Lecture Notes on Mathematical Statistical Physics

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Part I Classical Statistical Mechanics

1 The Basic Facts

"The goal of statistical mechanics is to predict the macroscopic properties of bodies, most especially their thermodynamic properties, on the basis of their microscopic structure." Luca Peliti¹

In statistical mechanics, one studies the macroscopic (i.e., large-scale) behavior of systems with a large number (typically > 10^{20}) of small components that interact according to certain laws of mechanics. "Mechanics" means the appropriate laws of motion, attraction and repulsion, but in some models will be replaced by other rather simple rules. In most of our considerations, the small components will be atoms or molecules (such as N_2), the macroscopic behavior concerns thermodynamics, and the laws of mechanics will be simplified and idealized models based on classical or quantum mechanics. (We will deal with the quantum case only in the second half of this course. Although we will briefly review the concepts from quantum mechanics that we need, we will require there some familiarity with quantum mechanics.)

The three basic facts of statistical mechanics.

- 1. Heat is an unordered motion of the atoms, and temperature measures the intensity of this motion.
- 2. A closed real-world system that at time t_0 has macro-state ν appears macroscopically in the future, but not the past, of t_0 like a system that at time t_0 is in a typical micro-state compatible with ν .
- 3. The real world as a whole (i.e., the universe) appears macroscopically like a system that at the big bang is in a typical micro-state compatible with the universe's macro-state at the big bang.

The first basic fact should be a clear statement, the others will be explained in due course when I discuss the concepts of "macroscopic appearance," "macro-state," "micro-state," and "typical." I call these statements "basic facts" and list them here because they are not logical consequences of the laws of mechanics. Rather, the laws of mechanics together with the three basic facts imply, by way of mathematics, the predictions of statistical mechanics. The basic facts thus provide the connection between mechanics and thermodynamics.

¹L. Peliti: Statistical Mechanics in a Nutshell. Princeton University Press (2011)

2 Review of Classical Mechanics

There are several theories that could be called classical mechanics. For the sake of concreteness, I formulate one precisely.

2.1 Definition of the Theory

Definition 1. Classical mechanics is a physical theory that states the following. The world consists of material points, called *particles*, moving with time $t \in \mathbb{R}$ in a 3-dimensional Euclidean space, here simply denoted \mathbb{R}^3 , so that the position $\boldsymbol{q}_k(t) \in \mathbb{R}^3$ of particle number $k \in \{1, \ldots, N\}$ (where N is the number of particles) obeys the equation of motion

$$m_k \frac{d^2 \boldsymbol{q}_k}{dt^2} = \sum_{j \neq k} G m_j m_k \frac{\boldsymbol{q}_j - \boldsymbol{q}_k}{|\boldsymbol{q}_j - \boldsymbol{q}_k|^3} - \sum_{j \neq k} \frac{e_j e_k}{4\pi\varepsilon_0} \frac{\boldsymbol{q}_j - \boldsymbol{q}_k}{|\boldsymbol{q}_j - \boldsymbol{q}_k|^3} \,. \tag{2.1}$$

Here, $m_k > 0$ is a constant called the mass of particle $k, e_k \in \mathbb{R}$ is a constant called the electric charge of particle $k, G = 6.67 \cdot 10^{-11} \text{ kg}^{-1} \text{ m}^3 \text{ s}^{-2}$ is a constant of nature called the constant of gravity, $\varepsilon_0 = 8.85 \cdot 10^{-12} \text{ kg}^{-1} \text{ m}^{-3} \text{ s}^4 \text{ A}^2$ is a constant of nature called the electric constant, the right-hand side is called the force acting on particle k, the first sum on the right is called the gravitational force, the *j*-th term in the sum is called the gravitational force exerted by particle *j* on particle *k*, and the second sum is called the electrostatic force or Coulomb force acting on particle *k*.

A d-dimensional Euclidean space is a metric space that is isometric to \mathbb{R}^d with the Euclidean distance

$$d(\boldsymbol{x}, \boldsymbol{y}) = |\boldsymbol{x} - \boldsymbol{y}| \tag{2.2}$$

with the Euclidean norm of $\boldsymbol{x} = (x_1, \ldots, x_d) \in \mathbb{R}^d$ given by

$$|\mathbf{x}| = \left(\sum_{a=1}^{d} x_a^2\right)^{1/2}.$$
(2.3)

Here, a metric space is a set X together with a distance function $d: X \times X \to [0, \infty)$ such that for all $x, y, z \in X$, $d(x, y) = 0 \Leftrightarrow x = y$, d(x, y) = d(y, x), and the triangle inequality $d(x, z) \leq d(x, y) + d(y, z)$. An isometry between metric spaces (X, d_X) and (Y, d_Y) is a surjective mapping $\varphi: X \to Y$ such that $d_Y(\varphi(x), \varphi(y)) = d_X(x, y)$ for all $x, y \in X$; an isometry is automatically bijective, and its inverse is also an isometry. Two metric spaces are *isometric* iff² there is an isometry between them. A Cartesian coordinate system of a Euclidean space is an isometry to \mathbb{R}^d with the Euclidean distance. We will often use a notation that does not distinguish between the physical Euclidean space and the coordinate space \mathbb{R}^3 , but we keep in the back of our minds that we could have made other choices of Cartesian coordinates. A similar remark applies to time: although we write \mathbb{R} for the time axis, it should really be regarded as a 1-dimensional

 $^{^{2}}$ iff = if and only if

Euclidean space. It can be shown that any two Cartesian coordinate systems (denoted x and \overline{x}) are related according to

$$\overline{\boldsymbol{x}} = R\boldsymbol{x} + \boldsymbol{a} \tag{2.4}$$

with $\boldsymbol{a} \in \mathbb{R}^d$ (providing a translation) and $R \in O(d)$, the group of orthogonal $d \times d$ matrices (providing a rotation and possibly reflection). It can be shown further that the equation of motion (2.1), if it holds in one Cartesian coordinate system (of physical space and of time), holds in every Cartesian coordinate system; if that were not the case, then Definition 1 would be ambiguous.

The theory provided by Definition 1 is an example of *microscopic laws* because it governs all details of all particles. This particular theory was never actually proposed to give the correct and complete laws of physics (although we can imagine a hypothetical world where it does); for example, it leaves out magnetism. An extension of this theory, which we will not consider further but which is also considered "classical physics," includes electromagnetic fields (governed by Maxwell's field equations) and gravitational fields (governed by Einstein's field equations, also known as the theory of general relativity). We know that all classical theories are empirically wrong because they predict the absence of quantum effects such as matter interference, discrete energy levels, and entanglement. Nevertheless, they are interesting to study for students and scientists alike because they are easier to understand than quantum theories and they already exhibit phenomena and mechanisms of interest, such as thermodynamics. (In addition, the correct theory of quantum gravity is not known, and quantum electrodynamics is at present still partly unclear.)

The greatest contributions from a single person to the development of Eq. (2.1) came from Isaac Newton (1643–1727), who suggested (in his *Philosophiae Naturalis Principia Mathematica* 1687) considering ODEs, in fact of second order, suggested "forces" and the form $m\frac{d^2q}{dt^2}$ = force, and introduced the form of the gravitational force, now known as "Newton's law of universal gravity." Eq. (2.1) was first written down, without the Coulomb term, by Leonhard Euler (1707–1783). The last term was proposed in 1784 by Charles Augustin de Coulomb (1736–1806). Nevertheless, we will often call (2.1) "Newton's equation of motion."

Eq. (2.1) is a system of ordinary differential equations (ODEs) in the unknown function $q(t) = (\mathbf{q}_1(t), \ldots, \mathbf{q}_N(t))$; we will often simply say "an ODE" instead of "a system of ODEs." Eq. (2.1) is said to be *of second order*, meaning it involves up to second time derivatives; it is called *non-linear* because the right-hand side is a nonlinear function of the unknown function. The function $t \mapsto \mathbf{q}_k(t)$ is also called the *trajectory* of particle k.

2.2 Phase Space and the Existence of Solutions

Since Newton's equation of motion (2.1) is of second order, one expects that, as initial data, one can specify the zeroth and first time derivatives arbitrarily, that is, the positions $\boldsymbol{q}_k(t=0)$ and velocities $\boldsymbol{v}_k(t=0)$, $\boldsymbol{v}_k = d\boldsymbol{q}_k/dt$ at a time that we regard as the

"initial" time and that we can conveniently choose to have time coordinate 0. Instead of velocities v_k , one often considers momenta

$$\boldsymbol{p}_k = m_k \boldsymbol{v}_k \tag{2.5}$$

(singular momentum), which is mathematically equivalent since $m_k \neq 0$. This leads to the mathematical question whether that is really so:

Is it true that the ODE (2.1) possesses a unique solution q(t) for all times $t \in \mathbb{R}$ for given q(0) and $v(0) = (\boldsymbol{v}_1(0), \dots, \boldsymbol{v}_N(0))$?

The standard result about the existence and uniqueness of solutions to ODEs is:

Theorem 1 (Picard–Lindelöf theorem). Consider the ODE initial-value problem

$$\frac{dx}{dt} = F(x,t), \quad x(t_0) = x_0$$
 (2.6)

with \mathbb{R}^n -valued unknown function x of a single variable t. If the \mathbb{R}^n -valued known function F is continuous and satisfies the Lipschitz condition

$$|F(x',t) - F(x,t)| \le K|x' - x|$$
(2.7)

with some Lipschitz constant K > 0 on some open set $\Omega \subseteq \mathbb{R}^{n+1}$, and if $(x_0, t_0) \in \Omega$, then there is a time interval $[t_0 - \varepsilon, t_0 + \varepsilon]$ with $\varepsilon > 0$ on which the initial-value problem (2.6) has a unique solution x(t).

The Lipschitz condition implies continuity; conversely, it follows if F is continuously differentiable and the first derivatives are bounded on Ω , and Ω is convex.

To apply the theorem to our case, we need a reduction of order: we translate the 3N equations of (2.1) of second order into 6N equations of first order by introducing further variables \boldsymbol{v}_k and writing $d^2\boldsymbol{q}_k/dt^2$ as $d\boldsymbol{v}_k/dt$; we obtain

$$\frac{d\boldsymbol{q}_k}{dt} = \boldsymbol{v}_k \tag{2.8}$$

$$\frac{d\boldsymbol{v}_k}{dt} = \sum_{j \neq k} \left(Gm_j - \frac{e_j e_k}{4\pi\varepsilon_0 m_k} \right) \frac{\boldsymbol{q}_j - \boldsymbol{q}_k}{|\boldsymbol{q}_j - \boldsymbol{q}_k|^3} \,.$$
(2.9)

We can thus bring (2.1) to the form (2.6) with x = (q, v) and n = 6N. The 6Ndimensional space whose coordinates are the components of q_k and v_k is called the *phase space* Γ . (Here, "phase" is supposed to mean "state.") The points in phase space $x \in \Gamma$ are called *phase points* or *micro-states*. The function $t \mapsto x(t) = (q(t), v(t))$ is also called the *trajectory in phase space*.

The function F is defined everywhere except where the denominators in (2.1) vanish, i.e., where $\mathbf{q}_j = \mathbf{q}_k$ for some $j \neq k$. Thus, writing \mathcal{Q}_{\neq} for the set of configurations $q \in \mathbb{R}^{3N}$ such that $\mathbf{q}_j \neq \mathbf{q}_k$ for all j and k with $j \neq k$, F is defined on $\mathcal{Q}_{\neq} \times \mathbb{R}^{3N+1}$. While F is continuously differentiable, its first derivatives are not bounded on $\mathcal{Q}_{\neq} \times \mathbb{R}^{3N+1}$, as some of them grow unboundedly when $\mathbf{q}_j - \mathbf{q}_k \to \mathbf{0}$. In fact, F does not obey the Lipschitz condition, regardless of how large K is. However, on any compact subset of $\mathcal{Q}_{\neq} \times \mathbb{R}^{3N+1}$, any continuous function (such as a first derivative of F) is bounded. Thus, for convex Ω contained in a compact subset of $\mathcal{Q}_{\neq} \times \mathbb{R}^{3N+1}$, a solution exists locally (i.e., at least for a short time). Such a set Ω cannot touch the subspace where $\mathbf{q}_j = \mathbf{q}_k$ but must keep a positive distance from it, which is equivalent to a positive minimum distance between \mathbf{q}_i and \mathbf{q}_k . But every (q_0, v_0, t_0) with $q_0 \in \mathcal{Q}_{\neq}$ lies in such an Ω !

So we obtain that (q, v) is indeed the appropriate specification of an initial condition, and that there is, at least for a short time, a unique solution of (2.1) with (q, v) as the initial condition. This fact makes it appropriate to call (q, v) the micro-state. ("State" because it uniquely determines the further motion, and "micro" because it includes all microscopic details, the exact positions and velocities of all particles.)

We will now look more closely into the question of *global existence*, i.e., whether the solutions exist for all t, although this question will play no role in the remainder of this course (where we will take global existence for granted).

It is helpful to talk about maximal solutions of the initial-value problem (2.6), which is a time interval I_{max} (which can be finite or infinite) containing t_0 and a solution $x_{\text{max}} : I_{\text{max}} \to \mathbb{R}^n$ of (2.6) such that every other solution of (2.6) is merely the restriction of x_{max} to a subinterval. From the Picard–Lindelöf theorem, one obtains the following result about maximal solutions.³

Corollary 1. If F is continuously differentiable on the open set $\Omega \subseteq \mathbb{R}^{n+1}$, then for each initial condition $(x_0, t_0) \in \Omega$ there exists a unique maximal solution x_{\max} of (2.6) on the (possibly infinite) open interval $I_{\max} = (t_-, t_+)$ with $t_{\pm} \in \mathbb{R} \cup \{-\infty, \infty\}$ and $t_0 \in I_{\max}$. If $t_{\pm} \neq \pm \infty$, then either $\limsup_{t \to t_{\pm}} |x(t)| = \infty$ (explosion in finite time) or $\lim_{t \to t_+} x(t) \in \partial\Omega$ (leaves Ω), where $\partial\Omega$ denotes the boundary of Ω .

This gives a partial answer to the question of global existence of solutions to (2.1): The solution can fail to exist for all t in two ways: either (q, v) is unbounded on a finite time interval, or it reaches $\partial \Omega = (\partial \mathcal{Q}_{\neq}) \times \mathbb{R}^{3N+1}$, that is, it reaches a configuration with $\mathbf{Q}_i = \mathbf{Q}_k$. Indeed, there are solutions that exist only for a finite time:

Example. Consider N = 2 uncharged particles with equal masses. For $t \leq 1$ (in suitable time units), the motion

$$\boldsymbol{q}_1(t) = \left(0, 0, (1-t)^{2/3}R\right), \quad \boldsymbol{q}_2(t) = \left(0, 0, -(1-t)^{2/3}R\right)$$
 (2.10)

with $R = \frac{1}{2}(9Gm)^{1/3}$ is a solution of (2.1). The two particles move towards each other until they collide at time t = 1. The velocities point in opposite radial directions and both have magnitude $\frac{2}{3}(1-t)^{-1/3}R$, which tends to ∞ as $t \to 1$.

Experts believe that only very few phase points lead to collisions or generally to finite t_+ . More precisely, they believe that the set of "explosive" phase points $\{(q, v) \in$

³See, e.g., p. 114 in W. Walter: *Gewöhnliche Differentialgleichungen*, 7. Auflage, Berlin: Springer (2000)

 $\mathcal{Q}_{\neq} \times \mathbb{R}^{3N} : (t_{-}, t_{+}) \neq (-\infty, +\infty)$ for which global existence fails has 6*N*-dimensional volume 0. However, to this day this conjecture has not been proven.

The problems with global existence arose from the expressions

$$\frac{\boldsymbol{q}_j - \boldsymbol{q}_k}{|\boldsymbol{q}_j - \boldsymbol{q}_k|^3}, \qquad (2.11)$$

which have magnitude $1/r^2$ if $r = |\mathbf{q}_j - \mathbf{q}_k|$ and therefore have first derivatives that are unbounded as $r \to 0$. If we replaced the right-hand side of Newton's equation of motion (2.1) by a function of q with bounded first derivatives (perhaps also defined even where $\mathbf{q}_j = \mathbf{q}_k$), then the Picard–Lindelöf theorem would yield the global existence of all solutions. For example, this would happen if we replaced (2.11) by

$$\frac{\boldsymbol{q}_{j} - \boldsymbol{q}_{k}}{\left(|\boldsymbol{q}_{j} - \boldsymbol{q}_{k}|^{2} + \ell^{2}\right)^{3/2}},$$
(2.12)

where ℓ is a constant with the dimension of length and a rather small value (such as $\ell = 10^{-15} \text{ m}$); see Figure 1.



Figure 1: Plots of the functions $1/r^2$ and $1/(r^2 + \ell^2)$ to illustrate (2.12), with r in units of ℓ .

2.3 Properties of the Theory

2.3.1 Time Reversal Invariance

If $t \mapsto q(t)$ is a solution of Newton's equation of motion (2.1), then so is $t \mapsto q(-t)$, which is called the *time reverse*. Its initial conditions at t = 0 are: positions equal to those in the original solution, all velocities opposite. Time reversal invariance, also known as *microscopic reversibility* is a rather surprising fact, as the time reverse solution looks like a movie shown backwards, and one would not have guessed that this is a possible course of events. While motion of the planets looks just as plausible backwards as forwards, this cannot be said of spilling water, cracking an egg, or the growth of a tree, which are very different forwards and backwards, and never observed backwards. This fact is known as *macroscopic irreversibility*. Specifically, time reversal invariance seems in conflict with the second law of thermodynamics, which asserts that entropy can only increase, but not decrease with time. This conflict is known as *Loschmidt's paradox*. So we will have to address this point when trying to derive laws of thermodynamics from mechanics.

2.3.2 Conserved Quantities

Definition 2. The *energy*, the *momentum*, and the *angular momentum* of the universe are defined to be, respectively,

$$E = \sum_{k=1}^{N} \frac{m_k}{2} \boldsymbol{v}_k^2 - \sum_{\substack{j,k=1\\j< k}}^{N} \left(Gm_j m_k - \frac{e_j e_k}{4\pi\varepsilon_0} \right) \frac{1}{|\boldsymbol{q}_j - \boldsymbol{q}_k|}$$
(2.13)

$$\boldsymbol{p} = \sum_{k=1}^{N} m_k \boldsymbol{v}_k \tag{2.14}$$

$$\boldsymbol{L} = \sum_{k=1}^{N} m_k \boldsymbol{q}_k \times \boldsymbol{v}_k \,, \tag{2.15}$$

where $v^2 = v \cdot v = |v|^2$, and × denotes the cross product in \mathbb{R}^3 . The first term in (2.13) is called *kinetic energy*, the second one *potential energy*.

Proposition 1. E, p, and L are conserved quantities, i.e., they are time independent (on the interval I_{max} on which the solution is defined).

Proof. Homework exercise.

2.4 Hamiltonian Systems

A *dynamical system* is another name for an ODE. It is one possibility for a time evolution law; other possibilities include stochastic laws (such as Brownian motion, which we will discuss later), or equations that involve an unknown function and its derivatives but are

not ODEs because they cannot be solved for the highest derivative (e.g., $(dx_1/dt)^2 + (dx_2/dt)^2 = 1$). A dynamical system can be characterized by specifying the function $F: \Omega \to \mathbb{R}^n$ in

$$\frac{dx}{dt} = F(x,t), \qquad (2.16)$$

with $\Omega \subseteq \mathbb{R}^{n+1}$. F can be called a time-dependent vector field on (a possibly timedependent domain in) \mathbb{R}^n . One often considers a more general concept of ODE, in which F is a time-dependent vector field on a differentiable manifold M. A manifold is, roughly speaking, a space that looks locally like \mathbb{R}^n but may differ globally. Manifolds include curved spaces such as spheres and toruses. For readers familiar with manifolds, I mention that the ODE can still be written in the form (2.16) if we now understand x(t) as a point in M, the mapping $t \mapsto x(t)$ as a curve in M, dx/dt as a tangent vector that lies in the tangent space $T_{x(t)}M$ at x(t), and F as a (time-dependent) vector field on M.

So classical mechanics as in Definition 1 has a time evolution that belongs to the class of dynamical systems. It also belongs to a narrower class, called *Hamiltonian* systems. Simply put, these are dynamical systems for which the vector field F is a certain type of derivative of a scalar function H called the *Hamiltonian function* or simply the *Hamiltonian*. Namely, n is assumed to be even, n = 2r, and denoting the n components of x by $(q_1, \ldots, q_r, p_1, \ldots, p_r)$, the ODE is of the form

$$\frac{dq_i}{dt} = -\frac{\partial H}{\partial p_i} \tag{2.17}$$

$$\frac{dp_i}{dt} = -\frac{\partial H}{\partial q_i}.$$
(2.18)

Classical mechanics as in Definition 1 fits this definition with $r = 3N, q_1, \ldots, q_r$ the 3N components of $q = (\boldsymbol{q}_1, \ldots, \boldsymbol{q}_N), p_1, \ldots, p_r$ the 3N components of $p = (\boldsymbol{p}_1, \ldots, \boldsymbol{p}_N)$ (the momenta $\boldsymbol{p}_k = m_k \boldsymbol{v}_k$), and H = H(q, p) the energy (2.13) expressed as a function of q and p, that is,

$$H(q,p) = \sum_{k=1}^{N} \frac{\boldsymbol{p}_{k}^{2}}{2m_{k}} - \sum_{\substack{j,k=1\\j< k}}^{N} \left(Gm_{j}m_{k} - \frac{e_{j}e_{k}}{4\pi\varepsilon_{0}} \right) \frac{1}{|\boldsymbol{q}_{j} - \boldsymbol{q}_{k}|} \,.$$
(2.19)

For readers familiar with manifolds I mention that the natural definition of a Hamiltonian system on a manifold M is as follows. M plays the role of phase space. Let the dimension n of M be even, n = 2r, and suppose we are given a symplectic form ω on M, i.e., a non-degenerate differential 2-form whose exterior derivative vanishes. (Non-degenerate means that it has full rank n at every point.) The equation of motion for $t \mapsto x(t) \in M$ reads

$$\omega\left(\frac{dx}{dt},\cdot\right) = dH\,,\tag{2.20}$$

where dH means the exterior derivative of H. To make the connection with the case $M = \mathbb{R}^n$ just described, dH is then the gradient of H and ω the $n \times n$ matrix

$$\omega = \begin{pmatrix} 0 & I \\ -I & 0 \end{pmatrix} \tag{2.21}$$

with I the $r \times r$ unit matrix and 0 the $r \times r$ zero matrix; $\omega(dx/dt, \cdot)$ becomes the transpose of ω applied to the *n*-vector dx/dt, and (2.21) reduces to (2.17) and (2.18).

For investigating thermodynamic properties, it is common to study *models*, i.e., simplified versions of the laws of nature. That is because the simpler the model, the easier it may be to obtain mathematical results about it, and because a phenomenon of interest (say, heat transport) may depend on some mechanisms (say, collisions between molecules) and not on others (say, the gravitational influence of Jupiter); a model exhibiting some mechanisms and neglecting others can bring this out clearly. Many models that are considered in statistical mechanics fall in the category of Hamiltonian systems.

2.5 Systems of Particles

After talking about dynamical systems and Hamiltonian systems, we also need to talk about a different kind of systems, *systems of particles*, also known as subsystems.

A system is a subset S of the set of all particles. It can be specified by listing the numbers $k \in \{1, \ldots, N\}$ of the particles belonging to the system. It is sometimes of interest to choose this set in a time-dependent way, and thus to consider a timedependent system. It is also often convenient to define a system as the set of particles in a given region $\Lambda \subseteq \mathbb{R}^3$,

$$S = \left\{ k \in \{1, \dots, N\} : \boldsymbol{q}_k \in \Lambda \right\}.$$
(2.22)

Also this system will in general be time-dependent.

A system is said to be *closed* or *isolated* if it behaves as if it were alone in the universe, but possibly with a different equation of motion or, correspondingly, a different Hamiltonian. Here, to behave the same way means to have the same trajectories of all particles. In the real world, a system is never exactly closed, but may be approximately. In a model, a system can be exactly closed. For example, the gravitational influence of Jupiter on a specific system of particles on Earth is nonzero but tiny; since it is also irrelevant to questions of thermodynamics, it is usually neglected in models. The gravitational influence of Earth on, say, the particles in a particular container, is usually not negligible, but the influence of those particles on the motion of Planet Earth as a whole is; thus, it is a useful approximation to suppose that those particles feel a particular fixed gravitational field that they do not influence. Such approximations correspond to a Hamiltonian system for the particle system (with n particles), in fact with H of the particular form

$$H = \sum_{k=1}^{n} \frac{\boldsymbol{p}_{k}^{2}}{2m_{k}} + V(\boldsymbol{q}_{1}, \dots, \boldsymbol{q}_{n}).$$
(2.23)

The function V is called the *potential energy* or simply *potential*. Hamilton's equations of motion (2.17) and (2.18) then become

$$\frac{d\boldsymbol{q}_k}{dt} = \frac{\boldsymbol{p}_k}{m} \tag{2.24}$$

$$\frac{d\boldsymbol{p}_k}{dt} = -\nabla_k V \,, \tag{2.25}$$

where $\nabla_k V$ means the 3-vector of the partial derivatives of V with respect to the 3 components of \boldsymbol{q}_k . Often, V is of the special form

$$V(\boldsymbol{q}_{1},\ldots,\boldsymbol{q}_{n}) = \sum_{k=1}^{n} V_{1}(\boldsymbol{q}_{k}) + \sum_{\substack{j,k=1\\j < k}}^{n} V_{2}(\boldsymbol{q}_{j},\boldsymbol{q}_{k}).$$
(2.26)

Then, V_1 is called an *external potential* and V_2 a *pair potential*. For example, the fixed gravitational field of Earth provides an external potential, and the Coulomb interaction a pair potential.

2.6 Flow

On the subset Ω of phase space where the solution curve x(t) exists globally in time (i.e., $t_{-} = -\infty$ and $t_{+} = +\infty$), it is convenient to define the solution map $T : \mathbb{R} \times \Omega \to \Omega$, written $T(t, x) = T^{t}x$, by

$$T^t x(0) = x(t)$$
. (2.27)

It is also known as the *flow map*. If F, the right-hand side of the ODE, is timeindependent (for a Hamiltonian system, if H is time independent), then T has the properties

$$T^0 = \mathrm{id}, \quad T^t T^s = T^{s+t}.$$
 (2.28)

For these two properties, $t \mapsto T^t$ is called a *one-parameter group* of mappings; the group multiplication is composition, the neutral element T^0 , and the inverse of T^t is T^{-t} , which actually is the inverse mapping of T^t because $T^{-t}T^t = T^{t-t} = T^0 = \text{id}$.

2.7 Billiards

Here is a specific model of a gas in a container, investigated particularly by Ludwig Boltzmann (1844–1906) around 1870 and called the *hard sphere gas*. Put briefly, one represents every gas molecule by a billiard ball of small radius a. The balls can fly around in the container volume $\Lambda \subseteq \mathbb{R}^3$ (possibly under the influence of an external potential such as Earth's gravity) and collide according to the laws of billiard ball collisions. The wall of the container is assumed to be fixed and hard; when a ball reaches the wall it gets reflected elastically there (see Figure 2). We make the idealizing assumption that the billiard balls do not spin.



Figure 2: Illustration of a phase point of the hard sphere gas. Arrows indicate velocities.

One may think of this model as a Hamiltonian system of the form (2.23) with (2.26) and

$$V_1(\boldsymbol{q}) = \begin{cases} 0 & \text{if } \boldsymbol{q} \in \Lambda \\ \infty & \text{if } \boldsymbol{q} \notin \Lambda \end{cases}$$
(2.29)

$$V_2(\boldsymbol{q}_1, \boldsymbol{q}_2) = \begin{cases} 0 & \text{if } |\boldsymbol{q}_1 - \boldsymbol{q}_2| \ge 2a \\ \infty & \text{if } |\boldsymbol{q}_1 - \boldsymbol{q}_2| < 2a . \end{cases}$$
(2.30)

This formal prescription could be regarded as a limit of smooth potentials V_1, V_2 that quickly tend to ∞ near the boundary of Λ and near the surface in \mathbb{R}^6 where $|\mathbf{q}_1 - \mathbf{q}_2| = 2a$.

A mathematical definition can be given as follows. Let $\Lambda \subseteq \mathbb{R}^3$ be a set with a piecewise smooth boundary (e.g., ball-shaped or a brick $[b_1, c_1] \times [b_2, c_2] \times [b_3, c_3]$). Whenever a billiard ball reaches the wall $\partial \Lambda$, its momentum component normal to the wall, $\mathbf{p} \cdot \mathbf{n}$, changes sign, whereas the momentum component parallel to the wall remains unchanged,

$$\boldsymbol{p} \to \boldsymbol{p}' = \boldsymbol{p} - 2[\boldsymbol{p} \cdot \boldsymbol{n}]\boldsymbol{n}$$
. (2.31)

Here, \boldsymbol{n} is the outward unit normal vector to the wall. This can be mathematically represented by identifying (glueing together) the phase point $(\ldots, \boldsymbol{q}_j, \ldots, \boldsymbol{p}_j, \ldots)$ when $\boldsymbol{q}_j \in \partial \Lambda$ with $(\ldots, \boldsymbol{q}_j, \ldots, \boldsymbol{p}_j - 2[\boldsymbol{p}_j \cdot \boldsymbol{n}]\boldsymbol{n}, \ldots)$. With this identification, the phase space Γ is no longer a subset of \mathbb{R}^n but a manifold with a different topology. That is an example of how the need for manifolds arises.

The rule for colliding balls can be formulated in a similar way.⁴ Between collisions, the momentum of each ball is constant, and at a collision of two balls, their momenta change discontinuously from p_1 and p_2 to p'_1 and p'_2 . As shown in a homework exercise, the conservation of energy, momentum, and angular momentum allows only two

⁴Our description follows H. Spohn: *Large Scale Dynamics of Interacting Particles*. Berlin: Springer-Verlag (1991)

possibilities for the values p'_1 and p'_2 (provided the balls do not spin): One is $p'_1 = p_1$ and $p'_2 = p_2$, which would, however, force the ball to pass through each other, and is thus excluded. Here is the other one (using that the balls have equal mass): Let q_1 and q_2 be such that $|q_2 - q_1| = 2a$, so the balls are just colliding, and let ω be the unit vector from ball 1 to ball 2, $\omega = (q_2 - q_1)/2a$. The ω -components of the momenta get exchanged,

$$p'_1 \cdot \boldsymbol{\omega} = \boldsymbol{p}_2 \cdot \boldsymbol{\omega}, \quad p'_2 \cdot \boldsymbol{\omega} = \boldsymbol{p}_1 \cdot \boldsymbol{\omega},$$
 (2.32)

while the components orthogonal to $\boldsymbol{\omega}$ remain unchanged,

$$(\mathbf{p}_1')^{\perp} = \mathbf{p}_1^{\perp}, \quad (\mathbf{p}_2')^{\perp} = \mathbf{p}_2^{\perp},$$
 (2.33)

where $p^{\perp} = p - (p \cdot \omega)\omega$ is the projection of p perpendicular to ω . In formulas:

$$\boldsymbol{p}_1 \rightarrow \boldsymbol{p}_1' = \boldsymbol{p}_1 - [(\boldsymbol{p}_1 - \boldsymbol{p}_2) \cdot \boldsymbol{\omega}] \boldsymbol{\omega}, \quad \boldsymbol{p}_2 \rightarrow \boldsymbol{p}_2' = \boldsymbol{p}_2 + [(\boldsymbol{p}_1 - \boldsymbol{p}_2) \cdot \boldsymbol{\omega}] \boldsymbol{\omega}, \quad (2.34)$$

provided that

$$(\boldsymbol{p}_1 - \boldsymbol{p}_2) \cdot \boldsymbol{\omega} > 0. \tag{2.35}$$

As before, we glue the pre- and post-collision phase points together, $(\boldsymbol{q}_1, \boldsymbol{q}_2, \ldots, \boldsymbol{p}_1, \boldsymbol{p}_2, \ldots)$ and $(\boldsymbol{q}_1, \boldsymbol{q}_2, \ldots, \boldsymbol{p}_1', \boldsymbol{p}_2', \ldots)$. After this glueing, there is no need anymore for a potential V governing collisions (ball-wall or ball-ball); we may sometimes want to keep some potential function V representing, e.g., an external gravitational field.

There are, in fact, some collisions for which we have not yet specified a rule: grazing collisions (such as when $(\mathbf{p}_1 - \mathbf{p}_2) \cdot \boldsymbol{\omega} = 0$), and simultaneous collisions of three or more balls. However, such rules are cumbersome and actually irrelevant because, in a suitable sense, the probability of ever running into such a situation is zero. More precisely:⁵

Theorem 2. One can delete a set Γ_b (of "bad points") of volume zero from the hard sphere phase space Γ_0 such that on $\Gamma := \Gamma_0 \setminus \Gamma_b$, the hard sphere motion x(t) as constructed above exists for all t, and thus a flow map $T : \mathbb{R} \times \Gamma \to \Gamma$ exists.

⁵Proofs of this theorem can be found in R.K. Alexander: Time evolution for infinitely many hard spheres. *Communications in Mathematical Physics* **49**: 217–232 (1976) and L.N. Vaserstein: On a system of particles with finite range and/or repulsive interactions. *Communications in Mathematical Physics* **69**: 35–56 (1979).

3 Review of Probability and Measure

Andrey Nikolaevich Kolmogorov (1903–1987) gave, in his 1933 book *Grundbegriffe der Wahrscheinlichkeitsrechnung*, the formulation of probability theory that we use today. It was a synthesis of three centuries of earlier work. It is perhaps surprising that this formulation gives no explanation of the nature of randomness. It states, put briefly, that probability is a normalized measure \mathbb{P} on a σ -algebra over the history space (sample space) Ω .

3.1 Definitions

Definition 3. A σ -algebra over a set Ω is a family \mathscr{F} of subsets of Ω such that

- $\bullet \ \ \emptyset \in \mathscr{F}$
- For every $A \in \mathscr{F}$, also its complement $A^c = \Omega \setminus A$ belongs to \mathscr{F} .
- If the countably many sets A_1, A_2, \ldots all belong to \mathscr{F} , then so does $\bigcup_{n=1}^{n} A_n$.

A pair (Ω, \mathscr{F}) is called a *measurable space*. A subset $A \subseteq \Omega$ is called *measurable* iff $A \in \mathscr{F}$.

It follows that $\Omega \in \mathscr{F}$, that also $A_1 \cup A_2$ belongs to \mathscr{F} (set $A_3 = \emptyset = A_4 = \ldots$), likewise any finite union, that also $\bigcap_{n=1}^{\infty} A_n \in \mathscr{F}$ (by de Morgan's law, $\bigcap A_n = (\bigcup (A_n^c))^c$), and likewise any finite intersection.

Definition 4. A measure μ on a measurable space (Ω, \mathscr{F}) is a mapping (set function) $\mu : \mathscr{F} \to [0, \infty]$ that is σ -additive, i.e., is such that, for any sequence $A_1, A_2, \ldots \in \mathscr{F}$ with $A_j \cap A_k = \emptyset$ for $j \neq k$,

$$\mu\left(\bigcup_{n=1}^{\infty} A_n\right) = \sum_{n=1}^{\infty} \mu(A_n).$$
(3.1)

The triple $(\Omega, \mathscr{F}, \mu)$ is called a *measure space*.

It follows that $\mu(A) \leq \mu(\Omega)$ for all $A \in \mathscr{F}$. μ is called *finite* iff $\mu(\Omega) < \infty$, normalized iff $\mu(\Omega) = 1$, and σ -finite iff there exist $A_1, A_2, \ldots \in \mathscr{F}$ with $\mu(A_n) < \infty$ for all n and $\bigcup_{n=1}^{\infty} A_n = \Omega$. A normalized measure space $(\Omega, \mathscr{F}, \mathbb{P})$ is also called a probability space.

In probability, elements of \mathscr{F} represent random events, elements of Ω the elementary events (simple events, individual histories, sample points); $\mathbb{P}(A)$ represents the probability of the event A. For example, if we flip a coin 100 times, then a simple choice of Ω would be the 2¹⁰⁰ sequences of head and tail, although Ω can also be chosen to be much larger (and comprise, e.g., the world history). Several traits of Kolmogorov's formulation may be surprising: (i) That not every set $A \subseteq \Omega$ of histories is attributed a probability, but only those in \mathscr{F} . For sets $A \notin \mathscr{F}$, we cannot ask what their probability is. (ii) That a measure that is merely *finitely* additive but not σ -additive cannot occur as \mathbb{P} . (iii) That \mathbb{P} is required to be suitably additive for countable families A_1, A_2, \ldots of events, but not for uncountable ones. More on this below.

On \mathbb{R}^d , the most frequently used σ -algebra is the *Borel* σ -algebra, which is defined as follows and whose elements are called the Borel measurable sets or simply Borel sets. Note first that the intersection of two σ -algebras over Ω is again a σ -algebra over Ω . This fact is not limited to two, but applies equally to any collection, even uncountably infinite, of σ -algebras over Ω : their intersection is again a σ -algebra over Ω , and one can say that it is the largest σ -algebra contained in all σ -algebras in the given collection. Given any family \mathscr{T} of subsets of Ω , consider the collection of all σ -algebras over Ω containing \mathscr{T} ; its intersection $\mathscr{F}(\mathscr{T})$ is the smallest σ -algebra containing \mathscr{T} (it is contained in every other σ -algebra containing \mathscr{T}) and is called the σ -algebra generated by \mathscr{T} . For \mathbb{R}^d (and any topological space), the Borel σ -algebra is the one generated by the family of the open sets. It contains, among other things, all one-element sets (because their complements are open), all Cartesian products of lower-dimensional Borel sets, and, in \mathbb{R}^1 , all intervals.

Another application of measures besides probability is the concept of volume in \mathbb{R}^d ; it is consensus among mathematicians that the precise formulation of this concept is the *Lebesgue measure*.

Theorem 3. ⁶ There exists exactly one measure λ on the Borel σ -algebra of \mathbb{R}^d that is translation invariant, $\lambda(A) = \lambda(A + \mathbf{a})$ with $A + \mathbf{a} = \{\mathbf{x} + \mathbf{a} : \mathbf{x} \in A\}$, and yields 1 on the unit cube, $\lambda([0, 1)^d) = 1$. It is called the Lebesgue measure.

Sets A with $\lambda(A) = 0$ are called *null sets*. As it should, λ is also invariant under rotations and reflections, $\lambda(RA) = \lambda(A)$ for $R \in O(d)$, and scales according to $\lambda(rA) = r^d \lambda(A)$ for scaling factor r > 0. The Lebesgue measure can also naturally be defined on a somewhat larger σ -algebra, the *Lebesgue* σ -algebra, which is the family of those sets $A \subseteq \mathbb{R}^d$ for which there exists a Borel set B such that both $A \setminus B$ and $B \setminus A$ are subsets of Borel null sets; one defines $\lambda(A) = \lambda(B)$. The idea is that once we have a Borel null set C, it is natural to attribute volume 0 to every subset of C, regardless of whether it is Borel measurable or not.

Even this larger σ -algebra does not contain *all* subsets of \mathbb{R}^d , and a notion of volume cannot be defined on *all* subsets, as the following Proposition shows.

Proposition 2. There exists no measure μ on the power set of [0, 1) that is translation invariant, $\mu(A) = \mu(A + a)$ in the periodic sense $A + a = \{x + a \mod 1 : x \in A\}$, and yields 1 on the whole, $\mu([0, 1)) = 1$.

Proof. We consider rational translations, $a \in \mathbb{Q}$, and introduce the equivalence relation $x \sim y \iff x - y \in \mathbb{Q}$; the equivalence classes are called the orbits under rational translations. Choose one element from each orbit, and collect them in a set A.⁷ Thus, A

⁶For a proof, see, e.g., Theorem 2.20 in W. Rudin: *Real and Complex Analysis.* London: McGraw-Hill (1970).

⁷We are using the axiom of choice, which asserts that for every nonempty set S of nonempty sets, there is a "choice function" f on S, i.e., a function such that $f(M) \in M$ for every $M \in S$.

has exactly one element in common with every orbit; put differently, for every $x \in [0, 1)$ there are unique $y \in A$ and $a \in \mathbb{Q}$ such that x = y + a. As a consequence, all rational translates of A mod 1 are mutually disjoint, and their union is all of [0, 1). Let A_1, A_2, \ldots be all rational translates of A mod 1. If μ as described existed, then

$$1 = \mu([0,1)) = \mu(\cup A_n) = \sum_{n=1}^{\infty} \mu(A_n), \qquad (3.2)$$

but all $\mu(A_n)$ are equal to each other by translation invariance, so the rightmost expression would have to be either 0 (if $\mu(A) = 0$) or ∞ (if $\mu(A) > 0$).

Thus, some sets are too wild to allow a meaningful attribution of a number as their volume.⁸ This is also the reason why, in probability theory, not all sets of elementary events can be attributed a number as their probability. We can also say more about why σ -additivity is the right kind of additivity. The Lebesgue measure on [0, 1) is obviously normalized, thus qualifies as a probability measure, and represents a uniform probability distribution over the unit interval. But it obviously violates unrestricted uncountable additivity because every one-element set has measure zero (and it should, as an interval of length zero!), so

$$\sum_{x \in [0,1)} \lambda(\{x\}) = 0 \neq 1 = \lambda([0,1)) = \lambda\left(\bigcup_{x \in [0,1)} \{x\}\right).$$
(3.3)

On the other hand, if we only require finite additivity of μ then it can happen that a descending sequence $A_1 \supseteq A_2 \supseteq \ldots$ has $\bigcap_{n=1}^{\infty} A_n = \emptyset$ but $\lim_{n\to\infty} \mu(A_n) > 0$, and that conflicts with our intuitions of volume and probability.

3.2 Cournot's Principle

As Kolmogorov made clear in his book, his formulation of probability as a normalized measure leaves out the connection to the empirical world. He summarizes this connection in two further principles. From Section 2 of Chapter 1 of the Grundbegriffe:

Unter gewissen Bedingungen, auf die wir hier nicht näher eingehen wollen, kann man voraussetzen, dass einem Ereignis A, welches infolge der Bedingungen \mathfrak{S} auftritt oder nicht, eine gewisse reelle Zahl $\mathbb{P}(A)$ zugeordnet ist, welche folgende Eigenschaften besitzt:

A. Man kann praktisch sicher sein, dass, wenn man den Komplex der Bedingungen \mathfrak{S} eine große Anzahl von n Malen wiederholt und dabei durch m die Anzahl der Fälle bezeichnet, bei denen das Ereignis A stattgefunden hat, das Verhältnis m/n sich von $\mathbb{P}(A)$ nur wenig unterscheidet.

⁸A statement similar to Proposition 2 is the *Banach-Tarski theorem*, which asserts that the unit sphere in \mathbb{R}^3 can be partitioned into 10 subsets A_1, \ldots, A_{10} , and there are 10 rotations $R_1, \ldots, R_{10} \in$ SO(3), such that R_1A_1, \ldots, R_5A_5 form a partition of the unit sphere and $R_6A_6, \ldots, R_{10}A_{10}$ form a partition of the unit sphere. From one sphere make two! Since rotations preserve area, this seems impossible. In fact, it would be impossible if A_1, \ldots, A_{10} were measurable, but they are not.

B. Ist $\mathbb{P}(A)$ sehr klein, so kann man praktisch sicher sein, dass bei einer einmaligen Realisation der Bedingungen \mathfrak{S} das Ereignis A nicht stattfindet.

Translation:

Under certain conditions, that we will not go into further here, we may assume that an event A that does or does not occur under conditions \mathfrak{S} is assigned a real number $\mathbb{P}(A)$ with the following properties:

- A. One can be practically certain that if the system of conditions \mathfrak{S} is repeated a large number of times, n, and the event A occurs m times, then the ratio m/n will differ only slightly from $\mathbb{P}(A)$.
- **B.** If $\mathbb{P}(A)$ is very small, then one can be practically certain that the event A will not occur on a single realization of the conditions \mathfrak{S} .

Principle (A) can be regarded, by means of the law of large numbers (more on this below), as a special case of (B). Principle (B) is also known as *Cournot's principle* after Antoine Augustin Cournot (1801–1877). Paul Lévy (1919): "Cournot's principle is the only connection between probability and the empirical world." While the principle is itself not a mathematical statement, it is part of the laws of correct thinking. It lies at the basis of statistical tests (as developed particularly by Jerzy Neyman, Egon Pearson, and Ronald A. Fisher) that reject a hypothesis H_0 about a variable X if the observed value x lies in a suitable region that, according to H_0 , has very small probability.

It is not easy to give a precise formulation of Cournot's principle because after the outcome of an experiment (say, 1000 coin tosses) is known, it is usually easy to name a particular event (say, this particular sequence of heads and tails) that has small probability and did occur. A practical formulation is that an event of very small probability singled out in advance will not happen. How small? Borel⁹ has argued that events with probability $< 10^{-200}$ can be assumed to never occur in our universe.

3.3 Integration

The definition of integral used by present-day mathematicians is that of Lebesgue (1902), which replaced an earlier and simpler one by Riemann (1854). We will not review these definitions here, but we note that for every non-negative measurable function $f: \Omega \to [0, \infty)$ on a measure space $(\Omega, \mathscr{F}, \mu)$, the Lebesgue integral $\int_{\Omega} \mu(d\omega) f(\omega)$ is defined as an element of $[0, \infty]$. A function between two measurable spaces is called *measurable* iff the pre-image $f^{-1}(A) = \{x : f(x) \in A\}$ of every measurable set A is measurable. If $\int_{\Omega} \mu(d\omega) f(\omega) < \infty$, then f is called *integrable*. If $f: \Omega \to \mathbb{R}$ has integrable positive part $f^+(\omega) = \max\{0, f(\omega)\}$ and integrable negative part $f^-(\omega) = \max\{0, -f(\omega)\}$ (so $f = f^+ - f^-$), then f is said to be *integrable*, and $\int_{\Omega} \mu(d\omega) f(\omega) =: \int f$ is defined as $\int f^+ - \int f^-$. When μ is the Lebesgue measure, it is common to write $\int dx f(x)$ for $\int \lambda(dx) f(x)$.

⁹Chapter 6 in E. Borel: *Probabilities and life.* London: Dover (1962).

A basic instance of integration is the concept of *probability density*: The measure ν on (Ω, \mathscr{F}) is said to have *density function* $\rho : \Omega \to [0, \infty)$ relative to the measure μ on (Ω, \mathscr{F}) iff ρ is measurable and

$$\nu(A) = \int_{A} \mu(d\omega) \,\rho(\omega) \tag{3.4}$$

for all $A \in \mathscr{F}$. In this case, ρ is also called the *Radon-Nikodym derivative* of ν relative to μ ,

$$\frac{d\mathbb{P}}{d\mu} = \rho \,. \tag{3.5}$$

Clearly, whenever $\int_{\Omega} \rho = 1$, then ν is a probability measure.

Theorem 4 (Radon-Nikodym theorem). If a σ -finite measure ν on the measurable space (Ω, \mathscr{F}) is absolutely continuous relative to another σ -finite measure μ on (Ω, \mathscr{F}) (i.e., if every μ -null set is a ν -null set), then ν possesses a density function ρ relative to μ , and ρ is unique up to changes on μ -null sets.

Another basic instance of integration is the *expectation value*: A random variable is a measurable function X on a probability space $(\Omega, \mathscr{F}, \mathbb{P})$. If X takes values in a vector space, then the expectation of X is

$$\mathbb{E}X = \langle X \rangle = \int_{\Omega} \mathbb{P}(d\omega) X(\omega) , \qquad (3.6)$$

whenever that is defined. (If X is real-valued and $X \ge 0$, then $\mathbb{E}X$ is always defined as an element of $[0, \infty]$.) We recall, by the way, that the *variance* of a real random variable X is

$$\operatorname{Var} X = \sigma_X^2 = \mathbb{E}\left[(X - \mathbb{E}X)^2 \right] = \mathbb{E}(X^2) - (\mathbb{E}X)^2 \in [0, \infty], \qquad (3.7)$$

whenever $\mathbb{E}X$ is defined and finite. The *covariance* of two real random variables X, Y is

$$\operatorname{Cov}(X,Y) = \mathbb{E}\Big[(X - \mathbb{E}X)(Y - \mathbb{E}Y)\Big] = \mathbb{E}(XY) - (\mathbb{E}X)(\mathbb{E}Y), \qquad (3.8)$$

whenever that is defined. Obviously, $\operatorname{Var} X = \operatorname{Cov}(X, X)$.

3.4 Product Measures

In the following, we will not make explicit the assumption that sets considered lie in the relevant σ -algebra, and often not even mention the σ -algebra. Let μ_1, \ldots, μ_n be measures on (measurable spaces) $\mathcal{M}_1, \ldots, \mathcal{M}_n$; the *product measure* $\mu_1 \times \cdots \times \mu_n$ on $\mathcal{M}_1 \times \cdots \times \mathcal{M}_n$ (with the σ -algebra generated by the products of measurable sets) is defined by the property

$$\mu_1 \times \dots \times \mu_n(A_1 \times \dots \times A_n) = \mu_1(A_1) \cdots \mu_n(A_n).$$
(3.9)

Such a measure always exists; it is unique if μ_1, \ldots, μ_n are σ -finite.

The distribution or marginal distribution of an \mathcal{M} -valued random variable X is the measure μ on \mathcal{M} given by

$$\mu(A) = \mathbb{P}(X \in A). \tag{3.10}$$

In symbols, $X \sim \mu$. The random variables X_1, \ldots, X_n are *independent* iff their joint distribution is the product of their individual (marginal) distributions. An infinite collection X_1, X_2, \ldots of random variables is *independent* iff every finite subcollection is.

Conversely, we will often want to construct a measure that represents the joint distribution of independent X_1, X_2, \ldots when the distributions μ_1, μ_2, \ldots are given. Such a *countable product measure* $\mu_1 \times \mu_2 \times \cdots$ exists when the μ_k are probability measures, but not necessarily if they are merely σ -finite. For example, there is no product of infinitely many copies of the Lebesgue measure or, in other words, there is no volume measure in $\mathbb{R}^{\mathbb{N}}$.

3.5 Conditional Probability

The conditional probability of the event A, given the event B, is defined by

$$\mathbb{P}(A|B) = \frac{\mathbb{P}(A \cap B)}{\mathbb{P}(B)}, \qquad (3.11)$$

provided $\mathbb{P}(B) \neq 0$. Correspondingly, if the random variable X is discrete (i.e., assumes only countably many values), then the *conditional distribution of* Y, given X = x, is given by

$$\mathbb{P}(Y \in A | X = x) = \frac{\mathbb{P}(Y \in A, X = x)}{\mathbb{P}(X = x)}$$
(3.12)

for every set A and every x for which $\mathbb{P}(X = x) \neq 0$.

In this case, X and Y are independent iff the conditional distribution of Y given X = x does not depend on x. Indeed, if X and Y are independent, then $\mathbb{P}(Y \in A, X = x) = \mathbb{P}(Y \in A) \mathbb{P}(X = x)$, so $\mathbb{P}(Y \in A | X = x) = \mathbb{P}(Y \in A)$ independently of x. Conversely, if $\mathbb{P}(Y \in A | X = x) = \nu(A)$ independently of x, then

$$\mathbb{P}(Y \in A, X \in B) = \sum_{x \in B} \mathbb{P}(Y \in A, X = x) = \sum_{x \in B} \nu(A) \mathbb{P}(X = x) = \nu(A) \mathbb{P}(X \in B).$$
(3.13)

For B the full set (i.e., the value space of X, with $\mathbb{P}(X \in B) = 1$) it follows that $\mathbb{P}(Y \in A) = \nu(A)$, so $\mathbb{P}(Y \in A, X \in B) = \mathbb{P}(Y \in A) \mathbb{P}(X \in B)$, which means that X and Y are independent.

Now if X is a continuous real random variable, the formula (3.12) cannot be applied because $\mathbb{P}(X = x) = 0$ for every $x \in \mathbb{R}$. However, if X and Y are jointly continuous with density $\rho_{X,Y}(x, y)$, then one can define the conditional distribution of Y, given X = x, as the distribution with density

$$\rho(Y = y | X = x) = \frac{\rho_{X,Y}(x,y)}{\int dy' \,\rho_{X,Y}(x,y')} \tag{3.14}$$

for every x for which the denominator is neither 0 nor ∞ . The denominator is, in fact, $\rho_X(x)$, which cannot be ∞ except on a null set of x's (or else $\rho_{X,Y}$ would have infinite integral); also the set B of x's where the denominator vanishes is unproblematical because $\mathbb{P}(X \in B) = 0.^{10}$

If $\rho(Y = y | X = x)$ does not depend on x, then X and Y are independent. Indeed, in this case

$$\mathbb{P}(Y \in A, X \in B) = \int_{B \times A} dx \, dy \, \rho_{X,Y}(x, y) \tag{3.15}$$

$$= \int_{B \times A} dx \, dy \, \rho(Y = y | X = x) \, \rho_X(x) \tag{3.16}$$

$$= \int_{A} dy \,\rho(Y = y | X = x) \,\int_{B} dx \,\rho_X(x) \tag{3.17}$$

$$=\nu(A)\mathbb{P}(X\in B),\qquad(3.18)$$

and $\nu(A)$ must be $\mathbb{P}(Y \in A)$ (this follows from considering the full space for B).

Conversely, if X and Y are jointly continuous and independent, then $\rho_{X,Y}(x,y)$ can be chosen to factorize, $\rho_{X,Y}(x,y) = \rho_X(x) \rho_Y(y)$, with the consequence that $\rho(Y = y|X = x) = \rho_Y(y)$ is independent of x.

The expectation value of a conditional distribution is called the *conditional expecta*tion and denoted $\mathbb{E}(Y|X=x)$.

3.6 The Gaussian Distribution

The most famous density function is perhaps that of the 1-dimensional Gaussian distribution, also known as the normal distribution $\mathcal{N}(\mu, \sigma^2)$, shown in Figure 3.



Figure 3: Density of a 1d Gaussian distribution

¹⁰A subtlety with (3.14) arises from the fact that $\rho_{X,Y}$ can be changed on a null set without changing the joint distribution of X and Y. As a consequence, $\rho(Y = y | X = x)$ is only defined up to changes on a null set of x's and for every x an x-dependent null set of y's.

It is given by

$$\rho(x) = \frac{1}{\sqrt{2\pi\sigma}} e^{-\frac{(x-\mu)^2}{2\sigma^2}},$$
(3.19)

its expectation by μ and its variance by σ^2 . We will also need Gaussian distributions in higher dimension.

Definition 5. A Gaussian distribution in \mathbb{R}^d is a continuous distribution whose density is of the form

$$\rho(\boldsymbol{x}) = \exp(P(\boldsymbol{x})), \qquad (3.20)$$

where P is a (real) second-order polynomial in d variables.



Figure 4: Density function of a 2d Gaussian distribution

This distribution, like any probability distribution on \mathbb{R}^d , can be regarded as the joint distribution of d random variables X_1, \ldots, X_d , or as the distribution of a random vector \boldsymbol{X} , which we also call an \mathbb{R}^d -valued random variable. The general form of a second-order polynomial is

$$P(x_1, \dots, x_d) = \sum_{k=1}^d \alpha_k x_k^2 + \sum_{k=2}^d \sum_{j=1}^{k-1} \beta_{jk} x_j x_k + \sum_{k=1}^d \gamma_k x_k + \delta.$$
(3.21)

It is often convenient to re-write this as

$$P(\boldsymbol{x}) = \sum_{j,k=1}^{d} a_{jk} x_j x_k + \sum_{k=1}^{d} \gamma_k x_k + \delta$$
(3.22)

by setting $a_{jj} = \alpha_j$ and $a_{jk} = \beta_{jk}/2$ for j < k and $a_{jk} = \beta_{kj}/2$ for j > k; the coefficients a_{jk} then form a symmetric matrix A. Conversely, any expression of the form (3.22) agrees with (3.21) according to $\alpha_j = a_{jj}$ and $\beta_{jk} = \frac{1}{2}(a_{jk} + a_{kj})$. It follows that even if A were not symmetric, we can replace it by its symmetric part $\frac{1}{2}(A + A^T)$ without changing P; here, A^T denotes the transpose of A.

It is furthermore convenient to write

$$P(\boldsymbol{x}) = \boldsymbol{x}^T A \boldsymbol{x} + \boldsymbol{\gamma} \cdot \boldsymbol{x} + \delta$$
(3.23)

with $\boldsymbol{\gamma} = (\gamma_1, \ldots, \gamma_d)$. One can show that for $\int e^{P(\boldsymbol{x})} d\boldsymbol{x} < \infty$, it is necessary that

$$\boldsymbol{x}^T A \boldsymbol{x} < 0 \tag{3.24}$$

for all $x \neq 0$; that is, A must be *negative definite*. Setting $\mu = -\frac{1}{2}A^{-1}\gamma$ (which exists because negative definite matrices are invertible), we can rewrite

$$P(\boldsymbol{x}) = (\boldsymbol{x} - \boldsymbol{\mu})^T A(\boldsymbol{x} - \boldsymbol{\mu}) + \delta'.$$
(3.25)

The constant δ' is fixed by the normalization of ρ . That is, the Gaussian distributions in \mathbb{R}^d are just the translates of those with density

$$\rho(\boldsymbol{x}) = \mathscr{N} e^{\boldsymbol{x}^T A \boldsymbol{x}} \tag{3.26}$$

with negative-definite, symmetric matrix A (and normalization constant \mathcal{N}).

Recall that the spectral theorem for symmetric matrices asserts: For every symmetric $d \times d$ matrix A there is an orthonormal basis (ONB) of \mathbb{R}^d that diagonalizes A. Relative to this ONB (i.e., in a new coordinate system $\overline{\boldsymbol{x}} = R\boldsymbol{x}$), the density assumes the form

$$\overline{\rho}(\overline{\boldsymbol{x}}) = \mathcal{N} \ e^{\sum_k a_k \overline{x}_k^2} \,, \tag{3.27}$$

where a_k are the eigenvalues of A, which are all negative here because A is negative definite and can thus be written as $a_k = -1/2\sigma_k^2$. We thus obtain

$$\overline{\rho}(\overline{\boldsymbol{x}}) = \prod_{k=1}^{d} \frac{1}{\sqrt{2\pi\sigma_k}} e^{-\frac{\overline{\boldsymbol{x}_k^2}}{2\sigma_k^2}}, \qquad (3.28)$$

using that the product of normalized densities must be normalized. That is, in the \overline{x} coordinates, the components $\overline{X}_1, \ldots, \overline{X}_d$ are independent 1d Gaussian random variables. In Figure 4, one can actually see that the density is the product of two 1d Gaussian densities. From the product form (3.28) it is clear that $\mathbb{E}\overline{X} = 0$, and by the linearity of the expectation also $\mathbb{E}X = \mathbb{E}(R^{-1}\overline{X}) = R^{-1}\mathbb{E}\overline{X} = 0$, which yields after the translation by μ that in the general case (3.25),

$$\mathbb{E}\boldsymbol{X} = \boldsymbol{\mu} \,. \tag{3.29}$$

It also becomes clear from (3.28) that the level surfaces of the density function ρ are ellipsoids whose axes coincide with the \overline{x} coordinate axes and thus with the eigenvectors of A (which remains true after rotation and translation, so it is a general fact).

One defines the *covariance matrix* C of a distribution on \mathbb{R}^d to have entries $C_{jk} = \text{Cov}(X_j, X_k)$. It is a symmetric matrix with the variances on the diagonal. For the Gaussian distribution, one finds

$$C = -\frac{1}{2}A^{-1}. (3.30)$$

The easiest way to see this is perhaps as follows. Since the covariance matrix does not change if we translate the distribution, we can assume $\boldsymbol{\mu} = 0$. When we rotate the coordinates, $\overline{\boldsymbol{x}} = R\boldsymbol{x}$ with $R^T = R^{-1}$, then $\overline{C} = (\operatorname{Cov}(\overline{X}_j, \overline{X}_k))_{jk} = RCR^T$. But when we have diagonalized A to obtain $\overline{A} = RAR^T = \operatorname{diag}(a_1, \ldots, a_d)$, then the components are independent (thus have vanishing covariance) with variances $\sigma_k^2 = -1/2a_k$, so $\overline{C} = -\frac{1}{2}\overline{A}^{-1}$, which implies (3.30).

In sum, the *d*-dimensional Gauss distribution is characterized by its expectation $\boldsymbol{\mu}$ and its covariance matrix C (an abritrary symmetric positive definite matrix); we denote this distribution by $\mathcal{N}^d(\boldsymbol{\mu}, C)$.

Example. Velocity Distribution in a Gas According to Maxwell. James Clerk Maxwell (1831–1879) suggested in 1866 that the statistical distribution of velocities in a gas in thermal equilibrium has distribution density

$$\rho(\boldsymbol{v}) = \mathscr{N} \exp\left(-\frac{m|\boldsymbol{v}|^2}{2kT}\right),\tag{3.31}$$

now called the *Maxwellian distribution*. Here, m is the mass of a molecule, k the Boltzmann constant = $1.38 \cdot 10^{-23}$ J/K, and T the absolute temperature. If several types of molecules occur (as in air, which primarily contains N_2 , O_2 , Ar, and H_2O), then each type is claimed to have a velocity distribution according to (3.31).

The Maxwellian distribution (3.31) is a 3d Gaussian distribution with $\mu = 0$ and

$$A = \begin{pmatrix} -m/2kT & & \\ & -m/2kT & \\ & & -m/2kT \end{pmatrix}, \quad C = \begin{pmatrix} kT/m & & \\ & kT/m & \\ & & kT/m \end{pmatrix}. \quad (3.32)$$

It is invariant under rotations $R \in SO(3)$. We will come back later to why this is the right distribution.

3.7 The Law of Large Numbers

We write δ_x (alluding to Dirac delta functions) for the normalized measure concentrated at x, i.e.,

$$\delta_x(A) = \begin{cases} 1 & \text{if } x \in A \\ 0 & \text{if } x \notin A \end{cases}.$$
(3.33)

Consider random variables X_1, \ldots, X_n . Their *empirical distribution* is

$$\mu^{\rm emp} = \frac{1}{n} \sum_{k=1}^{n} \delta_{X_k} \,. \tag{3.34}$$

It is a random measure, one that depends on the outcomes of X_1, \ldots, X_n . It is conveniently represented as a histogram (see Figure 5). A histogram of a measure μ on Ω is based on some partition $\mathscr{A} = \{A_1, \ldots, A_r\}$ of Ω that we choose and depicts the values $\mu(A_1), \ldots, \mu(A_r)$, also known as the *coarse-grained distribution* relative to \mathscr{A} .



Figure 5: Histogram of a realization of a large number of independent standard normal random variables

The law of large numbers asserts that if X_1, \ldots, X_n are independent and identically distributed (i.i.d.) and n is large then the empirical distribution is close to the marginal distribution (also called the theoretical distribution). A first version of the law of large numbers was developed by Jacob Bernoulli (1654–1705) in his book Ars conjectandi (the art of conjecturing), written between 1684 and 1689 and published in 1713.

Theorem 5 (Weak law of large numbers). Let \mathscr{M} be a measurable space, X_1, X_2, \ldots i.i.d. \mathscr{M} -valued random variables, $\mathscr{A} = \{A_1, \ldots, A_r\}$ a partition of \mathscr{M} , $\mathbf{P} = (P_1, \ldots, P_r)$ with $P_i = \mathbb{P}(X_1 \in A_i)$ the distribution of X_1 (and thus of any X_k) in terms of \mathscr{A} , and $\mathbf{Y}_n = (Y_{n1}, \ldots, Y_{nr})$ with $Y_{ni} = \#\{k \leq n : X_k \in A_i\}/n$ the histogram of X_1, \ldots, X_n in terms of \mathscr{A} . For every $\varepsilon > 0$, the probability that \mathbf{Y}_n is ε -close to \mathbf{P} tends to 1 as $n \to \infty$. In fact,

$$\mathbb{P}\Big(\forall i: |Y_{ni} - P_i| < \varepsilon\Big) \ge 1 - \frac{1}{n\varepsilon^2}.$$
(3.35)

Proof. The Markov inequality asserts that if $Y \ge 0$ then

$$\mathbb{P}(Y \ge a) \le \frac{\mathbb{E}Y}{a}.$$
(3.36)

("In a population with average income 1,000, no more than 10% can have an income of 10,000 or more.") For $Y = (X - \mathbb{E}X)^2$ and $a = \varepsilon^2$, one obtains the *Chebychev inequality*

$$\mathbb{P}\Big(|X - \mathbb{E}X| < \varepsilon\Big) \ge 1 - \frac{\operatorname{Var} X}{\varepsilon^2}.$$
(3.37)

Since $Y_{ni} = n^{-1} \sum_{k=1}^{n} \mathbb{1}_{X_k \in A_i}$, we have that

$$\mathbb{E}Y_{ni} = n^{-1} \sum_{k=1}^{n} \mathbb{E}1_{X_k \in A_i} = n^{-1} \sum \mathbb{P}(X_k \in A_i) = P_i$$
(3.38)

and, since the X_k are independent,

Var
$$Y_{ni} = n^{-2} \sum_{k=1}^{n} \operatorname{Var} \mathbb{1}_{X_k \in A_i} = n^{-1} P_i (1 - P_i).$$
 (3.39)

Thus, the event complementary to the one in (3.35) has probability

$$\mathbb{P}\Big(\bigcup_{i=1}^{r} \Big\{ |Y_{ni} - P_i| \ge \varepsilon \Big\} \Big) \le \sum_{i=1}^{r} \mathbb{P}\Big(|Y_{ni} - P_i| \ge \varepsilon \Big)$$
(3.40)

$$\leq \sum_{i=1}^{r} \frac{\operatorname{Var} Y_{ni}}{\varepsilon^2} \tag{3.41}$$

$$=\sum_{i=1}^{r}\frac{P_i(1-P_i)}{n\varepsilon^2} \le \frac{1}{n\varepsilon^2},\qquad(3.42)$$

which proves (3.35).

Theorem 6 (Strong law of large numbers¹¹). Under the same hypotheses as before,

$$\mathbb{P}\left(\forall i: \lim_{n \to \infty} Y_{ni} = P_i\right) = 1.$$
(3.43)

The strong LLN, proved by Émile Borel (1871–1956) in 1909, implies that the lefthand side of (3.35) tends to 1 as $n \to \infty$, but does not provide the estimate (3.35). For applications, the weak LLN is usually more relevant because we usually deal with a finite n (such as 10^{23}) and then need an estimate such as (3.35).

The name "law of large numbers" is often given to the following statements, which are closely related but not exactly equivalent to Theorems 5 and 6. Let Z_1, Z_2, \ldots be *i.i.d. real-valued random variables with finite expectation and variance. Then (weak law)* for every $\varepsilon > 0$, the probability that $n^{-1} \sum_{j=1}^{n} Z_j$ is ε -close to $\mathbb{E}Z_1$ tends to 1 as $n \to \infty$. In fact,

$$\mathbb{P}\left(\left|\frac{1}{n}\sum_{j=1}^{n}Z_{j}-\mathbb{E}Z_{1}\right|<\varepsilon\right)\geq1-\frac{\operatorname{Var}Z_{1}}{n\varepsilon^{2}}.$$
(3.44)

¹¹For a proof, see, e.g., H.-O. Georgii: *Stochastik.* Berlin: de Gruyter (2002)

Moreover (strong law),

$$\mathbb{P}\left(\lim_{n \to \infty} \frac{1}{n} \sum_{j=1}^{n} Z_j = \mathbb{E}Z_1\right) = 1.$$
(3.45)

There also exist variants of the statement with weaker assumptions. Clearly, the hypothesis "independent" in Theorem 5 can be replaced by $\operatorname{Cov}(1_{X_j \in A_i}, 1_{X_k \in A_i}) = 0$, and in the formulation around (3.44) by $\operatorname{Cov}(Z_j, Z_k) = 0$; also for the strong LLN it suffices that $\operatorname{Cov}(Z_j, Z_k) = 0$. Similar statements can be formulated when the Z_j have different distributions, and they still hold when $\operatorname{Cov} = 0$ is replaced by "Cov small."

4 The Maxwellian Distribution

4.1 Pressure

At this point, let us draw a rather simple but also somewhat subtle consequence of the Maxwellian (3.31) and compute, in a non-rigorous way, the pressure exerted by the molecules on the wall $\partial \Lambda$ of the container Λ . The pressure is the force (that the molecules bouncing off the wall exert on the wall) per area, more precisely the component of the force normal (orthogonal) to the wall; the force is best thought of as the momentum transferred per time. In the hard sphere model, the actual momentum transferred between t = 0 and t = T, $P_n(T)$ is a step function of T (and its time density therefore a sum of delta peaks), with one step (one peak) per molecule bouncing off. So we average over a time τ that is microscopically large but macroscopically small in the sense that very many molecules bounce off the wall during τ but τ is very short for humans, and consider $P_n(\tau)/\tau$. Consider a piece W of the wall that is large enough so that still very many collisions with it occur during τ and small enough so that it can be regarded as approximately flat. So we take W to be a piece of a plane, for simplicity of the plane $\{q_1 = 0\}$, with the interior of the container on the $q_1 > 0$ side. Assuming that the particles are uniformly distributed in position space and that the distribution in velocity is Maxwellian (with position-independent temperature), the number of molecules with velocity in a given volume element $d^3 \boldsymbol{v}$ around \boldsymbol{v} in velocity space and in a given volume element $d^3 q$ around q in position space is approximately

$$\frac{N}{\operatorname{vol}(\Lambda)}\rho(\boldsymbol{v})\,d^3\boldsymbol{x}\,d^3\boldsymbol{v}\,,\tag{4.1}$$

assuming that $d^3 \boldsymbol{x}$ and $d^3 \boldsymbol{v}$ are large enough to contain many molecules. The expression (4.1) can be regarded as an application of the law of large numbers. Among the balls with velocity in $d^3 \boldsymbol{v}$, which ones will hit W within time τ ? Those within the slanted prism over W with height τv_1 , which has volume $\operatorname{area}(W)\tau v_1$. How many are they? The integral of (4.1) in \boldsymbol{x} over the prism, which is, due to the uniformity in \boldsymbol{x} ,

$$\frac{N}{\operatorname{vol}(\Lambda)}\rho(\boldsymbol{v})\operatorname{area}(W)\tau v_1 d^3\boldsymbol{v}.$$
(4.2)

For each ball, the normal component of the momentum transferred is $2mv_1$ because the ball's momentum changes from $m(v_1, v_2, v_3)$ to $m(-v_1, v_2, v_3)$ at collision. Thus, keeping in mind that only \boldsymbol{v} 's with $v_1 < 0$ can contribute to the pressure, the total normal momentum transferred is

$$P_n(\tau) = \int_{-\infty}^0 dv_1 \int_{\mathbb{R}} dv_2 \int_{\mathbb{R}} dv_3 \, 2mv_1 \frac{N}{\operatorname{vol}(\Lambda)} \rho(\boldsymbol{v}) \operatorname{area}(W) \tau \, v_1 \tag{4.3}$$

$$= \frac{mN\operatorname{area}(W)\,\tau}{\operatorname{vol}(\Lambda)} \int_{\mathbb{R}^3} d^3 \boldsymbol{v} \, v_1^2\,\rho(\boldsymbol{v})\,. \tag{4.4}$$

The force is $P_n(\tau)/\tau$, and the pressure p is force/area, so

$$p = \frac{mN}{\operatorname{vol}(\Lambda)} \int_{\mathbb{R}^3} v_1^2 \,\rho(\boldsymbol{v}) \,d^3\boldsymbol{v} \,. \tag{4.5}$$

From the covariance matrix (3.32) of the Maxwellian, which is C = (kT/m)I, we read off that the variance of v_1 is kT/m; since the expectation of v_1 is 0, the average of v_1^2 must be

$$\langle v_1^2 \rangle = \frac{kT}{m} \,. \tag{4.6}$$

Thus,

$$p = \frac{mN}{\operatorname{vol}(\Lambda)} \frac{kT}{m} = \frac{NkT}{\operatorname{vol}(\Lambda)}, \qquad (4.7)$$

or, with the symbol V common in thermodynamics for $vol(\Lambda)$,

$$pV = NkT. (4.8)$$

This equation is known in thermodynamics as the *state equation of the ideal gas*. As a by-product, it also follows that the average kinetic energy of the molecules,

$$\overline{e} = \int \frac{m}{2} \boldsymbol{v}^2 \,\rho(\boldsymbol{v}) \,d^3 \boldsymbol{v} \,, \tag{4.9}$$

is given by

$$\overline{e} = \frac{3}{2}m \int v_1^2 \rho(\mathbf{v}) \, d^3 \mathbf{v} = \frac{3}{2}m \frac{kT}{m} = \frac{3}{2}kT \,.$$
(4.10)

Daniel Bernoulli (1700–1782) conjectured in his 1738 book *Hydrodynamica* that there is a ceaseless unordered motion of the atoms which causes the phenomenon of pressure; he figured out, as we just did in (4.5), that pV is proportional to the average kinetic energy \overline{e} of the molecules, and concluded that the average kinetic energy must be proportional to the temperature. Empirically, the ideal gas law (4.8) is well confirmed for dilute gases. For our purposes, the derivation of (4.8) confirms that the parameter T in the Maxwellian distribution is indeed temperature, as (4.8) forms the basis of a standard way of measuring temperature (the "gas thermometer").

4.2 The Maxwellian as a Marginal Distribution

We can say something about the reasons behind the Maxwellian. For simplicity, we consider an ideal gas. The expression *ideal gas* means a gas consisting of molecules that do not interact at all, neither through a Coulomb potential nor through hard-sphere collisions or anything else. For an ideal gas of N molecules in a container $\Lambda \subset \mathbb{R}^3$, the phase space is $\Gamma = \Lambda^N \times \mathbb{R}^{3N}$, and the Hamiltonian (in the interior of Λ) is simply given by

$$H = \sum_{k=1}^{N} \frac{p_k^2}{2m} \,. \tag{4.11}$$

Since energy is conserved, the phase point always stays on the surface of constant energy,

$$\Gamma_E = \left\{ (q, p) \in \Gamma : H(q, p) = E \right\}.$$
(4.12)

In our case,

$$\Gamma_E = \Lambda^N \times \mathbb{S}^{3N-1}_{\sqrt{2mE}}, \qquad (4.13)$$

where

$$\mathbb{S}_R^{d-1} = \{ \boldsymbol{x} \in \mathbb{R}^d : |\boldsymbol{x}| = R \}$$
(4.14)

is the sphere (around the origin) in \mathbb{R}^d of radius R. Since positions will play no role in the following, we drop the position variables and consider just the momentum space \mathbb{R}^{3N} . So the sphere $\mathbb{S}^{3N-1}_{\sqrt{2mE}}$ now plays the role of the energy surface.

Now the first three components of a random vector on \mathbb{S}_R^{d-1} have approximately a Gaussian distribution $\mathcal{N}^3(\mathbf{0}, R^2 d^{-1}I)$ (with I the 3×3 unit matrix) as $d \to \infty$. That is, let u_R^{d-1} be the normalized uniform measure on \mathbb{S}_R^{d-1} , i.e., the (d-1)-dimensional surface area measure divided by the surface area of the whole sphere. It is the unique rotationally invariant probability measure on the sphere. Then for large d the 3-dimensional marginal of u_R^{d-1} is close to $\mathcal{N}^3(\mathbf{0}, R^2 d^{-1}I)$. More precisely:

Theorem 7. Let $\sigma > 0$ be a constant, $k \in \mathbb{N}$ fixed, and $\rho_{\text{Gauss}} : \mathbb{R}^k \to \mathbb{R}$ the density of $\mathcal{N}^k(\mathbf{0}, \sigma^2 I)$. Consider d > k and $(X_1, \ldots, X_d) \sim u_R^{d-1}$ with $R = \sigma \sqrt{d}$. The marginal distribution $\mu_{k,d}$ of X_1, \ldots, X_k is absolutely continuous (relative to Lebesgue measure) with density $\rho_{k,d}$, and

$$\left\|\rho_{k,d} - \rho_{\text{Gauss}}\right\|_{L^1(\mathbb{R}^k)} \to 0 \tag{4.15}$$

as $d \to \infty$.

Before I give the proof, let me point out why this convergence is not surprising. Let Z_1, \ldots, Z_d be i.i.d. $\mathcal{N}(0, 1)$ -distributed, so $\mathbf{Z} = (Z_1, \ldots, Z_d) \sim \mathcal{N}^d(\mathbf{0}, I)$. Then $R\mathbf{Z}/|\mathbf{Z}| \in \mathbb{S}_R^{d-1}$, and its distribution is rotationally invariant, so it must be u_R^{d-1} . So we can think of $\mathbf{X} = (X_1, \ldots, X_d)$ as generated this way. For large d, since $|\mathbf{Z}|^2 = Z_1^2 + \ldots + Z_d^2$ is a sum of many i.i.d. random variables, the law of large numbers in the form (3.44) (with Z_j replaced by Z_j^2 and $\mathbb{E}Z_1$ by $\mathbb{E}Z_1^2 = 1$) entails that $|\mathbf{Z}|^2$ is very probably close to d, and thus $R/|\mathbf{Z}|$ close to σ , and thus (for $j = 1, \ldots, k$) $X_j = RZ_j/|\mathbf{Z}|$ close to σZ_j . Theorem 7 makes precise the type of convergence (L^1 or, equivalently, total variation distance).

Proof of Theorem 7. As shown in a homework exercise, the exact k-marginal of the uniform distribution on \mathbb{S}_{R}^{d-1} has density

$$\rho_{k,d,R}(\boldsymbol{x}) = \frac{A_{d-k}}{A_d R^{d-2}} \mathbf{1}_{\boldsymbol{x}^2 \le R^2} \left(R^2 - \boldsymbol{x}^2\right)^{(d-k)/2-1}.$$
(4.16)

Lemma 1. If ρ_d and ρ are normalized densities on \mathbb{R}^k and ρ_d converges uniformly to ρ as $d \to \infty$, then $\rho_d \to \rho$ also in L^1 , $\|\rho_d - \rho\|_{L^1(\mathbb{R}^k)} \to 0$ as $d \to \infty$.

Proof of Lemma 1. Let $0 < \varepsilon < 1$. Choose a ball *B* large enough so that $\int_B \rho > 1-\varepsilon$. By the uniform convergence, there is d_0 such that for $d \ge d_0$, $|\rho_d(\boldsymbol{x}) - \rho(\boldsymbol{x})| < \varepsilon / \operatorname{vol}(B)$ for all $\boldsymbol{x} \in \mathbb{R}^k$, therefore $\int_B |\rho_d - \rho| < \varepsilon$. As a consequence, $\int_B (-\rho_d + \rho) < \varepsilon$, so $\int_B \rho_d > 1-2\varepsilon$, and by normalization $\int_{B^c} \rho_d < 2\varepsilon$. Thus, $\int_{B^c} |\rho_d - \rho| < 3\varepsilon$ and $\int_{\mathbb{R}^k} |\rho_d - \rho| < 4\varepsilon$. Since ε was arbitrary, we obtain that $\|\rho_d - \rho\|_{L^1} \to 0$.

Lemma 2. Leaving aside the normalizing factors,

$$\tilde{\rho}_{k,d}(\boldsymbol{x}) := \mathbf{1}_{\boldsymbol{x}^2 \le \sigma^2 d} \left(1 - \frac{\boldsymbol{x}^2}{\sigma^2 d} \right)^{-k/2 - 1} \left(1 - \frac{\boldsymbol{x}^2/2\sigma^2}{d/2} \right)^{d/2} \longrightarrow e^{-\boldsymbol{x}^2/2\sigma^2} =: \tilde{\rho}(\boldsymbol{x}) \quad (4.17)$$

uniformly as $d \to \infty$.

Proof of Lemma 2. It is known that

$$\left(1+\frac{x}{n}\right)^n \to e^x \text{ as } n \to \infty \text{ uniformly on every compact set in } \mathbb{R}$$
 (4.18)

(in fact, also if we allow non-integer n). It is clear that $\tilde{\rho}_{k,d} \to \tilde{\rho}$ pointwise, and the remaining work is to show that the convergence is uniform.

For given $0 < \varepsilon < 1$, choose r > 0 so large that $\exp(-r^2/2\sigma^2) < \varepsilon/3$. Then for $|\mathbf{x}| \ge r, \, \tilde{\rho}(\mathbf{x}) < \varepsilon/3$ and

$$\tilde{\rho}_{k,d}(\boldsymbol{x}) \le \tilde{\rho}_{k,d}(r,0,\ldots,0) \le \tilde{\rho}(r,0,\ldots,0) + \frac{\varepsilon}{3}$$
(4.19)

from some d_0 onwards because of the pointwise convergence. (Note that d_0 depends on r but not on \boldsymbol{x} .) Thus,

$$\left|\tilde{\rho}_{k,d}(\boldsymbol{x}) - \tilde{\rho}(\boldsymbol{x})\right| \leq \tilde{\rho}_{k,d}(\boldsymbol{x}) + \tilde{\rho}(\boldsymbol{x}) < \varepsilon.$$
(4.20)

Let us turn to $|\boldsymbol{x}| \leq r$. For $d > r^2/\sigma^2$, the first factor in (4.17) equals 1, the second lies between 1 and

$$\left(1 - \frac{r^2}{\sigma^2 d}\right)^{-k/2-1} \tag{4.21}$$

and thus converges uniformly to 1, and the last factor converges uniformly to $\tilde{\rho}(\boldsymbol{x})$ by virtue of (4.18). Therefore, from some d'_0 onwards, $|\tilde{\rho}_{k,d}(\boldsymbol{x}) - \tilde{\rho}(\boldsymbol{x})| < \varepsilon$ on $B_r(\boldsymbol{0})$ and thus, with (4.20), on \mathbb{R}^k .

We now continue with the proof of Theorem 7. First, we need to check that the normalizing factor $\mathscr{N}_{k,d}$ of $\tilde{\rho}_{k,d}$ converges to the normalizing factor \mathscr{N} of $\tilde{\rho}$. Indeed, since (homework exercise)

$$A_d = \frac{2\pi^{d/2}}{\Gamma(d/2)}$$
(4.22)

with Γ the Gamma function,

$$\mathcal{N}_{k,d} = \frac{A_{d-k}}{A_d} \sigma^{-k} d^{-k/2} = (2\pi\sigma^2)^{-k/2} \left(\frac{2}{d}\right)^{k/2} \frac{\Gamma(d/2)}{\Gamma(\frac{d-k}{2})}.$$
(4.23)

Since $\Gamma(x+1) = x\Gamma(x)$, we obtain for even k = 2n that

$$\left(\frac{2}{d}\right)^{k/2} \frac{\Gamma(d/2)}{\Gamma(\frac{d-k}{2})} = \left(\frac{2}{d}\right)^n \left(\frac{d}{2} - 1\right) \left(\frac{d}{2} - 2\right) \cdots \left(\frac{d}{2} - n\right) \longrightarrow 1 \quad \text{as } d \to \infty, \tag{4.24}$$

and for odd k = 2n + 1 that

$$\left(\frac{2}{d}\right)^{k/2} \frac{\Gamma(d/2)}{\Gamma(\frac{d-k}{2})} = \left(\frac{2}{d}\right)^{1/2} \left(\frac{2}{d}\right)^n \left(\frac{d}{2}-1\right) \left(\frac{d}{2}-2\right) \cdots \left(\frac{d}{2}-n\right) \frac{\Gamma(\frac{d-2n}{2})}{\Gamma(\frac{d-2n-1}{2})} \longrightarrow 1 \quad (4.25)$$

because it is $known^{12}$ that

$$\lim_{n \to \infty} \frac{\Gamma(n+1/2)}{\Gamma(n)\sqrt{n}} = 1$$
(4.26)

(in fact, also if we allow non-integer n). Thus $\mathscr{N}_{k,d} \to (2\pi\sigma^2)^{-k/2} = \mathscr{N}$, as claimed.

It follows further that the normalized version of $\tilde{\rho}_{k,d}$, which is $\rho_{k,d,\sigma\sqrt{d}}$, converges uniformly to the normalized version of $\tilde{\rho}$, which is ρ_{Gauss} . By Lemma 1, it also converges in the L^1 norm.

Let us state the implication of Theorem 7 for the Maxwellian: For a purely random phase point, the distribution of v_i is Maxwellian.

More precisely, fix the average energy per molecule \overline{e} , consider a large number N of particles, and set the energy $E = N\overline{e}$. For a purely random phase point X = (Q, P) on Γ_E (i.e., uniformly distributed), Q and P are independent, Q is uniformly distributed in Λ^N and $P \sim u_R^{3N-1}$ with $R = \sqrt{2mE} = \sqrt{2mN\overline{e}}$. The distribution of the momentum p_1 of particle 1 (or, by permutation symmetry, of any other particle) is thus $\mathcal{N}^3(\mathbf{0}, \frac{2\overline{e}}{3m}I)$, which means that $\mathbf{v}_1 \sim \mathcal{N}^3(\mathbf{0}, \frac{2\overline{e}}{3m}I)$, which is the Maxwellian (3.31) by virtue of (4.10).

4.3 The Maxwellian as the Typical Empirical Distribution

We can make an even stronger statement that gives a more serious explanation of why the Maxwellian occurs: For most points on $\mathbb{S}_{\sqrt{2mE}}^{3N-1}$ in momentum space with large N, the empirical distribution of the velocities is close to the Maxwellian. This statement is a variant of the weak LLN. Here is a precise formulation with the notation \mathbf{X}_{Nj} for the \mathbb{R}^3 -valued random variable that is the momentum of particle j out of N particles.

Theorem 8. Let $\overline{e} > 0$ be a constant, $\mu = \mathcal{N}^3(\mathbf{0}, \frac{2}{3}m\overline{e}I)$ the Maxwellian distribution on momentum space \mathbb{R}^3 , and $\mathscr{A} = \{A_1, \ldots, A_r\}$ a partition of \mathbb{R}^3 . For any $N \in \mathbb{N}$, let $E = N\overline{e}$, $R = \sqrt{2mE}$, and $(\mathbf{X}_{N1}, \ldots, \mathbf{X}_{NN}) \sim u_R^{3N-1}$. Let (Y_{N1}, \ldots, Y_{Nr}) with $Y_{Ni} = \#\{k \leq N : \mathbf{X}_k \in A_i\}/N$ be the histogram of $(\mathbf{X}_{N1}, \ldots, \mathbf{X}_{NN})$ in terms of \mathscr{A} . For every $\varepsilon > 0$,

$$\mathbb{P}\Big(\forall i: |Y_{Ni} - \mu(A_i)| < \varepsilon\Big) \to 1 \tag{4.27}$$

as $N \to \infty$.

¹²See, e.g., Wikipedia, https://en.wikipedia.org/wiki/Gamma_function.

While the LLN as formulated in Theorem 5 assumed *independent* X_j , here we are dealing with *weakly dependent* X_j . The weakness of the dependence is visible from Theorem 7 for k = 6, which shows that X_1 and X_2 are approximately independent, or from the representation $X_k = RZ_k/|\mathbf{Z}|$ in the previous section, where $|\mathbf{Z}|$ is almost deterministic; it is plausible already since the condition $\sum_{k=1}^{3N} X_k^2 = 1$ should not put a strong demand on just a few of the X_k .

Proof. Let $P_{Ni} = \mathbb{P}(\mathbf{X}_{N1} \in A_i)$ be the distribution of \mathbf{X}_{Nk} in terms of \mathscr{A} . By Theorem 7,

$$P_{Ni} \to \mu(A_i) \quad \text{as } N \to \infty \,.$$
 (4.28)

As in the proof of Theorem 5, we have that $Y_{Ni} = N^{-1} \sum_{k=1}^{N} 1_{\mathbf{X}_k \in A_i}$ and $\mathbb{E}Y_{Ni} = P_{Ni}$. However, since the \mathbf{X}_j are no longer independent,

$$\operatorname{Var} Y_{Ni} = \operatorname{Cov}(Y_{Ni}, Y_{Ni}) \tag{4.29}$$

$$= N^{-2} \sum_{j,k=1}^{N} \operatorname{Cov}(1_{\boldsymbol{X}_{j} \in A_{i}}, 1_{\boldsymbol{X}_{k} \in A_{i}})$$
(4.30)

$$= N^{-2} \sum_{k=1}^{N} \operatorname{Var} \mathbf{1}_{\mathbf{X}_{k} \in A_{i}} + 2N^{-2} \sum_{1 \le j < k \le N} \operatorname{Cov}(\mathbf{1}_{\mathbf{X}_{j} \in A_{i}}, \mathbf{1}_{\mathbf{X}_{k} \in A_{i}})$$
(4.31)

$$= N^{-2} N \operatorname{Var} \mathbf{1}_{\mathbf{X}_{1} \in A_{i}} + N^{-2} (N^{2} - N) \operatorname{Cov}(\mathbf{1}_{\mathbf{X}_{1} \in A_{i}}, \mathbf{1}_{\mathbf{X}_{2} \in A_{i}})$$
(4.32)

$$\leq \frac{P_{Ni}(1-P_{Ni})}{N} + \left| \operatorname{Cov}(1_{\boldsymbol{X}_{1}\in A_{i}}, 1_{\boldsymbol{X}_{2}\in A_{i}}) \right|$$

$$(4.33)$$

$$\leq \frac{P_{Ni}(1 - P_{Ni})}{N} + \left| \mathbb{E}(1_{\mathbf{X}_{1} \in A_{i}} 1_{\mathbf{X}_{2} \in A_{i}}) - P_{Ni}^{2} \right|$$
(4.34)

$$= \frac{P_{Ni}(1 - P_{Ni})}{N} + \left| \mathbb{P}(\boldsymbol{X}_{1} \in A_{i}, \boldsymbol{X}_{2} \in A_{i}) - P_{Ni}^{2} \right|$$
(4.35)

$$= o(1) + o(1) \tag{4.36}$$

because,¹³ by Theorem 7 with k = 6,

$$\mathbb{P}(\boldsymbol{X}_1 \in A_i, \boldsymbol{X}_2 \in A_i) \to \mu(A_i)^2 \quad \text{for } N \to \infty.$$
(4.37)

We now have our tools together. Because of (4.28), we can choose N_0 so large that for all $N > N_0$ and all i = 1, ..., r, $|P_{Ni} - \mu(A_i)| < \varepsilon/2$. Thus, using the Chebyshev inequality, we obtain for $N > N_0$ that the event complementary to the one in (4.27) has

¹³The notation o(f(N)) denotes any sequence x_N such that $x_N/f(N) \to 0$ as $N \to \infty$. So o(1) means some sequence that tends to 0.

probability

$$\mathbb{P}\Big(\bigcup_{i=1}^{r} \Big\{ |Y_{Ni} - \mu(A_i)| \ge \varepsilon \Big\} \Big) \le \mathbb{P}\Big(\bigcup_{i=1}^{r} \Big\{ |Y_{Ni} - P_{Ni}| + |P_{Ni} - \mu(A_i)| \ge \varepsilon \Big\} \Big)$$
(4.38)

$$\leq \mathbb{P}\Big(\bigcup_{i=1}^{r} \Big\{ |Y_{Ni} - P_{Ni}| \geq \varepsilon/2 \Big\} \Big)$$
(4.39)

$$\leq \sum_{i=1}^{r} \mathbb{P}\Big(|Y_{Ni} - P_{Ni}| \geq \varepsilon/2\Big) \tag{4.40}$$

$$\leq \sum_{i=1}^{r} \frac{\operatorname{Var} Y_{Ni}}{\varepsilon^2/4} \tag{4.41}$$

$$= r o(1) = o(1), \qquad (4.42)$$

as $N \to \infty$, which proves (4.27).

Theorem 8 can be summarized by saying that *the Maxwellian is typical*; that is why such a kind of theorem is also called a *typicality theorem*. Here is a summary in the words of Boltzmann (1896):

... der Fall, dass alle Moleküle genau die gleiche, gleichgerichtete Geschwindigkeit haben, [ist] um kein Haar unwahrscheinlicher als der Fall, dass jedes Molekül genau die Geschwindigkeit und Geschwindigkeitsrichtung hat, die es wirklich in einem bestimmten Momente im Gase hat. Vergleichen wir aber die erstere Eventualität mit der, dass im Gase die Maxwell'sche Geschwindigkeitsvertheilung herrscht, so finden wir wieder, dass zu Gunsten der letzteren Eventualität viel mehr gleichmögliche Fälle sprechen.

Translation:

The case that all molecules have exactly the same velocity in the same direction is no more improbable than the case that every molecule have exactly the velocity and direction that it actually has in the gas in a certain instant. However, if we compare the former case to the case that the Maxwellian distribution of velocities applies, then we find again that the latter case comprises many more equally possible cases.

Theorem 8 provides a certain type of explanation of the Maxwellian, using that the particle number N in a gas is large: If the phase point of a gas is just "any old phase point," if there is nothing special about it, then the empirical distribution of the velocities will be Maxwellian with temperature $T = \frac{2}{3k}\overline{e}$, where $\overline{e} = E/N$ and Eis whatever the energy of the phase point happens to be. Most phase points behave like that, where "most" means the overwhelming majority in terms of the size of sets (quantified here by the uniform measure u_R^{3N-1}). One might have thought that since $e^{-mv^2/2kT}$ is just one particular function among

One might have thought that since $e^{-mv^2/2kT}$ is just one particular function among an infinitude of possible functions, it should be a very special situation, a rare exception,

that the velocity statistics will have this particular form. But on the contrary, it is a rare exception among phase points that the velocity statistics should *differ* significantly from this form. If we know nothing about the actual phase point, the velocity statistics we should expect is the Maxwellian. And if we encounter a gas with Maxwellian velocity statistics, then no further reason is needed for why this is so: this is just what happens "by chance alone."

5 Probability Spaces in Classical Mechanics

In a terminology going back to the influential book *Elementary Principles in Statistical Mechanics* (1902) by Josiah Willard Gibbs (1839–1903), probability measures in phase space are called *ensembles* (and often associated with a picture of a huge number of systems whose different phase points have, roughly speaking, this measure as their empirical distribution). Two basic ensembles he introduced were the ones he called the *micro-canonical ensemble* and the *canonical ensemble*, which I will discuss in this section.

The uniform distribution $u_{\sqrt{2mE}}^{3N-1}$ over a sphere in velocity space is an instance of the micro-canonical ensemble. Generally, the micro-canonical ensemble can be thought of as the uniform normalized measure over a surface Γ_E of constant energy E in phase space.

The canonical ensembles are a family of measures with density function

$$\rho_{\rm can}(x) = \frac{1}{Z} e^{-\beta H(x)} \tag{5.1}$$

(relative to phase space volume), parameterized by the *inverse temperature* $\beta = kT$. Here, H is the Hamiltonian, and the normalizing factor $Z = Z(\beta)$ is called the *partition function*. We will discuss the micro-canonical and canonical ensembles in more detail below.

5.1 Liouville's Theorem

Consider a Hamiltonian system with phase space \mathbb{R}^{2r} and smooth Hamiltonian function H(q, p), and suppose that every solution exists globally in time. For this it is sufficient, for example, that the level sets of H be compact. Then the flow map T^t exists for all t, and is a bijection $\mathbb{R}^{2r} \to \mathbb{R}^{2r}$ for every t.

Theorem 9 (Liouville's theorem). The flow preserves phase space volume: For any $A \subseteq \mathbb{R}^{2r}$,

$$\operatorname{vol}_{2r}(T^t A) = \operatorname{vol}_{2r}(A) \,. \tag{5.2}$$

Here is a more general version of this statement for dynamical systems in \mathbb{R}^d , defined by the equation dx/dt = F(x) (without explicit time dependence). Suppose that all solutions exists globally in time, and let T^t be again the flow map, $T^t(x(0)) = x(t)$.

Theorem 10. If $\nabla \cdot F = 0$, then T^t preserves volume.

Proof. For small t, the asymptotics of the flow map is¹⁴

$$T^{t}(x) = x + F(x)t + O(t^{2}).$$
(5.3)

¹⁴The notation O(f(t)) denotes any function g(t) such that g(t)/f(t) stays bounded in the relevant limit (here, $t \to 0$). So, $O(t^2)$ means some function that shrinks at least as fast as t^2 .

Fix $A \subseteq \mathbb{R}^d$, and let $v(t) = \operatorname{vol}_d(T^t A)$. We show first that

$$\left. \frac{dv}{dt} \right|_{t=0} = \int_A d^d x \, \nabla \cdot F \,. \tag{5.4}$$

Indeed, for any t the transformation formula for changing variables in a multiple integral yields

$$v(t) = \int_{A} d^{d}x \left| \det \frac{\partial T^{t}x}{\partial x} \right|.$$
(5.5)

For small t, the Jacobian matrix is

$$\frac{\partial T^t x}{\partial x} = I + \frac{\partial F}{\partial x} t + O(t^2) \,. \tag{5.6}$$

Now, for any square matrix M,

$$\det(I + Mt) = 1 + t \text{ tr } M + O(t^2) \quad \text{as } t \to 0.$$
(5.7)

(Use the Leibniz expansion formula

$$\det A = \sum_{\sigma \in S_d} \operatorname{sign}(\sigma) \prod_{i=1}^d a_{\sigma(i),i}$$
(5.8)

and sort by powers of t.)

In particular, the Jacobian determinant is positive for sufficiently small t (so the absolute bars in (5.5) can be dropped), and

$$\det \frac{\partial T^t x}{\partial x} = 1 + t \operatorname{tr} \frac{\partial F}{\partial x} + O(t^2)$$
(5.9)

$$= 1 + t \sum_{i=1}^{d} \frac{\partial F_i}{\partial x_i} + O(t^2)$$
(5.10)

$$= 1 + t\nabla \cdot F + O(t^2), \qquad (5.11)$$

and therefore,

$$v(t) = \int_{A} d^{d}x \left(1 + t \nabla \cdot F + O(t^{2}) \right), \qquad (5.12)$$

which proves (5.4). If $\nabla \cdot F$ vanishes everywhere, it follows that v(t) is constant. \Box *Proof of Theorem 9.* In the special case of a Hamiltonian system, we obtain that

$$\nabla \cdot F = \sum_{i=1}^{r} \left[\frac{\partial}{\partial q_i} \frac{\partial H}{\partial p_i} + \frac{\partial}{\partial p_i} \left(-\frac{\partial H}{\partial q_i} \right) \right] = 0.$$
 (5.13)
Corollary 2. Let T^t be again the flow map of the ODE dx/dt = F(x), and let x(0) be chosen randomly with probability density ρ_0 . Then the probability density ρ_t of x(t) obeys the continuity equation¹⁵

$$\frac{\partial \rho_t(x)}{\partial t} = -\sum_{i=1}^d \frac{\partial}{\partial x_i} \left(\rho_t(x) F_i(x) \right).$$
(5.14)

Proof. For every $A \subseteq \mathbb{R}^d$, those trajectories arrive in A at time t that started in $T^{-t}A$, so

$$\int_{A} d^{d} y \,\rho_{t}(y) = \int_{T^{-t}A} d^{d} x \,\rho_{0}(x) \,. \tag{5.15}$$

On the other hand, by the transformation formula for integrals with $y = T^t x$,

$$\int_{A} d^{d}y \,\rho_{t}(y) = \int_{T^{-t}A} d^{d}x \,\rho_{t}(T^{t}x) \left| \det \frac{\partial T^{t}x}{\partial x} \right|, \qquad (5.16)$$

with the Jacobian determinant for small t again given by (5.11). Since A is arbitrary, the integrands must be equal,

$$\rho_0(x) = \rho_t(T^t x) \left(1 + t \nabla \cdot F(x) + O(t^2) \right),$$
(5.17)

 \mathbf{SO}

$$\frac{\rho_t(T^t x) - \rho_0(x)}{t} \xrightarrow{t \to 0} -\rho_0(x) \nabla \cdot F(x)$$
(5.18)

while also

$$\frac{\rho_t(T^t x) - \rho_0(x)}{t} \xrightarrow{t \to 0} \left(\partial_t \rho_t(x) + F(x) \cdot \nabla \rho_t(x) \right) \Big|_{t=0}$$
(5.19)

by the chain rule.

For Hamiltonian systems defined on a manifold M, a notion of volume is not automatically given. However, Hamiltonian systems come equipped with a symplectic form ω , a 2-form that defines a natural notion of volume as follows. If the dimension of M is 2r, then the r-fold exterior product of ω ,

$$\varepsilon = \omega \wedge \omega \wedge \ldots \wedge \omega \tag{5.20}$$

defines a 2r-form or volume form which is non-degenerate, and thus a measure

$$\mu(A) = \int_{A} \varepsilon \tag{5.21}$$

that can be regarded as the volume. In $M = \mathbb{R}^{2r}$ with

$$\omega = \begin{pmatrix} 0 & I \\ -I & 0 \end{pmatrix}, \tag{5.22}$$

¹⁵The name "continuity equation" has stuck although it does not fit, as the equation expresses a local conservation law, not continuity.

we obtain that

$$= dq_1 \wedge dp_1 \wedge dq_2 \wedge dp_2 \wedge \ldots \wedge dq_r \wedge dp_r, \qquad (5.23)$$

and μ is just the Lebesgue measure. The flow map preserves the symplectic form and thus also the volume form ε and the volume measure μ .

For systems for which not every trajectory exists globally in time, it can happen that volume is *not* preserved. In fact, this happens if the set of phase points for which the solution does not exist globally in time has positive measure. For the billiard system that we considered in Section 2.7, those "bad" phase points have measure zero, and thus volume is preserved ("Liouville's theorem holds").¹⁶

One often says that the Lebesgue measure is *invariant* under the time evolution. As a consequence of Liouville's theorem, the canonical measure is also invariant under the time evolution. That is because the density $\rho(x) \propto e^{-\beta H(x)}$ depends on the phase point x only through H(x), which is conserved, so ρ is constant along every trajectory. More generally, any measure whose density depends on x only through conserved quantities will be invariant.

5.2 The Micro-Canonical Ensemble

ε

The micro-canonical measure is intended to be the uniform normalized measure, either on an *energy surface*

$$\Gamma_E = \left\{ x \in \Gamma : H(x) = E \right\}$$
(5.24)

or on an *energy shell*

$$\Gamma_{E,\Delta E} = \left\{ x \in \Gamma : E \le H(x) \le E + \Delta E \right\}$$
(5.25)

with thickness ΔE that is taken to be small, particularly in comparison to E. It is sometimes intended to be the resolution of energy when "measured macroscopically."

On the energy shell, it is easy to say what the uniform measure $\mu_{\rm mc}$ is, provided that $\operatorname{vol}(\Gamma_{E,\Delta E}) < \infty$. (This phase space volume is finite if the system is confined to a finite 3-volume $\Lambda \subset \mathbb{R}^3$, and kinetic energy is a quadratic function of the momenta.) Then

$$\mu_{\rm mc}(A) = \frac{\operatorname{vol}(A \cap \Gamma_{E,\Delta E})}{\operatorname{vol}(\Gamma_{E,\Delta E})}, \qquad (5.26)$$

i.e., the volume restricted to $\Gamma_{E,\Delta E}$ and normalized. In the language of probability theory, $\mu_{\rm mc}$ is the *conditional distribution* (if the unconditional distribution vol is normalized), conditional on the event $E \leq H(x) \leq E + \Delta E$. Equivalently, $\mu_{\rm mc}$ is the measure with density

$$\rho_{\rm mc}(x) = \mathcal{N} \, \mathbf{1}_{E \le H(x) \le E + \Delta E} \,. \tag{5.27}$$

¹⁶Proofs are given in R.K. Alexander: Time evolution for infinitely many hard spheres. *Communications in Mathematical Physics* **49**: 217–232 (1976) and L.N. Vaserstein: On a system of particles with finite range and/or repulsive interactions. *Communications in Mathematical Physics* **69**: 35–56 (1979).

To obtain an appropriate measure μ_E on the energy surface Γ_E , we would like to take the limit $\Delta E \to 0$. Formally, we want to replace (5.27) by

$$\rho_{\rm mc}(x) = \mathcal{N}\,\delta(E - H(x)) \tag{5.28}$$

with δ the Dirac delta function. The measure μ_E should be the normalized "slices" of volume,

$$\mu_E(A) = \frac{\lambda_E(A)}{\lambda_E(\Gamma_E)}, \qquad (5.29)$$

where the λ_E can be defined by the property

$$\operatorname{vol}(A) = \int_{-\infty}^{\infty} dE \,\lambda_E(A \cap \Gamma_E) \tag{5.30}$$

for all $A \subseteq \Gamma$. This property actually determines the λ_E up to arbitrary changes on a null set of E values. In the language of probability theory, this procedure is called "conditioning on the null event H = E." The measure λ_E is in general not the same as ((2r-1)-dimensional) surface area. Rather, the density of λ_E is

$$\frac{d\lambda_E}{d\operatorname{area}_{\Gamma_E}}(x) = \frac{1}{|\nabla H(x)|}.$$
(5.31)

This can be visualized by thinking of an infinitesimal $\Delta E = dE$ and noting that $\lambda_E(A \cap \Gamma_E) dE$ (the volume in this layer) should be surface area times the thickness of the layer. And the thickness at x is $|\nabla H(x)|^{-1} dE$ because ∇H is normal to Γ_E and

$$(\text{thickness}) \cdot |\nabla H(x)| = dE.$$
(5.32)

In the case of the ideal gas, $H = \sum_{i} p_i^2/2m$, the surface is $\Gamma_E = \Lambda^N \times \mathbb{S}_{\sqrt{2mE}}^{3N-1}$, and $|\nabla H|$ happens to be constant over Γ_E , so that μ_E happens to be proportional to surface area.

The measure μ_E is (also) called the micro-canonical measure. It is clearly invariant under the time evolution (as a limit $\Delta E \rightarrow 0$ of invariant measures).

Some further notation:

$$\Gamma_{\leq E} = \left\{ x \in \Gamma : H(x) \leq E \right\},\tag{5.33}$$

$$\gamma(E) = \frac{1}{N!} \operatorname{vol}(\Gamma_{\leq E}), \qquad (5.34)$$

$$\Omega(E) = \frac{d\gamma(E)}{dE} = \frac{1}{N!} \lambda_E(\Gamma_E) = \int \frac{dx}{N!} \,\delta(E - H(x)) \,. \tag{5.35}$$

The average of a function $Y: \Gamma \to \mathbb{R}$ over Γ_E can be expressed as

$$\langle Y \rangle_E = \frac{1}{\Omega(E)} \int \frac{dx}{N!} Y(x) \,\delta(E - H(x))$$
 (5.36)

$$= \frac{1}{\Omega(E)} \frac{d}{dE} \int_{\Gamma_{\leq E}} \frac{dx}{N!} Y(x) \,. \tag{5.37}$$

Since energy is conserved, investigations of the behavior of a classical system can often focus on just one energy surface Γ_E . Since the micro-canonical measure is such a natural and obvious choice of measure on this surface (being the analog of volume, and being preferred by the equations of motion as an invariant measure), it is often talked of in the literature as "the probability" on Γ_E . This language can be confusing and should not be taken too literally because there are situations in which the phase point cannot be regarded as random with distribution μ_E .

5.3 Measure-Preserving Dynamical Systems

Definition 6. A measure-preserving dynamical system in continuous time is $(\Omega, \mathscr{F}, \mathbb{P}, T)$, where $(\Omega, \mathscr{F}, \mathbb{P})$ is a probability space and T a flow on Ω (i.e., a mapping $T : \mathbb{R} \times \Omega \to \Omega$ with $T^0 = \text{id}$ and $T^s T^t = T^{s+t}$)¹⁷ such that

$$\mathbb{P}((T^t)^{-1}(A)) = \mathbb{P}(A)$$
(5.38)

for all $t \in \mathbb{R}$ and $A \in \mathscr{F}$.

A measure-preserving dynamical system in discrete time is $(\Omega, \mathscr{F}, \mathbb{P}, T)$, where $(\Omega, \mathscr{F}, \mathbb{P})$ is a probability space and $T : \Omega \to \Omega$ a bijection (with measurable T and T^{-1}) such that

$$\mathbb{P}(T^{-1}(A)) = \mathbb{P}(A)$$
(5.39)

for all $A \in \mathscr{F}$.

For a system in discrete time, it follows that (5.38) holds for all $t \in \mathbb{Z}$. The canonical and micro-canonical ensemble are, of course, instances of measure-preserving dyanmical system in continuous time.

Theorem 11 (Poincaré recurrence theorem). Let $(\Omega, \mathscr{F}, \mathbb{P}, T)$ be a measure-preserving dynamical system in either discrete or continuous time, and let A be a subset of Ω such that $\mathbb{P}(A) > 0$. Then for almost every $\omega \in A$ (i.e., except for a set of ω 's of \mathbb{P} -measure 0) there exist arbitrarily large t such that $T^t \omega \in A$.

Proof. First of all, if we prove this for all discrete-time systems then it also holds for continuous-time systems because we can simply restrict the values of t to the integer multiples of some time unit $\tau > 0$. A point $\omega \in A$ eventually returns to A if there is $k \ge 1$ for which $T^k \omega \in A$. Let B be the set of points of A which will never return to A; in particular, if $\omega \in B$, then $T^n \omega \notin B$ for all $n \ge 1$. Thus, $B \cap T^{-n}(B) = \emptyset$ and hence $T^{-k}(B) \cap T^{-n-k}(B) = \emptyset$ for all $n \ge 1$ and $k \ge 0$. So the sets $B, T^{-1}(B), T^{-2}(B), \ldots$ are pairwise disjoint and all have the same measure $\mathbb{P}(B)$. Since $\mathbb{P}(\Omega) = 1$, by additivity of the measure of disjoint sets, $\mathbb{P}(B)$ must be zero.

If $\omega \in A$ returns to A only a finite number of times ever, so that $T^n \omega \in A$ for some $n \geq 0$ but $T^k \omega \notin A$ for all k > n, then $T^n \omega \in B$ or $\omega \in T^{-n}(B)$. Thus, the points $\omega \in A$ that return to A only finitely often lie in the null set $\bigcup_{n=0}^{\infty} T^{-n}(B)$. \Box

¹⁷It follows that T^t is a bijection since $T^tT^{-t} = \mathrm{id} = T^{-t}T^t$.

The Poincaré recurrence theorem is surprising as it seems to imply that statistical mechanics can never reach its goal of deriving thermodynamics from mechanics ($Zer-melo's \ paradox$):

- For example, the "zeroth law of thermodynamics" asserts that every closed system sooner or later reaches thermal equilibrium and then remains there. Now let $M \subset \Gamma_E$ be the set of phase points in thermal equilibrium; it is not obvious which set that would be, but for all options, $M^c = \Gamma_E \setminus M$ has positive measure μ_E . Thus, it is impossible that phase points in $A = M^c$ reach M after a while and remain there, as they will return to A.
- For example, the second law of thermodynamics asserts that entropy increases, but does not decrease, with time. An instance of this is that heat flows from the hotter body to the cooler but not vice versa. However, regardless of which function $S: \Gamma_E \to \mathbb{R}$ entropy is, unless it is constant almost everywhere, there must be values S_0 such that both sets $\{x \in \Gamma_E : S(x) \leq S_0\}$ and $\{x \in \Gamma_E : S(x) > S_0\}$ have positive measure. If S(x(t)) increases from $\leq S_0$ to $> S_0$, and if the trajectory returns to $\{S(x) \leq S_0\}$, then S will also have to decrease.
- For example, suppose the initial phase point of a gas is such that all molecules (i.e., billiard balls) are located in the left half of the container Λ. The balls will soon be distributed over the whole container, but sooner or later the phase point will recur to the region (of positive measure) with all balls in the left half. That seems wrong, and a spontaneous concentration of a gas in the left half has never been observed.

The full answer to this puzzle, in particular with respect to entropy increase, will require a careful analysis later. But I will give away here that the right answer, given already by Boltzmann, is that there is no contradiction, and that it plays a role that the recurrence times are exorbitantly large. This means in particular that *thermal* equilibrium is not forever. Rather, a closed system may take a few hours to reach thermal equilibrium, then spend > 10^{1000} years in thermal equilibrium, and then suddenly depart from thermal equilibrium.

Another reasoning that seems to exclude a derivation of thermodynamics from mechanics is *Loschmidt's paradox*, which is based on time reversal: The mapping U: $(q, p) \mapsto (q, -p)$ of reversing velocities preserves phase space volume and maps Γ_E to itself (provided H is of the form $\sum p_i^2/2m_i + V(q)$), so it also preserves μ_E . Thus, for every set $A \subset \Gamma_E$ of phase points whose trajectories are macroscopically reasonable (and in agreement with the laws of thermodynamics) there is an equally large set U(A) of phase points whose trajectories are just the opposite. We will come back to this later.

5.4 Identical Particles

We often treat the molecules as just particles, that is, disregarding any internal structure they may have. If the particles in a given model are identical, then they have the same mass m and interact through the same pair potential V, so their motion is governed by the Hamiltonian

$$H = \frac{1}{2m} \sum_{j=1}^{N} \boldsymbol{p}_{i}^{2} + \sum_{j=1}^{N} V_{1}(\boldsymbol{q}_{j}) + \frac{1}{2} \sum_{j \neq k} V_{2}(\boldsymbol{q}_{j} - \boldsymbol{q}_{k}), \qquad (5.40)$$

a function on phase space $\Gamma = \mathbb{R}^{6N}$ which is symmetric under permutations of the particles. Since the particles are identical, no physical distinction can be made between points in phase space that differ only in the ordering of the particle phase points, such as

$$x = (x_1, \dots, x_N) \quad \text{and} x' = \sigma(x) = (x_{\sigma(1)}, \dots, x_{\sigma(N)}),$$
(5.41)

where $\sigma \in S_N$ is a permutation of the particle indices. That is, x and x' actually describe the same physical state because in reality particles are not numbered: There is no fact about which particle is particle 1. The numbering was, of course, just a mathematical convenience.

However, if that is so then the true phase space is not the ordered phase space \mathbb{R}^{6N} but rather an unordered phase space obtained by identifying phase points such as x and x'. As a mathematical definition of the unordered phase space, we can use the following. Let Γ_1 denote the 1-particle phase space. (In our case, $\Gamma_1 = \mathbb{R}^6$, but in other models we will want to allow other choices.) Then Γ_1^N (i.e., the N-fold Cartesian product) is the ordered phase space, and

$${}^{N}\Gamma_{1} := \left\{ x \subset \Gamma_{1} : \#x = N \right\}$$

$$(5.42)$$

the unordered phase space. The elements of ${}^{N}\Gamma_{1}$ are the N-element subsets of Γ_{1} . The mapping

$$\pi: (x_1, \dots, x_N) \mapsto \{x_1, \dots, x_N\}$$

$$(5.43)$$

that erases the ordering is defined on the set

$$\Gamma_1^{N\neq} = \left\{ (x_1, \dots, x_N) \in \Gamma_1^N : x_j \neq x_k \forall j \neq k \right\}$$
(5.44)

that has the coincidence phase points removed. Note that for hard spheres, the coincidence phase points are removed anyway, and for non-interacting point particles the possibility of ever running into a coincidence phase point has measure zero, so we will ignore them whenever that is convenient. (If we wanted to allow unordered phase points with coincidences, then we would have to replace the definition (5.42) by something more complicated.)

An equivalent definition of ${}^{N}\Gamma_{1}$ starts from $\Gamma_{1}^{N\neq}$ and divides out the action of the permutation group S_{N} given by (5.41),

$${}^{N}\Gamma_{1} = \Gamma_{1}^{N\neq} / S_{N} \,. \tag{5.45}$$

This means to identify x and x'; due to the exclusion of coincidences, every equivalence class actually has N! elements. This way of looking at ${}^{N}\Gamma_{1}$ has the advantage that one easily sees that ${}^{N}\Gamma_{1}$ inherits some structure from $\Gamma_{1}^{N\neq}$: If Γ_{1} is a manifold, then so is $\Gamma_{1}^{N\neq}$, and thus so is ${}^{N}\Gamma_{1}$ (because S_{N} acts in a good way, namely properly discontinuously and by diffeomorphisms). Note that π is then a local diffeomorphism (i.e., a diffeomorphism in every not-too-large region); in particular, $\boldsymbol{q}_{1}, \boldsymbol{p}_{1}, \ldots, \boldsymbol{q}_{N}, \boldsymbol{p}_{N}$ can serve as local coordinates (in an arbitrary but fixed ordering). If Γ_{1} is a Riemannian manifold (i.e., a manifold equipped with a Riemann metric $g_{\mu\nu}$) or a symplectic manifold, then so are $\Gamma_{1}^{N\neq}$ and ${}^{N}\Gamma_{1}$ (because the action of any $\sigma \in S_{N}$ preserves the metric or symplectic form).

Let us turn to the motion. As a consequence of the permutation symmetry of Newton's equation of motion (2.1), or more generally of the Hamiltonian (5.40), for any solution $t \mapsto x(t)$ and any $\sigma \in S_N$ also $t \mapsto \sigma(x(t))$ is a solution. That is, the numbering played no role. (If it did, that would have been a disaster because we do not actually know how we are supposed to number the particles.) As a consequence, the projection $t \mapsto \pi(x(t))$ to ${}^{N}\Gamma_{1}$ using the forgetful mapping (5.43) yields the same curve when we replace x(0) by $\sigma(x(0))$. Thus, all members of the equivalence class $\pi^{-1}(y)$ corresponding to an unordered configuration y lead to the same curve in ${}^{N}\Gamma_{1}$ starting at y. This curve is, in fact, the solution of Hamilton's equation of motion for the appropriate Hamiltonian function on ${}^{N}\Gamma_{1}$, which is $\pi_{*}H := H \circ \pi^{-1}$ ("H transported with π "); that function is well defined because H is permutation invariant. Since ${}^{N}\Gamma_{1}$ is the true phase space, $\pi_{*}H$ is the true Hamiltonian.

The upshot is that the use of Γ_1^N was merely rendundant but did not affect the motion, which is why it often does not receive attention. Let me quote a remark from Nino Zanghì:¹⁸

Misconceptions about identical particles: The fact that the phase space of N identical particles is ${}^{N}\Gamma_{1}$ and not Γ_{1}^{N} has usually been overlooked and is rarely mentioned in textbooks of classical mechanics and statistical mechanics. The textbooks tend to underline that the proper description of identical particles can be achieved only within the framework of quantum mechanics. The standard argument is something like this: Particles are identical if they cannot be distinguished by means of measurements. So, if particles have the same mass, charge, etc., they could be distinguished only by their location in space, as it is the case in classical mechanics. However, in quantum mechanics, particles do not have trajectories. Therefore they cannot be be distinguished if they have the same mass, charge, etc.. Thus the notion of identical particles is purely a quantum one without any classical equivalent. The conclusion is faulty and the argument is wrong.

The notion of identical particles was already recognized by Gibbs. In order to correctly calculate the entropy change in a process of mixing to identical fluids or gases (at the same temperature, etc.), Gibbs postulated

¹⁸From his course notes on Statistical Physics, available on his webpage http://www.ge.infn.it/ ~zanghi/. The clarification of the status of identical particles, both classical and quantum, is mainly due to J. Leinaas and J. Myrheim: On the theory of identical particles. *Il Nuovo Cimento* **37B**: 1–23 (1977).

that states differing only by permutations of identical particles should not be counted as distinct.

Here, "counting states" means assigning a measure to a set of points, which brings us to the question of measures on ${}^{N}\Gamma_{1}$. Any measure μ on Γ_{1}^{N} naturally projects to a measure $\pi_{*}\mu$ on ${}^{N}\Gamma_{1}$ according to

$$\pi_*\mu(A) = \mu(\pi^{-1}(A)) \tag{5.46}$$

for all $A \subseteq {}^{N}\Gamma_{1}$. Thus, there is a natural concept of volume in ${}^{N}\Gamma_{1}$ and of microcanonical measure on $\pi(\Gamma_{E})$. However, since $\pi_{*} \operatorname{vol}_{\Gamma_{1}^{N}}$ in a sense counts every point in ${}^{N}\Gamma_{1}$ repeatedly, in fact N! times, one defines

$$\operatorname{vol}_{N_{\Gamma_1}} = \frac{1}{N!} \pi_* \operatorname{vol}_{\Gamma_1^N} .$$
(5.47)

This also agrees with the volume in local coordinates $\boldsymbol{q}_1, \boldsymbol{p}_1, \ldots, \boldsymbol{q}_N, \boldsymbol{p}_N$. As a consequence, the micro-canonical "density" no longer assumes the form (with $\Omega(E) = (d/dE) \operatorname{vol}(\Gamma_{\leq E})/N!$)

$$\rho_{\rm mc}(x) = \frac{1}{N! \,\Omega(E)} \delta(E - H(x)) \tag{5.48}$$

that it had on Γ_1^N , but instead, on ${}^N\Gamma_1$,

$$\rho_{\rm mc}(x) = \frac{1}{\Omega(E)} \delta(E - \pi_* H(x)) \,. \tag{5.49}$$

That is why the factor N! was included in the definition of $\Omega(E)$: To ensure that $\Omega(E) dE$ is the physically appropriate phase space volume of the energy shell $E \leq H(x) \leq E + dE$.

In quantum mechanics, the difference between ordered and unordered configuration plays a bigger role than in classical mechanics, as it plays a role for the dynamics. The wave function $\psi(\boldsymbol{q}_1, \ldots, \boldsymbol{q}_N)$ is affected by the global properties of the configuration space. We will come back to this point when we discuss quantum mechanics.

5.5 Systems with a Variable Number of Particles

In many situations, one considers a variable number of particles:

- Due to chemical reactions, certain types of molecules disappear while other types of molecules appear.
- When considering a system defined to comprise the particles in a certain region Λ , then the number of particles can change simply because particles may enter or leave Λ .

The appropriate (unordered) phase space for a variable number of particles is

$$\Gamma = \bigcup_{N=0}^{\infty} {}^{N}\Gamma_{1} = \left\{ x \subset \Gamma_{1} : \# x < \infty \right\},$$
(5.50)

the set of finite subsets of Γ_1 . The obvious concept of volume in this space is

$$\operatorname{vol}(A) = \sum_{N=0}^{\infty} \operatorname{vol}_{{}^{N}\Gamma_{1}} \left(A \cap {}^{N}\Gamma_{1} \right)$$
(5.51)

for all $A \subseteq \Gamma$. (Note that this measure is rather far away from the intuitive idea of "volume.") Sometimes, one wishes to enjoy the simplicity that comes with *ordered* phase spaces and therefore uses instead the definitions

$$\Gamma_{\rm ord} = \bigcup_{N=0}^{\infty} \Gamma_1^N \tag{5.52}$$

and

$$\operatorname{vol}(A) = \sum_{N=0}^{\infty} \frac{1}{N!} \operatorname{vol}_{\Gamma_1^N} \left(A \cap \Gamma_1^N \right).$$
(5.53)

5.6 The Canonical Ensemble

The canonical ensemble for a system \mathscr{S} arises as the marginal distribution of the microcanonical ensemble μ_E (also called the Liouville measure) for a bigger system $\mathscr{S} \cup \mathscr{B}$ under the following assumptions:

- The system \mathscr{B} , called the *heat bath*, is an ideal gas with a large number $N = N_{\mathscr{B}}$ of particles.
- The interaction between ${\mathscr S}$ and ${\mathscr B}$ is negligible.¹⁹

This fact can be formulated as the following generalization of Theorem 7. (In fact, these assumptions can be relaxed; the marginal for \mathscr{S} will still be close to canonical if the assumptions are only approximately satisfied.)

Theorem 12. Let T > 0 be a constant, set $\beta = 1/kT$, and let system \mathscr{S} have phase space $\Gamma_{\mathscr{S}}$ and smooth Hamiltonian $H_{\mathscr{S}} : \Gamma_{\mathscr{S}} \to \mathbb{R}$ such that

$$Z = \int_{\Gamma_{\mathscr{S}}} dx_{\mathscr{S}} e^{-\beta H_{\mathscr{S}}(x_{\mathscr{S}})} < \infty \,.$$
(5.54)

The canonical density is defined to be $\rho_{can}(x_{\mathscr{S}}) = Z^{-1} \exp(-\beta H_{\mathscr{S}}(x_{\mathscr{S}}))$. For $N \in \mathbb{N}$, let system \mathscr{B} have phase space $\Gamma_{\mathscr{B}} = \Lambda^N \times \mathbb{R}^{3N}$ and Hamiltonian $H_{\mathscr{B}}(x_{\mathscr{B}}) = H_{\mathscr{B}}(q_{\mathscr{B}}, p_{\mathscr{B}}) = p_{\mathscr{B}}^2/2m$, and let $E = \frac{3}{2}NkT$. Consider, for the composite system $\mathscr{S} \cup \mathscr{B}$ with phase space $\Gamma = \Gamma_{\mathscr{S}} \times \Gamma_{\mathscr{B}}$ and Hamiltonian

$$H_{\mathscr{S}\cup\mathscr{B}}(x_{\mathscr{S}}, x_{\mathscr{B}}) = H_{\mathscr{S}}(x_{\mathscr{S}}) + H_{\mathscr{B}}(x_{\mathscr{B}}), \qquad (5.55)$$

¹⁹That is, in the computation that follows we treat the interaction energy as zero. At the same time, the physically relevant case is that the interaction energy is small but non-zero; this will lead to small perturbations away from the canonical ensemble which we ignore here. In the case in which the interaction is exactly zero, we are less interested in the micro-canonical ensemble for $\mathscr{S} \cup \mathscr{B}$, for reasons that we will discuss later in connection with ergodicity.

the micro-canonical measure μ_E . Its marginal distribution $\mu_{\mathscr{S},N}$ for \mathscr{S} is absolutely continuous with density $\rho_{\mathscr{S},N}(x_{\mathscr{S}})$, and

$$\left\|\rho_{\mathscr{S},N} - \rho_{\operatorname{can}}\right\|_{L^{1}(\Gamma_{\mathscr{S}})} \to 0 \tag{5.56}$$

as $N \to \infty$.

Proof. For $i = \mathscr{S}, \mathscr{B}, \mathscr{S} \cup \mathscr{B}$ we write $\Gamma_{\leq E}^{(i)} = \{x \in \Gamma_i : H_i(x) \leq E\}$. The \mathscr{S} -marginal of μ_E has density

$$\rho_{\mathscr{S},N}(x_{\mathscr{S}}) \propto \frac{\partial}{\partial E} \operatorname{vol}_{\mathscr{B}} \left\{ x_{\mathscr{B}} \in \Gamma_{\mathscr{B}} : H(x_{\mathscr{S}}, x_{\mathscr{B}}) \le E \right\}$$
(5.57)

$$= \frac{\partial}{\partial E} \operatorname{vol}_{\mathscr{B}} \left\{ x_{\mathscr{B}} \in \Gamma_{\mathscr{B}} : H_{\mathscr{S}}(x_{\mathscr{S}}) + H_{\mathscr{B}}(x_{\mathscr{B}}) \le E \right\}$$
(5.58)

$$= \frac{\partial}{\partial E} \operatorname{vol}_{\mathscr{B}} \Gamma^{(\mathscr{B})}_{\leq E - H_{\mathscr{S}}(x_{\mathscr{S}})}.$$
(5.59)

Now

$$\operatorname{vol}_{\mathscr{B}} \Gamma_{\leq E}^{(\mathscr{B})} = \operatorname{vol}(\Lambda)^N \operatorname{vol}_{3N}(B^{3N}_{\sqrt{2mE}})$$
(5.60)

$$= \operatorname{vol}(\Lambda)^{N} V_{3N} (2mE)^{3N/2}$$
(5.61)

with V_{3N} the volume of the unit ball in \mathbb{R}^{3N} . Thus, using $E = \frac{3}{2}NkT$ and allowing proportionality constants that can depend on N, m, and T but not on $x_{\mathscr{S}}$,

$$\rho_{\mathscr{S},N}(x_{\mathscr{S}}) \propto \left(E - H_{\mathscr{S}}(x_{\mathscr{S}})\right)^{3N/2-1} \tag{5.62}$$

$$= \left(\frac{3}{2}NkT - H_{\mathscr{S}}(x_{\mathscr{S}})\right)^{3N/2-1}$$
(5.63)

$$\propto \left(1 - \frac{H_{\mathscr{S}}(x_{\mathscr{S}})}{\frac{3}{2}NkT}\right)^{3N/2-1}$$
(5.64)

$$\longrightarrow \exp\left(-\frac{H_{\mathscr{S}}(x_{\mathscr{S}})}{kT}\right) \text{ as } N \to \infty.$$
 (5.65)

Now the claim follows in the same way as in the proof of Theorem 7.

A kind of equivalence of ensembles is visible here: If we started from a canonical (rather than micro-canonical) ensemble for $\mathscr{S} \cup \mathscr{B}$, then we would (easily!) have obtained a canonical ensemble for \mathscr{S} , so canonical or micro-canonical ensemble for $\mathscr{S} \cup \mathscr{B}$ yield the same consequence (canonical for \mathscr{S}). Indeed, if $\rho_{\mathscr{S} \cup \mathscr{B}}$ is canonical, then

$$\rho_{\mathscr{S}\cup\mathscr{B}}(x_{\mathscr{S}}, x_{\mathscr{B}}) = \frac{1}{Z} e^{-\beta(H_{\mathscr{S}}(x_{\mathscr{S}}) + H_{\mathscr{B}}(x_{\mathscr{B}}))}$$
(5.66)

$$=\frac{1}{Z}e^{-\beta H_{\mathscr{S}}(x_{\mathscr{S}})}e^{-\beta H_{\mathscr{B}}(x_{\mathscr{B}})},\qquad(5.67)$$

so the \mathscr{S} -marginal is clearly canonical, even without taking the limit $N \to \infty$.

The phenomenon of equivalence of ensembles has many aspects. It means that the two ensembles "behave similarly" in various ways, one of which is discussed in one of the homework exercises.

5.7 The Maxwell–Boltzmann Distribution

From the above statements about the marginal distribution one can also deduce typicality statements. The simplest case is the one of n non-interacting systems $\mathscr{S}_1, \ldots, \mathscr{S}_n$, perhaps together with a bath \mathscr{B} : If the phase point X of the composite system $\mathscr{S}_1 \cup \ldots \cup \mathscr{S}_n \cup \mathscr{B}$ obeys a canonical distribution

$$\rho_{\operatorname{can}}(x_1,\ldots,x_n,x_{\mathscr{B}}) = \frac{1}{Z} e^{-\beta(H_{\mathscr{S}}(x_1)+\ldots+H_{\mathscr{S}}(x_n)+H_{\mathscr{B}}(x_{\mathscr{B}}))}, \qquad (5.68)$$

then its components X_1, \ldots, X_N are i.i.d. with distribution

$$\rho_1(x) = \frac{1}{Z_{\mathscr{S}}} e^{-\beta H_{\mathscr{S}}(x)} \,. \tag{5.69}$$

If n is large (which would be expected to occur when each system \mathscr{S}_i is small, for example a single particle), then by the law of large numbers the empirical distribution is typically close to ρ_1 . In this case, ρ_1 is called the *Maxwell-Boltzmann distribution* of the phase point x_1 and forms a generalization of the Maxwellian velocity distribution.

Let us look at the case in which \mathscr{S}_i is a single particle with phase space $\Lambda \times \mathbb{R}^3$ and

$$H_{\mathscr{S}}(\boldsymbol{q},\boldsymbol{p}) = \frac{\boldsymbol{p}^2}{2m} + V_1(\boldsymbol{q}).$$
(5.70)

For $V_1 = 0$ we obtain the Maxwellian; for an external gravitational field, in the linear approximation

$$V_1(\boldsymbol{q}) = mgq_3 \tag{5.71}$$

(g = field strength), we obtain that

$$\rho_1(\boldsymbol{q}, \boldsymbol{p}) = \frac{1}{Z} e^{-\frac{mgq_3}{kT}} e^{-\frac{\boldsymbol{p}^2}{2mkT}}.$$
(5.72)

The physical statement about this formula is that it describes the joint statistics of \boldsymbol{q} and \boldsymbol{p} in thermal equilibrium at temperature T. It will be a recurrent theme that thermal equilibrium is the behavior that occurs for most phase points on Γ_E .

A few consequences of the Maxwell–Boltzmann formula (5.69):

- (a) The temperature is constant throughout the volume occupied by the system. The obvious fact that mountain tops are cooler than lower altitudes means that the atmosphere is actually not in thermal equilibrium.²⁰
- (b) The pressure p(q) at a boundary point $q \in \partial \Lambda$ can now vary. Applying Bernoulli's reasoning (4.5) locally, we obtain that

$$p(\boldsymbol{q}) = \frac{2N}{3V} \int_{\mathbb{R}^3} \frac{m}{2} \boldsymbol{v}^2 \,\rho(\boldsymbol{q}, \boldsymbol{v}) \,d^3 \boldsymbol{v} \,, \qquad (5.73)$$

²⁰Roughly speaking, when air masses move to higher altitudes, they expand due to lower pressure, which leads to lower temperature, and the exchange of energy through collisions of molecules is too slow to equalize the temperature, although it would do so if given enough time without any input of energy (such as sunshine).

where the integral represents the mean kinetic energy per molecule at q. In the case of a gravitational field, we can evaluate this from (5.72) to yield

$$p(q) = p_0 e^{-\frac{mgq_3}{kT}}$$
(5.74)

with

$$p_0 = \frac{N}{V} kT \left[\int_{\Lambda} d^3 \boldsymbol{q}' \exp\left(-\frac{mgq'_3}{kT}\right) \right]^{-1}$$
(5.75)

the pressure at altitude $q_3 = 0$. Equation (5.74) is known as the *barometric* formula. It is approximately correct in the atmosphere over regions in which T does not vary too much, although the atmosphere is not in thermal equilibrium. (And keep in mind that a difference of 10° C means a difference of only about 3%.)

(c) The equipartition theorem. Realistic molecules consisting of several atoms are not like the hard spheres in that they can rotate, oscillate (atoms can move towards or away from each other), or bend (angles between three atoms can change). The Maxwell–Boltzmann distribution can easily take this fact into account by replacing the over-idealized phase space $\Gamma_1 = \Lambda \times \mathbb{R}^3$ by a higher-dimensional Γ_1 that includes these internal degrees of freedom. Often, Γ_1 is still of the form $\mathcal{Q}_1 \times \mathcal{P}_1$ with \mathcal{Q}_1 the (1-molecule) configuration space and \mathcal{P}_1 the corresponding momentum space, or of the form $T\mathcal{Q}_1$, the tangent bundle (or if desired cotangent bundle) of \mathcal{Q}_1 (because velocities should be tangent vectors to configuration space). For example, a rigid body has configuration space $\Lambda \times SO(3)$, and tangent vectors to SO(3) can be represented as the rotational velocity vector $\boldsymbol{\omega}$. And often, the Hamiltonian of the internal degrees of freedom is (approximately) quadratic. For example, for a rigid body the Hamiltonian is constant over SO(3) and depends on $\boldsymbol{\omega}$ according to the following formula for rotational energy:

$$H_{\rm rot} = \frac{1}{2} \boldsymbol{\omega}^T \mathcal{I} \boldsymbol{\omega}$$
 (5.76)

with \mathcal{I} the moment of inertia tensor (a positive definite symmetric 3×3 matrix). Now let us leave aside external potentials and assume that H is a positive semidefinite quadratic form on the vector space Γ_1 ,

$$H(x) = x^{T} A x. (5.77)$$

Then the Maxwell–Boltzmann distribution takes the form

$$\rho_1(x) = \frac{1}{Z} e^{-\beta x^T A x} = \frac{1}{Z} e^{-\beta \sum_j a_j \overline{x}_j^2}$$
(5.78)

with a_k the eigenvalues of A and \overline{x} a coordinate system that diagonalizes A. That is, the distribution is uniform in those directions with $a_k = 0$ (such as, over SO(3)) for a rigid body) and Gaussian in those directions with $a_k > 0$. The width in these directions is such that

$$\langle a_j \overline{x}_j^2 \rangle = \frac{1}{2\beta} = \frac{1}{2} kT \,. \tag{5.79}$$

This statement is known as the equipartition theorem: Every degree of freedom receives on average a kinetic energy of $\frac{1}{2}kT$ by thermal motion.

Above, I mentioned how the Maxwell–Boltzmann distribution arises from the canonical distribution as the typical empirical distribution. Not surprisingly, it also arises from the *micro-canonical* distribution, if either we combine $S_1 \cup \ldots \cup S_n$ with a heat bath, or if n-1 of the S_i provide a heat bath for S_i . That is, most phase points on Γ_E have an empirical distribution of the x_i close to the Maxwell–Boltzmann distribution.

5.8 The Ising Model

The Ising model is of a rather different type than all the models we have considered so far in that it has *no dynamics*. It was invented by Wilhelm Lenz in 1920 and is named after Ernst Ising, a student of Lenz who studied the model in his doctoral dissertation in 1925. It was devised as a tool to study the thermodynamic properties of a ferromagnet in thermal equilibrium, but its relevance nowadays goes far beyond ferromagnetism.

Physical space \mathbb{R}^3 is replaced here by a lattice \mathbb{Z}^d (in case d = 1 one speaks of an "Ising chain"), at each lattice site *i* there is located an atom (or elementary magnet, sometimes called "a spin" although the model is purely classical) that can have two different states (orientations, often thought of as "pointing up" and "pointing down"),

$$\sigma_{\boldsymbol{i}} = +1 \text{ or } \sigma_{\boldsymbol{i}} = -1. \tag{5.80}$$

We will often want to consider only a set Λ of finitely many lattice sites, for example a box of side length L:

$$\Lambda_L = \left\{ \boldsymbol{i} = (i_1, \dots, i_d) \in \mathbb{Z}^d : |i_k| < L/2 \, \forall k = 1 \dots d \right\}.$$
(5.81)

The sample space is

$$\Omega = \{+1, -1\}^{\Lambda}, \tag{5.82}$$

and on it one defines a "Hamiltonian" or "energy function" $H: \Omega \to \mathbb{R}$, for example

$$H(\sigma) = -J \sum_{\boldsymbol{i}, \boldsymbol{j}: |\boldsymbol{i}-\boldsymbol{j}|=1} \sigma_{\boldsymbol{i}} \sigma_{\boldsymbol{j}} , \qquad (5.83)$$

where the sum is over all nearest neighbors, and J is a constant called a coupling constant (although in the case (5.83) it is not coupling anyting). The Hamiltonian does not define any equation of motion, but it does define a canonical ensemble, the measure with probability mass function

$$\mathbb{P}_{\beta}\{\sigma\} = \frac{1}{Z}e^{-\beta H(\sigma)}.$$
(5.84)

To study the Ising model means to study the properties of the measure \mathbb{P}_{β} . We will come back to it later.

5.9 Ergodicity and Mixing

These are two mathematical properties of a measure-preserving dynamical system (MPDS) that come up repeatedly in statistical mechanics.

Definition 7. A MPDS $(\Omega, \mathscr{F}, \mathbb{P}, T)$ (let us say in continuous time) is *ergodic* iff for all $A \in \mathscr{F}$ and almost all $\omega \in \Omega$,

$$\lim_{\tau \to \infty} \frac{1}{\tau} \lambda \Big\{ t \in [0, \tau] : T^t \omega \in A \Big\} = \mathbb{P}(A) \,, \tag{5.85}$$

where λ means the Lebesgue measure.

That is, almost every trajectory of an ergodic system spends time, in the long run, in every region of phase space according to their sizes. Other names for "ergodic" are "metrically indecomposable" or "metrically transitive."

Theorem 13.²¹ The following are equivalent for a MPDS:

- (i) It is ergodic.
- (ii) For all $f \in L^1(\Omega)$ and almost all $\omega \in \Omega$,

$$\lim_{\tau \to \infty} \frac{1}{\tau} \int_0^\tau dt \, f(T^t \omega) = \mathbb{E}f \,. \tag{5.86}$$

(time average = ensemble average)

- (iii) Every conserved quantity is almost constant. That is, every measurable $f: \Omega \to \mathbb{R}$ that is constant along every trajectory differs from a constant only on a null set.
- (iv) Every invariant set has either measure 0 or measure 1: $\forall t \in \mathbb{R} : T^t A = A \implies \mathbb{P}(A) \in \{0, 1\}.$
- (v) Every set that is invariant up to null sets, $\mathbb{P}(T^t A \triangle A) = 0$ with \triangle the symmetric difference $(A \triangle B = (A \setminus B) \cup (B \setminus A))$, has either measure 0 or measure 1.
- (vi) For every $A \subseteq \Omega$ with $\mathbb{P}(A) > 0$, $\mathbb{P}(\bigcup_{t>0} T^t A) = 1$.
- (vii) If $A, B \subseteq \Omega$ have $\mathbb{P}(A) > 0$ and $\mathbb{P}(B) > 0$, then there is t > 0 such that $\mathbb{P}(A \cap T^t B) > 0$.

Example. Rotation on a circle, $\Omega = \{z \in \mathbb{C} : |z| = 1\}$ and $T^t z = e^{it} z$, is ergodic. That has to do with the fact that the whole space is only one trajectory, so every conserved quantity has to be constant. Thus, ergodicity still holds if the rotation occurs at a different speed, $T^t z = e^{i\alpha t} z$ with $\alpha \neq 0$.

²¹For a proof see, e.g., Theorems 1.5, 1.6, and 1.14 in P. Walters: An Introduction to Ergodic Theory. New York: Springer (1982).

Example. Ergodicity can also be considered in discrete time by allowing only integer t. The rotation on a circle through an angle α , $Tz = e^{i\alpha}z$, is ergodic iff $\alpha \notin \pi \mathbb{Q}^{22}$ (This statement generalizes the result of a homework exercise.)

Example. The motion on an *n*-dimensional torus in a fixed direction (when viewed as a rectangle with identified boundaries, as considered in a homework exercise) is ergodic for most directions.²²

Example. The hard sphere gas with N spheres confined to a box in 3d is believed to be ergodic on each energy surface, but this conjecture is not proven. Yakov Grigorevich Sinai (born 1935) announced in 1963 to have a proof, but he never published a complete proof and declared in 1987 that the announcement was premature.

Theorem 14. ²³ Every MPDS for which $(\Omega, \mathscr{F}, \mathbb{P})$ is sufficiently nice²⁴ can be (essentially uniquely) decomposed into ergodic components.

Since energy is a conserved quantity, only energy surfaces have a chance of being ergodic. If conservation of momentum or angular momentum hold, the ergodic components must lie in their level sets. Most models in statistical mechanics, however, do not conserve momentum or angular momentum. It is believed that most models with a sufficiently complex interaction are actually ergodic, although ergodicity has been proved only for some very special examples.²⁵ Boltzmann was the first to suggest that reasonable models of interacting gases (such as the hard sphere model) are ergodic on every energy surface. (He had at first suggested, perhaps speaking loosely, that the whole energy surface is just a single trajectory; however, this turned out to be mathematically impossible.) Oxtoby and Ulam²⁶ have given a heuristic argument to the effect that "almost every" MPDS should be ergodic, as well as a proof that it is generic (in a certain topological sense) for a MPDS in discrete time with continuous T on a compact Ω to be ergodic. In one of the homework exercises, we have essentially made an assumption of ergodicity for estimating the Poincaré recurrence times.

²²H. Weyl: Über die Gleichverteilung von Zahlen mod. Eins. Mathematische Annalen **77(3)**: 313–352 (1916). See also V.I. Arnold and A. Avez: Ergodic Problems of Classical Mechanics. New York: W.A. Benjamin (1968).

 $^{^{23}}$ V.A. Rokhlin: On the decomposition of a dynamical system into transitive components. *Matematicheski Sbornik* **25(2)**: 235–249 (1949) (in Russian). V.A. Rokhlin: Selected topics from the metric theory of dynamical systems. *Uspekhi Mat. Nauk* **4(2)**: 57–128 (1949). English translation in Transl. Amer. Math. Soc. Ser. 2, **49**: 171–240 (1966). A brief summary is also contained in P. Walters: *An Introduction to Ergodic Theory*. New York: Springer (1982), pp. 33–34.

²⁴More precisely, a "Lebesgue space." In fact, every complete separable metric space Ω with \mathbb{P} a probability measure on the Borel σ -algebra and \mathscr{F} its completion by \mathbb{P} is a Lebesgue space. This includes all manifolds (with countably many connected components of finite dimension).

²⁵Such results can be found in Y. Sinai: *Introduction to ergodic theory*. Princeton University Press (1976).

 $^{^{26}}$ J.C. Oxtoby and S.M. Ulam: Measure-preserving homeomorphisms and metrical transitivity. Annals of Mathematics 42(4): 874–920 (1941)

Definition 8. A MPDS is *strongly mixing* or simply *mixing* iff for all $A, B \in \mathscr{F}$,

$$\lim_{t \to \infty} \mathbb{P}(A \cap T^t B) = \mathbb{P}(A) \mathbb{P}(B).$$
(5.87)

Every mixing system is ergodic, but not vice versa.²⁷ The rotation on a circle is ergodic but not mixing; same with the motion on the *n*-torus in a generic fixed direction. A simple example of a mixing MPDS in discrete time (but with non-injective T) is provided by the "dyadic transformation": $\Omega = [0, 1]$, $\mathbb{P} =$ Lebesgue measure, and $T\omega = 2\omega \mod 1$. It is also believed that most interacting models in statistical mechanics are mixing on each energy surface, although this seems more dubious than for ergodicity (and was not proven for any serious model).

Many books try to derive thermodynamic behavior (such as approach to thermal equilibrium) from ergodicity (or mixing) on Γ_E . As I will discuss later, these derivations are actually flawed, and ergodicity (and likewise mixing) is neither necessary nor sufficient for thermodynamic behavior. However, thermodynamic behavior depends on the presence of little interactions, and the little interactions also tend to make the dynamics ergodic and mixing on Γ_E . Moreover, mixing plays a role for generating macroscopic randomness, i.e., for why a die has probability 1/6 to end up on any particular side.

²⁷P. Walters: An Introduction to Ergodic Theory. New York: Springer (1982)

6 Review of Thermodynamics

I will collect a few concepts and teachings of thermodynamics that will be relevant to us.

- Although the number N of molecules in a macroscopic system is, of course, an integer, it can reasonably be treated as a continuous variable. After all, realistic values of N are larger than 10^{20} , so even if we specify N to an accuracy of five digits, we are nowhere near noticing the discreteness of N.
- A quantity Q is called *extensive* if it is additive when disjoint systems get combined. For example, volume, mass, and charge are extensive. For a homogeneous system, Q is proportional to the volume of the system (this follows from considering disjoint subsystems).
- Energy is extensive to an excellent degree of approximation. Indeed, energy usually has the form

$$E = \sum_{k=1}^{N} \frac{\boldsymbol{p}_{k}^{2}}{2m} + \sum_{k=1}^{N} V_{1}(\boldsymbol{x}_{k}) + \sum_{1 \le j < k \le N} V_{2}(\boldsymbol{x}_{j} - \boldsymbol{x}_{k})$$
(6.1)

with external potential V_1 and pair potential V_2 . What keeps E from being exactly extensive are terms $V_2(\boldsymbol{x}_j - \boldsymbol{x}_k)$ with particle j belonging to system \mathscr{S}_A and k to system \mathscr{S}_B . However, these terms are tiny except for particles very close to the surface where \mathscr{S}_A and \mathscr{S}_B touch, and even for those the terms are not large; since those particles are few in number, the terms are usually small compared to the energies of \mathscr{S}_A and \mathscr{S}_B .

- A quantity R is called *intensive* if it is independent of the size of a homogeneous system. In particular, it has the same value for every subsystem of a homogeneous system. For example, temperature, pressure, and mass density are intensive.
- Zeroth law of thermodynamics: Every isolated system will, after sufficient waiting time, reach a state of thermal equilibrium.
- First law of thermodynamics: In an isolated system, energy is conserved.
- Consider a simple system \mathscr{S} (i.e., a homogeneous system \mathscr{S} without external fields) consisting of a single compound (i.e., a single chemical substance). The thermal equilibrium states of \mathscr{S} can be parametrized by the number N of molecules, the energy E, and the volume V (do not confuse with the potential). That is, (E, V, N) together define a bijection from the set of thermal equilibrium states to $(0, \infty)^3 \subset \mathbb{R}^3$.
- If a system \mathscr{S} is in thermal equilibrium, the temperature T is the same everywhere in \mathscr{S} . In particular, for a single-compound simple system, T is a function on the set of thermal equilibrium states, T(E, V, N).

- There is an extensive quantity S called entropy.
- Second law of thermodynamics: The entropy of an isolated system is an increasing function of time.
- Every thermal equilibrium state has a unique entropy value. This value S(E, V, N) is a concave function²⁸ of E, V, N and increasing in E. The specification of S as a function of E, V, N was called by Gibbs the *fundamental equation* of the system. For example, for the ideal mono-atomic gas,

$$S(E, V, N) = kN \log \frac{V}{Nv_0} + \frac{3}{2}kN \log \frac{E}{Ne_0},$$
(6.2)

where log means the natural logarithm, v_0 is an arbitrarily chosen unit of 3-volume (or comparison volume), and e_0 a unit of energy.

• Since all of E, V, N, S are extensive, S(E, V, N) is a homogeneous function of degree 1.²⁹ Thus, writing e = E/N, v = V/N, and s = S/N, s is a function s(e, v) of e and v alone, in fact a concave function. For example, for the ideal mono-atomic gas,

$$s(e,v) = k \log \frac{v}{v_0} + \frac{3}{2}k \log \frac{e}{e_0}.$$
(6.3)

• Moreover,

$$\frac{\partial S(E,V,N)}{\partial E} = \frac{1}{T(E,V,N)} \,. \tag{6.4}$$

Since S(E, V, N) is increasing in E, $T(E, V, N) \ge 0$. The relation (6.4) was expressed by Rudolf Clausius (1822–1888) in 1865 in the form

$$dS = \frac{dQ}{T}, \qquad (6.5)$$

where dQ is the heat added to a system (while V and N are kept constant and thus no work is done), and dS is the resulting change in entropy.

• The equation $S(E, V, N) = S_0$ can be solved for E; the result is commonly denoted $U(S_0, V, N)$ or simply U(S, V, N). It follows that

$$\frac{\partial U(S,V,N)}{\partial S} = T(U(S,V,N),V,N) =: T(S,V,N).$$
(6.6)

(Indeed, keeping V and N fixed, taking the S_0 -derivative of the relation $S(U(S_0)) = S_0$ yields $\frac{1}{T} \frac{\partial U}{\partial S} = 1$.) Moreover,

$$\frac{\partial U(S, V, N)}{\partial V} = -p(S, V, N) \quad \text{the negative pressure}$$
(6.7)

²⁸A real-valued function $f(x_1, \ldots, x_n)$ is called concave iff -f is convex or, equivalently, the set above the graph of -f in \mathbb{R}^{n+1} is convex. If f is twice continuously differentiable, then f is concave iff everywhere its Hessian matrix is negative semi-definite.

²⁹A function $f(x_1, \ldots, x_n)$ is said to be homogeneous of degree s iff for every $\lambda > 0$, $f(\lambda x_1, \ldots, \lambda x_n) = \lambda^s f(x_1, \ldots, x_n)$.

and

$$\frac{\partial U(S, V, N)}{\partial N} = \mu(S, V, N) \quad \text{the chemical potential.}$$
(6.8)

For (6.6), (6.7), and (6.8) together, one often writes

$$dU = T dS - p dV + \mu dN, \qquad (6.9)$$

where d can be taken to mean the gradient (or the exterior derivative). In fact, (6.9) can be understood independently of any choice of coordinates as an equation between 1-forms (covector fields) on the manifold of thermal equilibrium states.

• Among all thermal equilibrium states available to an isolated system, the one with maximal entropy will occur.

Example. If two systems \mathscr{S}_A and \mathscr{S}_B , with initial total energy $E_{\text{tot}} = E_{iA} + E_{iB}$, are brought into thermal contact and thus allowed to exchange energy while $\mathscr{S}_A \cup \mathscr{S}_B$ is isolated, then the total entropy of the final equilibrium state will be

$$S_{\text{tot}} = \sup_{\substack{(E_A, E_B) \in [0, \infty)^2 \\ E_A + E_B = E_{\text{tot}}}} \left[S_A(E_A) + S_B(E_B) \right],$$
(6.10)

where the dependence on the variables V_A , N_A , V_B , N_B was omitted because they are constant. Here, the states available to $\mathscr{S}_A \cup \mathscr{S}_B$ are those with any value of E_A (because energy can be exchanged between \mathscr{S}_A and \mathscr{S}_B) while $E_A + E_B$ is fixed by energy conservation.

Note that, if S_A and S_B are differentiable functions of the energy variables, then the maximizer of (6.10) occurs where

$$0 = \frac{\partial}{\partial E_A} \left[S_A(E_A) + S_B(E_{\text{tot}} - E_A) \right], \qquad (6.11)$$

unless it occurs at one of the extremes

$$E_A = 0, E_B = E_{\text{tot}} \text{ or } E_A = E_{\text{tot}}, E_B = 0.$$
 (6.12)

Suppose that (6.11) holds. Then, by (6.4),

$$0 = \frac{1}{T_A} - \frac{1}{T_B}, \qquad (6.13)$$

in agreement with the statement above that the temperature is spatially constant within a system in thermal equilibrium. (The case (6.12) of a maximum on the boundary does not occur in practice: for if the maximum occurs at $E_A = 0$, then the right-hand side of (6.11) must be ≤ 0 , so $1/T_A - 1/T_B \leq 0$ or $T_A \geq T_B$ despite $E_A = 0$ and $E_B > 0$; if $T_A > T_B$, it would be impossible to cool \mathscr{S}_A beyond T_A .)

Another remark concerns the physical relevance of the fact that s(e, v) is a concave function: a non-concave function would lead to thermodynamic instability. Consider



Figure 6: A function S(E) that is not concave and satisfies (6.14)

for example again the two systems \mathscr{S}_A and \mathscr{S}_B that can exchange energy. The simplest case would consist of two identical systems:

If $E \mapsto S(E)$ were not concave at $E = E_0/2$, see Figure 6, say

$$S(E) < \frac{1}{2}S(E + \Delta E) + \frac{1}{2}S(E - \Delta E),$$
 (6.14)

then the state at $E_A = E_B = E$ would not be stable, as it would be preferable to increase entropy by transporting the amount of energy ΔE from B to A:

$$S(\underbrace{E}_{E_A}) + S(\underbrace{E}_{E_B}) < S(\underbrace{E + \Delta E}_{E_A}) + S(\underbrace{E - \Delta E}_{E_B}).$$
(6.15)

For $N_B \neq N_A$, the same situation can be created at other energies than $E_0/2$.

7 Macro States, Macro Variables, Thermal Equilibrium, and Entropy

I begin this section with an outline of the key claims, and provide some supporting reasoning afterward. Further support will be provided by a case study of the hard sphere gas in Section 8, whose key element is the Boltzmann equation.

7.1 Overall Picture

We now discuss the concepts of macro state and macro variable for a macroscopic system. A difficult aspect of these concepts is that they are not sharply defined. However, their vagueness does not indicate that they would be inappropriate or unscientific; rather, this vagueness arises from the vagueness inherent in the idea of "macroscopic": How many atoms would a system need to have in order to count as a "macroscopic system"? And in such a system, by how much could we change the positions and momenta of how many atoms before the change would be "macroscopically noticeable"? It seems clear that there is no "right" answer to these questions; that different people, if we made them name specific numbers, would give different answers, and all of them could be reasonable; that these people will nevertheless draw basically the same conclusions about the macroscopic behavior; and that there is nothing wrong with this situation. Often, the concepts of macro state and macro variable can be given precise definitions in the limit $N \to \infty$, but such definitions are then of limited value if we know that the real system we are dealing with has $N = 10^{24}$ atoms.

7.1.1 Macro States

A macro state is one of the possibilities what a phase point can "look like macroscopically." The set of phase points ("micro states") compatible with a particular macro state ν will be denoted $\Gamma_{\nu} \subset \Gamma$ in the following and called a macro set. One might say that they are the equivalence classes of the relation "looking macroscopically the same," and we may take them to form a partition of the phase space or of the energy surface (depending on how we want to set them up). (Of course, it is not at all clear that "looking macroscopically the same" should be transitive, as we may think that phase point do look macroscopically the same when they are sufficiently close to each other, but a chain of points, each close to its predecessor, may have considerable length.) So the idea is that the choice of where to draw the borderline between the Γ_{ν} is somewhat arbitrary, but that this arbitrariness is unproblematical, and many choices can be reasonable.

7.1.2 Macro Variables

A specific approach to choosing the macro sets makes use of *macro variables*, which are those functions on the phase space that are quantities that "can macroscopically be measured." To flesh this idea out, I will describe two explicit schemes for modelling macro variables below. In general, we expect the following picture. Due to the limitations of "macroscopic measurements," there should only be finitely many macro variables $M_j : \Gamma \to \mathbb{R}, j = 1, ..., K$. Since macro measurements have limited accuracy (say, $\Delta M_j > 0$), we want to think of the M_j as suitably coarse-grained with a discrete set of values, say, $\{k\Delta M_j : k \in \mathbb{Z}\}$. Then two phase points $x_1, x_2 \in \Gamma$ will look macroscopically the same if $M_j(x_1) = M_j(x_2)$ for all j = 1, ..., K. In this way, the collection of functions $\{M_1, \ldots, M_K\}$ defines a partition of phase space Γ into equivalence classes

$$\Gamma_{\nu} = \left\{ x \in \Gamma : M_j(x) = \nu_j \,\forall j \right\},\tag{7.1}$$

one for every macro state $\nu = (\nu_1, \ldots, \nu_K)$ described by the list of values of all M_j .



Figure 7: Coarse graining function g with $\Delta E = 0.1$

More specifically, since a coarse-grained version of the energy is usually among the macro variables, say $M_1(x) = g(H(x))$ with coarse-graining function $g(E) = [E/\Delta E] \Delta E$ and [s] denoting the nearest integer to $s \in \mathbb{R}$ (see Figure 7), every macro set Γ_{ν} belongs to a particular micro-canonical energy shell $\Gamma_{\rm mc}$, so that $\Gamma_{\rm mc}$ is partitioned into macro sets Γ_{ν} .

7.1.3 Thermal Equilibrium

Different Γ_{ν} often have dramatically different volumes (examples later), with the differences getting even more dramatic as N gets larger. Some of the Γ_{ν} represent thermal equilibrium. The key observation about them is perhaps due to Maxwell:

Rule of the Dominant Macro State. In most macroscopic systems, there is, for every energy shell $\Gamma_{\rm mc}$, one macro set Γ_{ν_0} that contains most of the phase space volume of $\Gamma_{\rm mc}$. This ν_0 is the thermal equilibrium state, $\Gamma_{\nu_0} = \Gamma_{\rm eq}$.

"Most" means "a fraction close to 1." One says that Γ_{eq} is the "dominant macro set," see Figure 8. We will discuss exceptions to this rule in Section 7.3. The system is in thermal equilibrium whenever its phase points lies in Γ_{eq} . The situation of a dominant



Figure 8: Schematic representation of the partition of an energy shell $\Gamma_{\rm mc}$ in the phase space of a macroscopic classical system into subsets Γ_{ν} corresponding to different macro states ν . One of the subsets, $\Gamma_{\rm eq}$, contains more than 99.99% of the volume (not drawn to scale) and corresponds to thermal equilibrium.

macro set is an example of the dramatic difference of volumes: Γ_{eq} is much larger than all other Γ_{ν} in Γ_{mc} together. In fact, usually each Γ_{ν} is much larger than all smaller $\Gamma_{\nu'}$ together.

Since the phase point x(t) cannot leave the energy shell, and since phase space volume is conserved by Liouville's theorem, most $x \in \Gamma_{eq}$ stay during their time evolution in Γ_{eq} for a long time (in fact, usually for an *extraordinarily* long time), though not forever.

The existence of a dominant macro set is equivalent to saying that the macro variables are nearly constant functions on the energy shell. That is, for each macro variable M_j there is a particular value m_j such that $M_j(x) = m_j$ for a fraction of x's close to 1; this value is the thermal equilibrium value of M_j . As a consequence, m_j is close to the average of M_j over the energy surface or energy shell,

$$\langle M_j \rangle_E \approx m_j \approx \langle M_j \rangle_{\rm mc} \,,$$

$$(7.2)$$

which can be useful for computing the thermal equilibrium values. By equivalence of ensembles, also

$$m_j \approx \langle M_j \rangle_{\rm can}$$
 (7.3)

for suitable choice of β .

Since there is some arbitrariness in the choice of the functions M_j , there is also some arbitrariness about which set exactly Γ_{eq} is. However, any reasonable choice of $\Gamma_{\rm eq}$ will take up most of the volume of $\Gamma_{\rm mc}$. In fact, there is no reason to expect a unique criterion for exactly which phase points are in thermal equilibrium, just as there is no unique criterion for exactly which strings of 0's and 1's should count as "purely random-looking."

7.1.4 Boltzmann Entropy

Entropy was introduced by Rudolf Clausius in 1865 as a particular thermodynamic function, i.e., as a function on the set of all thermal equilibrium states of a system, that was useful for certain thermodynamic considerations. Clausius extended the definition of this quantity also to states of *local* thermal equilibrium that are not in (global) thermal equilibrium.

Boltzmann gave the following mechanical definition of entropy, the *fundamental entropy formula*:

$$S(x) = S(\nu) = k \log \operatorname{vol} \Gamma_{\nu} \quad \text{for } x \in \Gamma_{\nu} \,. \tag{7.4}$$

This is one of the key equations of statistical mechanics. Here, vol means the volume in ${}^{N}\Gamma_{1}$ (or $N!^{-1}$ times the volume in the ordered phase space). The use of the logarithm fits well with the situation that some Γ_{ν} have dramatically different volumes. According to Boltzmann's definition, entropy is not a precisely defined quantity because the partition of phase space into macro sets Γ_{ν} is not precisely defined.

One may hesitate about (7.4) because logarithms can be taken only of dimensionless numbers, and phase space volumes have dimension ([length]·[momentum])^{3N}. In quantum mechanics, this issue disappears because phase space volumes get replaced by dimensions of subspaces of Hilbert space, which in fact are dimensionless. In classical mechanics, one can take the attitude of choosing some unit of [length]·[momentum] (with $h = 2\pi\hbar$ a popular choice) and noting that any other choice will change S(x)only by addition of a constant independent of x, so entropy differences are still uniquely determined. In fact, in the thermodynamic formalism, entropy is only defined up to addition of a constant. If we ignore additive constants anyway, then we can also take vol in (7.4) to mean the surface measure λ_E or μ_E (the normalized version of λ_E) on an energy surface Γ_E because for $\Gamma_{\rm mc} = \Gamma_{E,\Delta E}$ with small ΔE , for $\Gamma_{\nu} \subset \Gamma_E$, and for $\Gamma_{\nu}^{\Delta E}$ the "fattening" of Γ_{ν} or " $\Gamma_{\nu} \times [E, E + \Delta E]$ " we obtain that

$$S(\nu) = k \log \operatorname{vol} \Gamma_{\nu}^{\Delta E} = k \log[\lambda_E(\Gamma_{\nu})\Delta E] = k \log \lambda_E(\Gamma_{\nu}) + \operatorname{const.}.$$
 (7.5)

If we replace λ_E by μ_E and thus introduce a normalizing factor, $S(\nu)$ will change by another additive constant, which however now depends on E; such a constant is harmless if we only compare macro sets on the same energy surface but incorrect if we consider Γ_{ν} on different surfaces.

As a first consequence of (7.4), if there is a dominant macro set Γ_{eq} in an energy shell Γ_{mc} then it has the maximal entropy among all macro sets in Γ_{mc} . Moreover, we can compute its entropy: From $vol(\Gamma_{eq})/vol(\Gamma_{mc}) > 1 - \varepsilon$ with $\varepsilon \ll 1$ we obtain that

$$S(\text{eq}) \approx k \log \operatorname{vol} \Gamma_{\text{mc}}$$
. (7.6)

Since vol $\Gamma_{\rm mc} \approx \Omega(E) \Delta E$, this can also be expressed as

$$S(\text{eq}) \approx k \log \Omega(E)$$
 (7.7)

up to an additive constant.

This relation is of considerable practical relevance because it allows the computation of Clausius' entropy function S(E, V, N). The specification of this function is called the *fundamental equation* for the system considered. A basic property of S(eq) is that, in the absence of external fields, it is (very nearly) independent of the shape of Λ , which makes an expression of the form S(E, V, N) possible.

It is a homework exercise to derive the form (6.2) of S(E, V, N) for an ideal gas from (7.7). Let me focus here on the energy dependence. Since $\Gamma_{\leq E} = \Lambda^N \times B_{\sqrt{2mE}}^{3N}$, we have that $\gamma(E) \propto E^{3N/2}$ and

$$\Omega(E) = C E^{3N/2 - 1}. \tag{7.8}$$

with some C = C(V, N) > 0. Taking for granted $S(E) = k \log \Omega(E)$, it follows that

$$S(E) = \frac{3k(N-2)}{2}\log E + \text{const.}$$
 (7.9)

with a constant that depends on V and N but not on E, so

$$\frac{\partial S}{\partial E} = \frac{3k(N-2)}{2E} = \frac{3k}{2\overline{e}} - \frac{3k}{\overline{e}N}$$
(7.10)

with $\overline{e} = E/N$ the average energy per molecule. Since $\overline{e} = \frac{3}{2}kT$ for an ideal gas, see (4.10), it follows that

$$\frac{\partial S}{\partial E} = \frac{1}{T} + O(N^{-1}). \tag{7.11}$$

Since the last term is negligible, we have derived the relation (6.4) for the ideal gas.

Extensivity of entropy is expressed by the relation

$$S_{A\cup B}(\nu_A, \nu_B) = k \log \operatorname{vol}(\Gamma_{\nu_A} \times \Gamma_{\nu_B}) = S_A(\nu_A) + S_B(\nu_B), \qquad (7.12)$$

which follows from Boltzmann's formula (7.6) if the macro sets of $A \cup B$ are the Cartesian products of those of A and those of B. When are they Cartesian products? As a rule of thumb, they are if A and B occupy disjoint regions of space or comprise different types of particles (because then permutation of particles does not play a role) and the interaction energy between A and B is negligible (because then the Hamiltonian of $A \cup B$ is approximately the sum of those of A and B). The latter is in practice often justified when the two systems are in thermal contact along a surface and the interaction has short range. ("Most of the energy is in the bulk, little at the surface.")

7.1.5 Boltzmann's Qualitative Explanation of the Second Law

The second law of thermodynamics states that entropy can only increase with time, not decrease. Here is Boltzmann's qualitative explanation (a more detailed, quantitative

explanation will be considered in Section 8 in connection with the Boltzmann equation): Consider the set Γ_{ν} at time t_0 and evolve all phase points there until time $t_1 = t_0 + t$, resulting in the set $A_t = T^t \Gamma_{\nu}$. By Liouville's theorem, $\operatorname{vol}(A_t) = \operatorname{vol}(\Gamma_{\nu})$. Set

$$\Gamma_{<\nu} = \bigcup_{\nu': S(\nu') < S(\nu)} \Gamma_{\nu'} \tag{7.13}$$

and correspondingly $\Gamma_{>\nu}$. Usually

$$\operatorname{vol}(\Gamma_{<\nu}) \ll \operatorname{vol}(\Gamma_{\nu}).$$
 (7.14)

(The number of small macro sets does not compensate their smallness.) Thus,

$$\frac{\operatorname{vol}(A_t \cap \Gamma_{<\nu})}{\operatorname{vol}(A_t)} \ll 1.$$
(7.15)

That is, only a minority of points in A_t will have entropy smaller than $S(\nu)$. That is, for most points $x(t_0) \in \Gamma_{\nu}$,

$$S(x(t_1)) \ge S(x(t_0)).$$
 (7.16)

Thus, one should expect entropy not to decrease.

This explanation appeals to typicality, as it refers to how most phase points behave. According to this explanation, entropy does not have to go up, but it typically does. Also, it does not enforce that entropy as a function of time, $t \mapsto S(t) = S(x(t))$, increases monotonically, but it does suggest that the valleys in S(t) ("fluctuations") are typically shallow, short-lived, and infrequent; in other words, entropy valleys that are either deep or long-lived or frequent occur only for a small set of exceptional phase points, in fact more strongly so as N gets larger.



Figure 9: A typical entropy curve S(x(t)) according to Boltzmann's qualitative reasoning: It should go up except for infrequent, shallow, short-lived valleys; frequency, depth, and duration of the valleys are exaggerated for better visibility. After very long times, the entropy should go down considerably.

This picture also illuminates Zermelo's recurrence paradox: If deep entropy valleys are infrequent, then they will still occur if we wait long enough (see Figure 9)—not

much sense of paradox left. We can also say something about Loschmidt's time reversal paradox: Consider for simplicity the case that $A_0 = \Gamma_{\nu}$ evolves to $A_t \subset \Gamma_{\nu'}$ with $S(\nu') > S(\nu)$. Then all phase points in Γ_{ν} move to $\Gamma_{\nu'}$, but only a small minority of phase points in $\Gamma_{\nu'}$ would under time reversal evolve to Γ_{ν} .

A puzzle remains, however: If non-equilibrium state are so unlikely, why do we ever observe them? We will come back to this question in Section 9.

7.2 Examples

We begin with some examples for how to choose macro variables, and then turn to the existence of a dominant macro set.

7.2.1 Hydrodynamic Variables as Macro Variables

Hydrodynamic variables are those used in hydrodynamic equations such as the Euler or Navier–Stokes equations. Key examples are the particle number density $n(\mathbf{r})$, the energy density $e(\mathbf{r})$, and the momentum density $\mathbf{p}(\mathbf{r})$ for $r \in \Lambda \subset \mathbb{R}^3$. These are treated as continuous functions of \mathbf{r} and t in hydrodynamic equations; they are coarse-grained descriptions of the exact (empirical) densities

$$n_x(\boldsymbol{r}) = \sum_{j=1}^N \delta^3(\boldsymbol{r} - \boldsymbol{q}_j)$$
(7.17)

$$e_{x}(\boldsymbol{r}) = \sum_{j=1}^{N} \left(\frac{\boldsymbol{p}_{j}^{2}}{2m} + V_{1}(\boldsymbol{q}_{j}) + \frac{1}{2} \sum_{k \neq j} V_{2}(\boldsymbol{q}_{j} - \boldsymbol{q}_{k})\right) \delta^{3}(\boldsymbol{r} - \boldsymbol{q}_{j})$$
(7.18)

$$\boldsymbol{p}_{x}(\boldsymbol{r}) = \sum_{j=1}^{N} \boldsymbol{p}_{j} \,\delta^{3}(\boldsymbol{r} - \boldsymbol{q}_{j}) \tag{7.19}$$

for a given phase point $x = (\boldsymbol{q}_1, \ldots, \boldsymbol{q}_N, \boldsymbol{p}_1, \ldots, \boldsymbol{p}_N) \in \Gamma = (\Lambda \times \mathbb{R}^3)^N$. There are two kinds of coarse-graining involved: First, a coarse-graining in space that leads to a histogram. That is, we partition Λ into cells Δ_i , $i = 1, \ldots, K$ (for simplicity, of equal size that represents the "macroscopic resolution of space," e.g., cubes of side length 1 mm) and form the corresponding histogram: For every $\Delta = \Delta_i$,

$$N_x(\Delta) = \sum_{j: q_j \in \Delta} 1 \tag{7.20}$$

$$E_x(\Delta) = \sum_{j: \boldsymbol{q}_j \in \Delta} \left(\frac{\boldsymbol{p}_j^2}{2m} + V_1(\boldsymbol{q}_j) + \frac{1}{2} \sum_{k \neq j} V_2(\boldsymbol{q}_j - \boldsymbol{q}_k) \right)$$
(7.21)

$$\boldsymbol{P}_{x}(\Delta) = \sum_{j:\boldsymbol{q}_{j}\in\Delta} \boldsymbol{p}_{j}.$$
(7.22)

Second, we coarse-grain further by rounding the values of these quantities according to the macroscopic resolution, i.e., by applying a coarse-graining function g as in Figure 7; for example, we may round particle numbers to integer multiples of 10^{12} .

7.2.2 Boltzmann's Macro Variables

Boltzmann's proposal (that he made in connection with the Boltzmann equation) amounts to

- choosing a partition A_1, \ldots, A_r of Γ_1 (e.g., cubic millimeters in Λ and cubic m/s in velocity space, dividing each velocity axis from -10^3 m/s to $+10^3$ m/s, along with a bin for $< -10^3$ m/s and one for $> 10^3$ m/s, so $r \approx 10^{16}$ for a liter of gas);
- then determining the fraction $f_x(A_i)$ of particles in each cell A_i ,

$$f_i = f_x(A_i) = \frac{1}{N} \# \left\{ j = 1, \dots, N : x_j \in A_i \right\},$$
(7.23)

• and finally coarse-graining this quantity to "macroscopic resolution" Δf (e.g., $\Delta f = 10^{-18}$).

(The numbers in brackets are mine, not Boltzmann's.)

These coarse-grained histograms are, I would say, already pretty fine grained and quite a bit more detailed than what one could realistically hope to "measure macro-scopically." However, it only strengthens the case if the scheme works even for rather fine-grained macro variables. Again, it is sometimes convenient to write this coarse-grained histogram as if it were a continuous function f(q, p) on Γ_1 .

7.2.3 Dominant Macro State and Size Differences

We derive in some examples the existence of a dominant macro set and compute size differences between different macro sets.

Example. Suppose two gases A, B are in separate containers but in thermal contact. We neglect the interaction energy and treat them as ideal gases. Their particle numbers N_A, N_B and volumes V_A, V_B are fixed but their energies are not. The total phase space is $\Gamma = \Gamma_A \times \Gamma_B$ with $\Gamma_i = (\Lambda_i \times \mathbb{R}^3)^{N_i}$, i = A, B. Fix an energy surface $\Gamma_{E_0} \subset \Gamma$, so the energies of A and B are constrained by $E_A + E_B = E_0$. For simplicity, we consider only one macro variable, the coarse graining of E_A with some small resolution ΔE . How big are the macro sets?

While $\Omega_A(E_A)$ and $\Omega_B(E_B)$ are of the ideal gas form (7.8), the total energy surface has measure

$$\Omega(E_0) = \int_0^E dE_A \,\Omega_A(E_A) \,\Omega_B(E_0 - E_A) \,. \tag{7.24}$$

The volume of Γ_{ν} with a given $\nu = E_A$ is

$$\Omega_A(E_A)\,\Omega_B(E_0 - E_A)\,\Delta E + o(\Delta E)\,. \tag{7.25}$$

To find the largest Γ_{ν} , we maximize the volume and thus consider

$$0 = \frac{\partial}{\partial E_A} \Omega_A(E_A) \,\Omega_B(E_0 - E_A) \tag{7.26}$$

$$= \Omega'_{A}(E_{A}) \,\Omega_{B}(E_{0} - E_{A}) - \Omega_{A}(E_{A}) \,\Omega'_{B}(E_{0} - E_{A})$$
(7.27)

or

$$\frac{\Omega_A'(E_A)}{\Omega_A(E_A)} = \frac{\Omega_B'(E_0 - E_A)}{\Omega_B(E_0 - E_A)}$$
(7.28)

or

$$\frac{d}{dE}\Big|_{E=E_A}\log\Omega_A(E) = \frac{d}{dE}\Big|_{E=E_0-E_A}\log\Omega_B(E)$$
(7.29)

or

$$\frac{\partial S_A}{\partial E}(E_A, V_A, N_A) = \frac{\partial S_B}{\partial E}(E_0 - E_A, V_B, N_B).$$
(7.30)

Note that we have arrived at the same equation as (6.11), the one considered in thermodynamics, which led to the conclusion that thermal equilibrium is reached when the two systems have the same temperature.

We still need to verify that we have found the unique global maximizer. First, we note that the condition (7.30) can always be satisfied, and is satisfied by a unique value \widehat{E}_A of E_A , as it amounts to, in view of (7.10),

$$\frac{3kN_A}{2E_A} = \frac{3kN_B}{2(E_0 - E_A)},$$
(7.31)

which has the unique solution

$$\widehat{E}_A = \frac{N_A}{N_A + N_B} E_0 \tag{7.32}$$

(i.e., energy gets distributed evenly over the molecules). For the second-derivative test, it is convenient to take as the quantity to maximize not the volume of Γ_{ν} but its logarithm

$$S(\nu) = S(E_A) = k \log \Omega_A(E_A) + k \log \Omega_B(E_0 - E_A) = S_A(E_A) + S_B(E_0 - E_A), \quad (7.33)$$

where we have dropped the irrelevant constant $\log \Delta E$. (We see an instance of additivity of entropies.) The second-derivative test then reads

$$\frac{\partial^2}{\partial E_A^2} \Big(S_A(E_A) + S_B(E_0 - E_A) \Big) = S_A''(E_A) + S_B''(E_0 - E_A) < 0$$
(7.34)

because each term individually is negative: By (7.10),

$$S''(E) = \frac{\partial}{\partial E} \frac{3k(N-2)}{2E} = -\frac{3k(N-2)}{2E^2} < 0$$
(7.35)

for N > 2, so S(E) is a strictly concave function, as it should be according to Section 6. To sum up, the smooth function $E_A \mapsto S(E_A)$ as in (7.33) has a unique local extremum, which is a strict local maximum, in the open interval $(0, E_0)$; thus, it is a global maximum.

Now let us figure out the size differences between different macro sets. To bring out clearly that these size differences are exponentially large, I choose a suitable notation:

 $N = N_A + N_B$, $\hat{\alpha} = N_A/N = \hat{E}_A/E_0$, and $\alpha = E_A/E_0$. Thus (replacing N - 2 by N for simplicity),

$$S(E_A) = S(\alpha) = \frac{3kN}{2} \left[\hat{\alpha} \log \alpha + (1 - \hat{\alpha}) \log(1 - \alpha) + \log E_0 \right].$$
 (7.36)

With $\nu = E_A$ and $\hat{\nu} = \hat{E}_A$, the ratio of sizes is

$$\frac{\operatorname{vol}\Gamma_{\nu}}{\operatorname{vol}\Gamma_{\hat{\nu}}} = \exp\left(\frac{1}{k}(S(E_A) - S(\widehat{E}_A))\right)$$
(7.37)

$$= \exp\left(\frac{3N}{2}s(\alpha)\right) \tag{7.38}$$

with

$$s(\alpha) = \hat{\alpha} \log \frac{\alpha}{\hat{\alpha}} + (1 - \hat{\alpha}) \log \frac{1 - \alpha}{1 - \hat{\alpha}}, \qquad (7.39)$$

whose graph for $\hat{\alpha} = \frac{1}{2}$ is depicted in Figure 10.



Figure 10: Graph of the function $s(\alpha)$ as in (7.39) that represents the entropy difference per particle for the example at hand for $\hat{\alpha} = 1/2$

Since the above calculation for $S(E_A)$ also shows that $s(\alpha)$ assumes its global maximum value at $\hat{\alpha}$, and since this value is 0, any $\alpha \neq \hat{\alpha}$ in (0,1) will have $s(\alpha) < 0$. It follows that every Γ_{ν} is exponentially smaller than $\Gamma_{\hat{\nu}} = \Gamma_{eq}$; it also follows that generally Γ_{ν} and $\Gamma_{\nu'}$ have dramatically different sizes except when $s(\alpha(\nu)) = s(\alpha(\nu'))$. \Box

Example. We would like to get a rough idea of how close the size of Γ_{eq} is to that of Γ_{mc} . I present a simple estimate suggesting that

$$\frac{\operatorname{vol}\Gamma_{\mathrm{eq}}}{\operatorname{vol}\Gamma_{\mathrm{mc}}} \approx 1 - \exp(-10^{-15}N) \,. \tag{7.40}$$

To obtain this estimate, we ignore velocities and focus on positions; that is, we consider simply the configuration space Λ^N instead of phase space. We partition the available 3-volume $\Lambda \subset \mathbb{R}^3$ into m (say, 10^9) cells Λ_i of equal volume, use the uniform distribution over Λ^N , and take the macro variables to be $M_j = [N_j/N \Delta M_j] \Delta M_j$, where N_j is the number of particles in Λ_j (and, say, $\Delta M_j = 10^{-12}$). Then M_j has equilibrium value $\nu_j^{\text{eq}} = 1/m$ (and the relative resolution is $\Delta M_j/\nu_j^{\text{eq}} = 10^{-3}$). The distribution of N_j is binomial with parameters N and m^{-1} ;³⁰ that is because N_j can be thought of as the number of successes in N independent trials in which (the position of one particle is chosen randomly and thus) success (i.e., a position in Λ_j) occurs with probability m^{-1} . The theorem of de Moivre–Laplace asserts, roughly speaking, that the binomial distribution with parameters n and p is close, for large n, to a Gaussian distribution with the same expectation (i.e., np) and variance (i.e., np(1-p)). Thus, since N is large, the distribution of N_j is approximately Gaussian with mean $\mu = N/m$ and variance $\sigma^2 = Nm^{-1}(1-m^{-1}) \approx N/m$. For M_j to deviate from its equilibrium value requires that N_j deviates from μ by more than $N \Delta M_j$, i.e., by more than $\sqrt{mN} \Delta M_j$ standard deviations. It is a fact about the Gaussian distribution³¹ that for all z > 0

$$\mathbb{P}(|Z| > z) \le e^{-z^2/2} \quad \text{for} \quad Z \sim \mathcal{N}(0, 1).$$

$$(7.41)$$

As a consequence, for $Y \sim \mathcal{N}(\mu, \sigma^2)$, $\mathbb{P}(|Y - \mu| > z\sigma) \leq e^{-z^2/2}$. Thus, the probability that M_j deviates from its equilibrium value is $\leq \exp(-mN\Delta M_j^2/2) =: p_0$. Hence, the probability that *any* of the M_j deviates from its equilibrium value is

$$\mathbb{P}\Big(\exists j: M_j \neq \frac{1}{m}\Big) = \mathbb{P}\Big(\bigcup_j \{M_j \neq \frac{1}{m}\}\Big) \le \sum_j \mathbb{P}\big(M_j \neq \frac{1}{m}\big) \le mp_0, \qquad (7.42)$$

which here is still of rough order of magnitude $\exp(-10^{-15}N)$.

The question remains whether N-particle systems with interaction also have a dominant macro set. The answer is basically yes, and we will report results about this question in Section 7.3.5.

7.2.4 Entropy for Boltzmann's Macro Variables

We now compute S(f) according to (7.4) for Boltzmann's macro variables $M_i = f_i$. Let us specify carefully the definition of f_i . A_1, \ldots, A_r form a partition of Γ_1 ; set $\Delta_i := \operatorname{vol}_6(A_i)$. For every $x \in \Gamma = {}^N\Gamma_1$, let

$$N_i(x) = \#(x \cap A_i)$$
 (7.43)

denote the occupation number of cell *i*; so the histogram f_i is $N_i/N\Delta_i$ coarse-grained to resolution Δf ,

$$f_i = \left[\frac{N_i}{N\,\Delta f\,\Delta_i}\right] \Delta f \,. \tag{7.44}$$

³⁰The binomial distribution with parameters n and p is the distribution of the number X of successes among n independent trials of a random experiment that succeeds with probability p. It has expectation np and variance np(1-p).

³¹See, e.g., https://en.wikipedia.org/wiki/Error_function.

For a given list of occupation numbers N_1, \ldots, N_r , the volume in Γ of the set of phase points x with these occupation numbers is

$$\frac{1}{N!} \begin{pmatrix} N \\ N_1 & \dots & N_r \end{pmatrix} \prod_{i=1}^r \Delta_i^{N_i} = \prod_{i=1}^r \frac{\Delta_i^{N_i}}{N_i!} , \qquad (7.45)$$

where the bracket is a multinomial coefficient, i.e., the number of functions $\{1, \ldots, N\} \rightarrow \{1, \ldots, r\}$ such that the value *i* occurs N_i times. Now a given value of f_i corresponds to a certain range of possible values of N_i , viz.,

$$N(f_i - \Delta f/2)\Delta_i \le N_i < N(f_i + \Delta f/2)\Delta_i.$$
(7.46)

This range has length $N\Delta f \Delta_i$; this is the number of possible values of N_i for given f_i . We make the approximation of taking $\Delta_i^{N_i}$ and N_i ! to be constant over this interval and obtain that the size of the set in Γ corresponding to a given histogram f is $(\nu = f)$

$$\operatorname{vol}\Gamma_{\nu} \approx \prod_{i=1}^{r} N \,\Delta f \,\Delta_{i} \frac{\Delta_{i}^{N_{i}}}{N_{i}!} \,. \tag{7.47}$$

We now insert $N_i = N f_i \Delta_i$ and take $x! = \Gamma(x+1)$ if x is not an integer; furthermore, we use *Stirling's formula*

$$\Gamma(x+1) = \sqrt{2\pi x} e^{-x} x^x (1+o(1)) \text{ as } x \to \infty$$
 (7.48)

in the form

$$\log n! = n \log n - n + o(n) \tag{7.49}$$

to obtain

$$S(f) = k \log \operatorname{vol} \Gamma_{\nu}$$

$$\approx kr \log N + kr \log \Delta f + k \sum_{i=1}^{r} \left((Nf_{i}\Delta_{i} + 1) \log \Delta_{i} - Nf_{i}\Delta_{i} \log(Nf_{i}\Delta_{i}) + Nf_{i}\Delta_{i} \right)$$

$$= kr \log N + kr \log \Delta f + k \sum_{i=1}^{r} \log \Delta_{i} - k \sum_{i=1}^{r} Nf_{i}\Delta_{i} \log(Nf_{i}) + k \sum_{i=1}^{r} Nf_{i}\Delta_{i} .$$

$$(7.51)$$

From (7.44),

$$\sum_{i=1}^{r} N f_i \Delta_i \approx N \,. \tag{7.52}$$

Now the idea is that N is large, corresponding to the limit $N \to \infty$, while r and Δf are fixed; that is, $N \gg r$, which we need for each bin to contain many particles. So when we neglect terms of lower order, it is lower order <u>in N</u> that counts. Thus,

$$S(f) = -kN \log N + kN - kN \sum_{i=1}^{r} \Delta_i f_i \log f_i + o(N).$$
 (7.53)

This is the formula for the entropy for Boltzmann's macro variables. It is often useful to rewrite it for the entropy per particle

$$s(f) = \frac{S(f)}{N} = -k \log N + k - k \sum_{i=1}^{r} \Delta_i f_i \log f_i.$$
 (7.54)

Since we consider different macro states f for the same N, we can drop the terms that do not depend on f. In the continuum limit $r \to \infty$ of shrinking cells in Γ_1 , then the last expression becomes

$$s(f) = -k \int_{\Gamma_1} dx_1 f(x_1) \log f(x_1) \,. \tag{7.55}$$

Remarks.

• Since

$$\lim_{u \searrow 0} u \log u = 0, \qquad (7.56)$$

(7.57)

the function $u \log u$ possesses a continuous extension to $[0, \infty)$, which is often (and will be in the following) denoted also simply by $u \log u$; in other words, we use the convention

 $0 \log 0 := 0.$



Figure 11: Graph of the function $u \log u$

• Boltzmann actually wrote (7.55) (with the term $-k \log N$) in the form

$$S(f) = -k \int_{\Gamma_1} dx_1 N f(x_1) \log(N f(x_1)), \qquad (7.58)$$

which is misleading insofar as it suggests that we take the continuum limit $r \to \infty$ before $N \to \infty$, while we actually need $r \ll N$ for the density $f(x_1)$ to be meaningful. (Besides, Boltzmann wrote f for what we called Nf.)

• Also (7.55) implies the existence of dramatice size differences: Whenever two macro states f, \tilde{f} have different values of s, then

$$\frac{\operatorname{vol}\Gamma_f}{\operatorname{vol}\Gamma_{\tilde{f}}} = e^{N[s(f) - s(\tilde{f})]/k}$$
(7.59)

is exponentially large in N.

7.2.5 Dominant Macro State in Boltzmann's Macro Variables

If the interaction energy is negligible compared to the kinetic energies (i.e., in the approximation of an ideal gas),

$$H(x_1, \dots, x_N) \approx \sum_{j=1}^N H_1(x_j),$$
 (7.60)

then the energy of a micro state x with macro state f can be computed as follows:

$$E \approx N \int_{\Gamma_1} dx_1 H_1(x_1) f(x_1)$$
 (7.61)

or, before taking the continuum limit,

$$E \approx N \sum_{i} \Delta_{i} H_{i} f_{i} \tag{7.62}$$

with H_i the (approximately constant) value of $H_1(x_1)$ on the cell $A_i \subset \Gamma_1$. Thus, finding the largest macro set in an energy shell amounts to finding $f_i \ge 0$, $i = 1, \ldots, r$ that maximize $S(f) = -kN \sum_i \Delta_i f_i \log f_i$ under the constraints $\sum_i \Delta_i f_i = 1$ and $\sum_i \Delta_i H_i f_i = e$, where e = E/N is a given constant. For lighter notation, we will maximize S(f)/kNinstead of S(f). For maximization with constraints, one adds the constraints to the objective function with Lagrange multipliers α, β as prefactors:

$$-\sum_{i} \Delta_{i} f_{i} \log f_{i} + \alpha \left[1 - \sum_{i} \Delta_{i} f_{i}\right] + \beta \left[e - \sum_{i} \Delta_{i} H_{i} f_{i}\right] = \max!$$
(7.63)

The gradient vanishes where

$$0 = \frac{\partial}{\partial f_k} \sum_i \Delta_i f_i \Big[-\log f_i - \alpha - \beta H_i \Big]$$
(7.64)

$$= \Delta_k \left[-\log f_k - \alpha - \beta H_k \right] + \Delta_k f_k \left[-\frac{1}{f_k} \right]$$
(7.65)

$$= \left(-\log f_k - \alpha - 1 - \beta H_k\right) \Delta_k \tag{7.66}$$

or

$$f_k = e^{-\alpha - 1 - \beta H_k} = \frac{1}{Z} e^{-\beta H_k}, \qquad (7.67)$$

the Maxwell–Boltzmann distribution! This should not come as a big surprise, of course, as we know already that for an ideal gas most phase points on Γ_E have empirical distribution in Γ_1 given by the Maxwell–Boltzmann distribution. Since Boltzmann's macro variables correspond exactly to the empirical distribution in Γ_1 , this known typicality statement means just that among the corresponding macro sets Γ_{ν} the one for which fhas the Maxwell–Boltzmann form is dominant.

Let us finish the maximization problem. Let us write $\Omega(f_1, \ldots, f_r)$ for the objective function on the left-hand side of (7.63). First, we have to satisfy the constraints by choosing α such that $Z = e^{\alpha+1}$ becomes the normalizing constant and β such that $\langle H_i \rangle = e$. Second, we have to check that the critical point (7.67) is indeed the global maximum. As the second derivative test, we observe that $\partial/\partial f_i$ of (7.66) is $\partial_i \partial_k \Omega =$ $-\delta_{ik}\Delta_k/f_k$, so the Hessian matrix of second derivatives is diagonal and negative definite. Thus, the critical point is a strict local maximum. We can even show that it is a strict global maximum: Since the Hessian of Ω is negative definite everywhere on $(0, \infty)^r$ (i.e., where all $f_i > 0$), the left-hand side of (7.63) is strictly concave on $(0, \infty)^r$. Note that Ω is defined and continuous on $[0, \infty)^r$ (i.e., where $f_i \ge 0$) but differentiable only on $(0, \infty)^r$ (i.e., in the interior); but at least it follows by continuity that Ω is still concave on $[0, \infty)^r$. For any concave function Ω , if it has two local maxima $f^{(1)}, f^{(2)}$, then

$$\Omega(f^{(1)}) = \Omega(f^{(2)}) = \Omega\left(tf^{(1)} + (1-t)f^{(2)}\right)$$
(7.68)

for all $t \in [0, 1]$ because if (say) $\Omega(f^{(1)}) < \Omega(f^{(2)})$ then, for all $t \in (0, 1)$,

$$\Omega(f^{(1)}) < t\Omega(f^{(1)}) + (1-t)\Omega(f^{(2)}) \le \Omega\left(tf^{(1)} + (1-t)f^{(2)}\right)$$
(7.69)

with the consequence (using t near 1) that $f^{(1)}$ cannot be a local maximum. Since we know that the critical point (7.67) (call it $f^{(1)}$) is a *strict* local maximum, the situation (7.68) with $f^{(1)} \neq f^{(2)}$ cannot occur, so $f^{(1)}$ must be the unique global maximum.

7.3 Discussion

7.3.1 The Case of an Autonomous Evolution of the Macro State

In general, the macro state at time t depends not only on the macro state at time 0 but on the micro state at time 0. In some setups, however, this is different, and the macro state evolves autonomously and deterministically. Strictly, this happens only in the limit $N \to \infty$, and various macroscopic equations have been developed for such situations, e.g., the Euler equations of hydrodynamics without dissipation, the Navier– Stokes equations of hydrodynamics with dissipation, the Boltzmann equation, and the heat equation. To formulate the situation for finite N, if ν and t are such that $T^t\Gamma_{\nu}$ is approximately a subset of $\Gamma_{\nu'}$, i.e.,

$$\operatorname{vol}(T^t\Gamma_{\nu} \setminus \Gamma_{\nu'}) \ll \operatorname{vol}\Gamma_{\nu}, \qquad (7.70)$$

then $S(\nu') \gtrsim S(\nu)$, so for most phase points in Γ_{ν} the Boltzmann entropy does not decrease significantly (but may well increase).³² The value $S(\nu')$ can often be determined from the equation governing the macro evolution. To sum up, deterministic macro evolution implies the second law.

7.3.2 Ergodicity

The fact that the observed values m_j^{eq} of macro variables M_j in thermal equilibrium coincide with their micro-canonical averages $\langle M_j \rangle$ has sometimes been explained with the following reasoning: Any macro measurement takes a time that is long compared to the time that collisions take or the time of free flight between collisions. Thus, it can be taken to be infinite on the micro time scale. Thus, the measured value is actually not the value of $M_j(x(t))$ at a particular t but rather its time average. By ergodicity, the time average is equal to the ensemble average, QED.

This reasoning is incorrect. In fact, ergodicity is neither necessary nor sufficient for $m_j^{\text{eq}} = \langle M_j \rangle$. Not necessary because M_j is nearly constant over Γ_E , and thus most phase points will yield a value close to $\langle M_j \rangle$ even if the motion is not ergodic. And not sufficient because the time needed for the phase point of an ergodic system to explore Γ_E is of the order 10^N years (as we saw in a homework exercise estimating recurrence times), and thus much longer than the duration of the measurement. This point is also illustrated by the fact that in a macro system with non-uniform temperature, you can clearly measure unequal temperatures in different places with a thermometer faster than the temperature equilibrates.

Here are some properties in the direction of ergodicity that are relevant to thermal equilibrium. Recall that ergodicity means the absence of further conserved quantities besides energy, and let us contrast this with the property that none of the further conserved quantities are macro variables. Suppose that one of the macro variables (other than energy) is conserved, say M_2 . Then it is sometimes a consequence that no macro state is dominant. But even if one macro state Γ_{eq} in Γ_{mc} is dominant, something will go wrong because if the initial phase point x has $M_2(x) \neq m_2^{eq}$, then x(t) will never reach Γ_{eq} . For example, in the example of Section 7.2.3 involving energy exchange between two gases A, B, we assumed that the interaction Hamiltonian is small but nonzero. If it were exactly zero, then each energy E_A and E_B would separately be conserved, and coarse-grained versions thereof would be conserved macro variables. In both cases, whether a dominant macro state exists or not, the energy shell Γ_{mc} should be split into invariant subsets corresponding to M_2 .

³²This reasoning is discussed in detail in S. Goldstein and J. L. Lebowitz: On the (Boltzmann) Entropy of Nonequilibrium Systems. *Physica D* 193: 53-66 (2004) http://arxiv.org/abs/cond-mat/ 0304251. See also P. Garrido, S. Goldstein, and J. L. Lebowitz: The Boltzmann Entropy for Dense Fluids Not in Local Equilibrium. Physical Review Letters 92: 050602 (2004) http://arxiv.org/abs/ cond-mat/0310575
On the other hand, a conserved quantity might exist that is not a macro variable; it might be a complicated quantity that is hard to access and to measure in practice. The existence of such a quantity would violate ergodicity but not necessarily pose an obstacle to the approach to thermal equilibrium.

Nevertheless, most systems are presumably ergodic, and the typical situation appears to be as follows. A small interaction term in the Hamiltonian, even if too small to change the phase space volumes of the Γ_{ν} significantly, will drive the system to thermal equilibrium. The same kind of interaction term will make the dynamics ergodic in Γ_E . That is, the same small terms in the Hamiltonian that ensure that most non-equilibrium phase points reach Γ_{eq} (often in a matter of hours) will make it ergodic (which concerns a time scale of 10^N years). So, ergodicity is neither cause nor consequence of thermodynamic behavior, but the two have a common cause.

7.3.3 Gibbs Entropy

We saw in Section 7.2.5 above that the Maxwell–Boltzmann distribution

$$f_i = Z^{-1} e^{-\beta H_i} \tag{7.71}$$

maximizes the entropy

$$s(f) = -k \sum_{i} \Delta_i f_i \log f_i \,. \tag{7.72}$$

The continuum limit of this statement is that the continuous Maxwell–Boltzmann distribution

$$f(x_1) = \frac{1}{Z} e^{\beta H_1(x_1)} \tag{7.73}$$

maximizes the entropy functional

$$s(f) = -k \int_{\Gamma_1} dx_1 f(x_1) \log f(x_1)$$
(7.74)

under suitable constraints. Since the reasoning made no specific assumptions about what kind of space Γ_1 is (for example, we did not require it to have dimension 6), we may carry the consideration one step further and replace Γ_1 by the full phase space Γ : The canonical distribution

$$\rho(x) = \frac{1}{Z} e^{-\beta H(x)} \tag{7.75}$$

maximizes, under suitable constraints, the functional

$$S_{\text{Gibbs}}(\rho) = -k \int_{\Gamma} dx \,\rho(x) \,\log\rho(x) \,, \qquad (7.76)$$

known as the *Gibbs entropy* of ρ . It can sometimes be useful to characterize the canonical (or its cousin, the grand-canonical) distribution by a variational principle.

A more important role for the Gibbs entropy will be explained below. But first let me note a basic observation about S_{Gibbs} . For a probability distribution that is uniform over some set $\Delta \subset \Gamma$,

$$\rho(x) = \operatorname{vol}(\Delta)^{-1} \mathbf{1}_{x \in \Delta}, \qquad (7.77)$$

the Gibbs entropy yields

$$S_{\text{Gibbs}}(\rho) = k \log \operatorname{vol} \Delta.$$
 (7.78)

So for $\Delta = \Gamma_{\nu}$, we get $S_{\text{Gibbs}}(\rho) = S(\nu)$, and for the micro-canonical distribution, $\Delta = \Gamma_{\text{mc}}$, we get $S_{\text{Gibbs}}(\rho_{\text{mc}}) \approx S(\text{eq})$. More generally, S_{Gibbs} quantifies logarithmically the *width* or *spread* of the distribution ρ , as it is the average of $\log(1/\rho(x))$. Put differently, $S_{\text{Gibbs}}(\rho)$ is k times the log of the volume over which ρ is effectively spread.

Now I come to the important role. Consider the ideal gas again, that is, suppose there is no interaction between the molecules. Then the canonical distribution factorizes into N copies of the Maxwell–Boltzmann distribution,

$$\rho_{\rm can}(x_1,\ldots,x_N) = f(x_1)\cdots f(x_N),$$
(7.79)

and the Gibbs entropy then splits according to

$$S_{\text{Gibbs}}(\rho_{\text{can}}) = -k \int_{\Gamma} dx_1 \cdots dx_N f(x_1) \cdots f(x_N) \sum_i \log f(x_i)$$
(7.80)

$$= -k \sum_{i} \int_{\Gamma_1} dx_i f(x_i) \log f(x_i)$$
(7.81)

$$= N s(f) = S(f) = k \log \operatorname{vol} \Gamma_{eq}.$$
(7.82)

That is, the Gibbs entropy of the canonical distribution agrees with the entropy of the equilibrium macro state, and thus (up to small error) with $k \log \operatorname{vol} \Gamma_{\mathrm{mc}} = S_{\mathrm{Gibbs}}(\rho_{\mathrm{mc}})$. This is another facet of equivalence of ensembles: For large N and suitable $\beta(E)$, ρ_{mc} and ρ_{can} have equal Gibbs entropy. And this situation is not limited to the ideal gas. As a consequence, the thermodynamic equilibrium entropy S(E, V, N) can be computed as the Gibbs entropy of the canonical distribution, which is often easier than computing $\Omega(E)$. That is the important role.

The Gibbs entropy has led to some confusion when it was identified with the thermodynamic entropy also for other ρ than $\rho_{\rm mc}$, $\rho_{\rm can}$, or $\rho(x) = \operatorname{vol}(\Gamma_{\nu})^{-1} \mathbf{1}_{x \in \Gamma_{\nu}}$. By taking (7.76), rather than $S(x) = k \log \operatorname{vol} \Gamma_{\nu(x)}$, as the definition of entropy, the impression arose that entropy is not a function on phase space but rather a functional of a probability distribution ρ . This idea does not make much sense to begin with because every system has an x but not a ρ . After all, it is not clear what should be meant by "the probability distribution" of a system: Is it simply the uniform distribution $\rho_{\rm mc}$ over the energy shell $\Gamma_{\rm mc}$ containing x? But then it does not depend on which state x is, and thus yields wrong values for non-equilibrium x. Or is "the probability distribution" the belief of an observer about where the phase point x is likely to be? This view is sometimes expressed in the literature, but the Gibbs entropy understood in this subjective way does not have the explanatory power of Boltzmann entropy: Consider for example the phenomenon that by thermal contact, heat always flows from the hotter to the cooler body, not the other way around. The usual explanation of this phenomenon is that entropy decreases when heat flows to the hotter body, and the second law excludes that. Now that explanation would not get off the ground if entropy meant subjective entropy: In the absence of observers, does heat flow from the cooler to the hotter? In distant stars, does heat flow from the cooler to the hotter? In the days before humans existed, did heat flow from the cooler to the hotter? If not, why would observers be relevant at all to the explanation of the phenomenon?

Moreover, the Gibbs entropy of a belief represented by ρ has nothing to do with the physical properties of the phase points that ρ gives significant weight to. After all, the Gibbs entropy just measures the spread of ρ , and another distribution with equal spread but concentrated on very different phase points will have equal Gibbs entropy.

Moreover, the Gibbs entropy of a belief represented by ρ often yields wrong values. For example, suppose an isolated room contains a battery-powered heater, and we do not know whether it is on or off. If it is on, then after ten minutes the air will be hot, the battery empty, and the entropy of the room has a high value S_3 . Not so if the heater is off; then the entropy has the low initial value $S_1 < S_3$. In view of our ignorance, we may attribute a subjective probability of 50 percent to each of "on" and "off"; correspondingly, we may distribute our subjective credence ρ about the final phase point so that 50 percent of it is spread uniformly over the macro set that arises from "on" and 50 percent over the macro set that arises from "off." Then, $S_{\text{Gibbs}}(\rho)$ will have a value S_2 between S_1 and S_3 . But the correct thermodynamic value is not S_2 , it is either S_1 (if the heater was off) or S_3 (if the heater was on). So subjective entropy yields a wrong value.

Also, there is a problem with time evolution. If we assume that ρ gets transported with the motion of phase points and thus evolves according to the continuity equation (5.14), then the Gibbs entropy does not increase with time, it is constant (homework exercise). (In view of this fact, some authors³³ have even claimed that it was impossible that entropy could increase with time.) This is another example in which the Gibbs entropy yields wrong values.

In sum, the Gibbs entropy yields correct values when ρ is taken to be the canonical or micro-canonical ensembles, but it is mistaken to take it as the definition of entropy also for non-equilibrium states, as some textbooks do.³⁴

³³E.g., A. I. Khinchin: *Matematičeskie osnovanija statističeskoj mechaniki*, Moscow (1941). English translation by G. Gamow: *Mathematical foundations of statistical mechanics*, New York: Dover (1949)

³⁴For further discussion see S. Goldstein, J. L. Lebowitz, R. Tumulka, and N. Zanghi: Gibbs and Boltzmann Entropy in Classical and Quantum Mechanics. In: V. Allori (editor), *Statistical Mechanics and Scientific Explanation: Determinism, Indeterminism and Laws of Nature*, Singapore: World Scientific (2020) http://arxiv.org/abs/1903.11870 and S. Goldstein: Individualist and Ensemblist Approaches to the Foundations of Statistical Mechanics. To appear in *The Monist* (2019).

7.3.4 Ensemblist and Individualist Views

A related confusion concerns the concept of thermal equilibrium when the latter is assumed to mean that "the probability distribution" ρ coincides with $\rho_{\rm mc}$ or $\rho_{\rm can}$ or μ_E ("ensemblist view"), rather than that $x \in \Gamma_{\rm eq}$ ("individualist view"). Again, the basic problem with this idea is that any system has an x but not a ρ . Note also that ρ never becomes $\rho_{\rm mc}$ if it was not $\rho_{\rm mc}$ to start with (because $\rho_{\rm mc}$ is invariant under T^t), so it would seem that no system can ever reach thermal equilibrium. Some authors appeal here to mixing (see Definition 8 on page 52): The condition $\mu_E(A \cap T^tB) \longrightarrow \mu_E(A) \mu_E(B)$ means that the distribution $\mu(\cdot) = \mu_E(\cdot \cap B)$ (i.e., with density $1_{x \in B}$), which evolves to $\mu_t(\cdot) = \mu(\cdot \cap T^tB)$, converges according to $\mu_t(A) \longrightarrow (\text{const.}) \mu_E(A)$ as $t \to \infty$.³⁵ They thus arrive at the conclusion that μ_t reaches thermal equilibrium at $t = \infty$ although the (Gibbs) entropy has not increased for any finite t, and regard the transition to thermal equilibrium as an idealization that never actually occurs in the real world.³⁶

7.3.5 Systems with Interaction and the Thermodynamic Limit

Our computations so far were limited to the simplest case, the ideal gas. We now look at results about systems with interaction between the molecules in the *thermodynamic limit* in which

$$E, V, N \to \infty, \quad \frac{E}{N} \to e, \quad \frac{V}{N} \to v$$
 (7.83)

with constants $e, v \in (0, \infty)$. This means in particular that the vessel $\Lambda \subset \mathbb{R}^3$ depends on N.

I will report two types of results:

- 1. In the thermodynamic limit, the equilibrium entropy $S(E, V, N) = k \log \Omega(E)$ is of the asymptotic form S = Ns(e, v) + o(N). The function s(e, v) is concave and independent of the shape of Λ . We have equivalence of ensembles in the sense that also $S_{\text{Gibbs}}(\rho_{\text{can}}) = Ns(e, v) + o(N)$ for suitable $\beta(e)$.
- 2. In the thermodynamic limit, there is a dominant macro state. Moreover, using an *N*-independent description of ν (such as Boltzmann's macro variables), $S(\nu) = k \log \operatorname{vol} \Gamma_{\nu}$ is of the asymptotic form $S(\nu) = Ns(\nu) + o(N)$, also for non-equilibrium ν ("dramatically different sizes").

A major result of type 1 was proved by David Ruelle (1963) and Michael Fisher (1964). In the version I present below, the interaction is assumed to be *of short range*,

³⁵In fact, in mixing systems any finite measure absolutely continuous relative to the preserved normalized measure \mathbb{P} will converge setwise to a multiple of \mathbb{P} . Equivalently, any density function $\rho \in L^2(\Omega, \mathbb{P})$ converges weakly to a constant $C = \langle \rho \rangle$, i.e., $\int \mathbb{P}(dx) f(x) \rho_t(x) \longrightarrow C \int \mathbb{P}(dx) f(x)$ as $t \to \infty$ for all test functions $f \in L^2(\Omega, \mathbb{P})$.

³⁶For further discussion see S. Goldstein, J. Lebowitz, R. Tumulka, and N. Zanghì: Long-Time Behavior of Macroscopic Quantum Systems. *European Physical Journal H* **35**: 173–200 (2010) http://arxiv.org/abs/1003.2129 and S. Goldstein, D. Huse, J. Lebowitz, and R. Tumulka: Macrocsopic and Microscopic Thermal Equilibrium. *Annalen der Physik* **529**: 1600301 (2017) http://arxiv.org/abs/1610.02312

which excludes the Coulomb interaction; a corresponding result for Coulomb interactions was proved by Joel Lebowitz and Elliott Lieb in 1969.³⁷ We assume that there are no external forces and limit ourselves to pair interactions (although more general classes of potentials can be treated); also for the pair potential $V_2(\boldsymbol{q}_j - \boldsymbol{q}_k)$ we will not formulate the most general possible condition. A sufficient condition is the conjunction of the following:

• "tempered": There are constants A > 0, $R_0 > 0$, and $\varepsilon > 0$ such that

$$V_2(\boldsymbol{q}) \le A |\boldsymbol{q}|^{-3-\varepsilon} \quad \text{for } |\boldsymbol{q}| > R_0.$$
 (7.84)

• "stable": There is a constant B > 0 such that for all N > 1 and all $q_1, \ldots, q_N \in \mathbb{R}^3$,

$$\sum_{1 \le j < k \le N} V_2(\boldsymbol{q}_j - \boldsymbol{q}_k) \ge -NB.$$
(7.85)

A sufficient condition for being stable is the conjunction of the following: (i) V_2 has a hard core of radius a > 0,

$$V_2(\boldsymbol{q}) = \infty \quad \text{for } |\boldsymbol{q}| < a \,, \tag{7.86}$$

and (ii) there is a positive decreasing function φ on $[a, \infty)$ such that

$$\int_{a}^{\infty} \varphi(r) \, 4\pi r^2 \, dr < \infty \tag{7.87}$$

and

$$V_2(\boldsymbol{q}) \ge -\varphi(|\boldsymbol{q}|) \quad \text{for } |\boldsymbol{q}| > a.$$
 (7.88)

In particular, V_2 is tempered and stable if it has a hard core (7.86), has finite range, $V_2(\mathbf{q}) = 0$ for $|\mathbf{q}| > R_0$, and is bounded between a and R_0 . For example, hard spheres are tempered and stable.

We now need to define what it means for a sequence of regions $\Lambda_N \subset \mathbb{R}^3$ to tend to infinite "in a reasonable way," viz., such that it does not have too much surface compared to the bulk.

Definition 9. For $\varepsilon > 0$, let $\partial_{\varepsilon} \Lambda$ denote the set of points with distance $\leq \varepsilon$ to $\partial \Lambda$, and let $d(\Lambda) = \sup\{|\boldsymbol{q} - \boldsymbol{q}'| : \boldsymbol{q}, \boldsymbol{q}' \in \Lambda\}$ denote the diameter of Λ . One says that $\Lambda_N \to \infty$ in the sense of Fisher³⁸ iff

$$\operatorname{vol}(\Lambda_N) \longrightarrow \infty \quad \text{as } N \to \infty$$
 (7.89)

³⁷J.L. Lebowitz and E. Lieb: The Existence of Thermodynamics for Real Matter with Coulomb Forces. *Physical Review Letters* **22**: 631-634 (1969)

³⁸M.E. Fisher: The Free Energy of a Macroscopic System. Archive for Rational Mechanics and Analysis **17**: 377–410 (1964)

and there exists a "shape function" π such that

$$\lim_{\alpha \to 0} \pi(\alpha) = 0 \tag{7.90}$$

and for sufficiently small α and all N,

$$\frac{\operatorname{vol}(\partial_{\alpha d(\Lambda_N)}\Lambda_N)}{\operatorname{vol}(\Lambda_N)} \le \pi(\alpha).$$
(7.91)

For example, if we keep the shape constant with smooth boundary and just scale Λ , $\Lambda_N = N^{1/3}\Lambda$, then $\Lambda_N \to \infty$ in the sense of Fisher. If, however, Λ_N is a cylinder of length N and fixed radius, then (7.91) is violated, as the numerator grows like $\alpha^2 N^3$ but the denominator only like N.

Theorem 15. ³⁹ Let $\Lambda_N \to \infty$ in the sense of Fisher, $\operatorname{vol}(\Lambda_N)/N \to v$, $E/N \to e$, $\Gamma = (\Lambda_N \times \mathbb{R}^3)^N$, V_2 be tempered and stable, $H(q, p) = p^2/2m + \frac{1}{2} \sum_{j \neq k} V_2(\boldsymbol{q}_j - \boldsymbol{q}_k)$, $\Gamma_{\mathrm{mc}} = \{x \in \Gamma : E - \Delta E \leq H(x) \leq E\}$. Then, independently of the value of $\Delta E > 0$ and the sequence Λ_N ,

$$\frac{k}{N}\log \operatorname{vol}\Gamma_{\mathrm{mc}} \longrightarrow s(e,v) \quad as \ N \to \infty$$
(7.92)

for some function s that is concave, finite in the region $\{(e,v) : v \ge v_0, e > e_0(v)\}$ (where v_0 is the minimum volume per particle required for non-overlapping hard cores, "close packing volume"), and $-\infty$ otherwise.

There are cases in which the thermodynamic limit does not exist: (a) If the molecules are charged and the ratio of positive and negative charges is significantly different from 1, then they tend to accumulate near $\partial \Lambda$. (b) Gravitational systems (and generally systems with potentials V_2 not bounded from below near **0**) tend to clump into galaxies, stars, and planets.

I now turn to a result of type 2 due to Oscar Lanford (1973).⁴⁰ His proof focuses on macro variables M_j (j = 1, ..., K) of the form⁴¹

$$M_j(x) = \frac{1}{N} \sum_{1 \le i < k \le N} \Phi_j(\boldsymbol{q}_i - \boldsymbol{q}_k), \qquad (7.93)$$

where the function Φ_j is continuous, even $(\Phi(-q) = \Phi(q))$, and has finite range,

$$\Phi(\boldsymbol{q}) = 0 \quad \text{for } |\boldsymbol{q}| > R_0.$$
(7.94)

Such a variable M_j could count, for example, how many pairs of particles are closer than R_0 to each other (by taking Φ to be a continuous approximation to $1_{|\mathbf{q}| < R_0}$). This is perhaps not a very realistic or relevant example of a macro variable, but one for which a proof is possible.

³⁹For the proof see D. Ruelle: *Statistical Mechanics: Rigorous Results.* Benjamin (1969)

⁴⁰O. E. Lanford: Entropy and Equilibrium States in Classical Statistical Mechanics. Pages 1–113 in A. Lenard (ed.), *Statistical Mechanics and Mathematical Problems*. Lecture Notes in Physics **20**. Berlin: Springer-Verlag (1973)

⁴¹Actually, his proof is a bit more general than that. I am simplifying matters here.

Theorem 16. Let Λ_N , E, Γ , H, $\Gamma_{\rm mc}$ be as in Theorem 15, M_j as above, and assume that V_2 has a finite range. Then, for given bounded intervals $I_j \subset \mathbb{R}$ and independently of the value of $\Delta E > 0$ and the sequence Λ_N ,

$$\frac{k}{N}\log\operatorname{vol}\left\{x\in\Gamma_{\mathrm{mc}}:M_{j}(x)\in I_{j}\;\forall j\right\}\longrightarrow s(e,v,\underline{\Phi},\underline{I})\quad as\;N\to\infty\tag{7.95}$$

for some function s that is everywhere either finite or $-\infty$, with the notation $\underline{\Phi} = (\Phi_1, \ldots, \Phi_K)$ and $\underline{I} = (I_1, \ldots, I_K)$. Moreover,

$$s(e, v, \underline{\Phi}, \underline{I}) = \sup_{m_j \in I_j \ \forall j} s(e, v, \underline{\Phi}, \underline{m})$$
(7.96)

for a suitable function $s(e, v, \underline{\Phi}, \underline{m})$.

The last statement essentially means that after the thermodynamic limit, we can also let the resolution $\Delta M_j \rightarrow 0$ and still get a meaningful entropy function.

7.3.6 Without a Dominant Macro State

There are exceptional situations in which no dominant macro state exists. First, certain symmetries can enforce that every macro set has a mirror image that is another macro set of the same size, with the consequence that the largest macro set and its mirror image each have nearly 50% of the volume of $\Gamma_{\rm mc}$ (such a situation occurs at certain phase transitions).

Second, if N is not very large (e.g., $N = 10^2$), or the number of macro variables M_i is not much smaller than N (e.g., if the number r of Boltzmann's cells $A_i \subset \Gamma_1$ is not much smaller than N), or the resolution ΔM_j is chosen very small, then the largest macro set will not be dominant. To illustrate the last point, consider again only configurations, partition Λ into r cells Λ_i of equal volume, and consider a purely random (i.e., uniformly distributed) configuration $x \in \Lambda^N$. Then the occupation number N_i of Λ_i is binomial with parameters N and 1/r, so its expectation is N/r and its variance is $N(1/r)(1-1/r) \approx N/r$ if $r \gg 1$. In other words, the deviations in the histogram N_i from uniformity (i.e., from the value N/r) that occur "by chance alone" (i.e., even for a typical x) are of the order $\sqrt{N/r}$. Before, we took the range of N_i -values included in one Γ_{ν} to have length $N\Delta f$, which for fixed Δf and r is much larger than $\sqrt{N/r}$ for large N. However, if for a fixed N we choose Δf so small that $N\Delta f = \sqrt{N/r}$ or even $N\Delta f < \sqrt{N/r}$, then we should expect to find, for maybe half of all i, N_i outside of the interval $[N/r - N\Delta f, N/r + N\Delta f]$ that defines the largest macro set (the one of the uniform histogram). The statement that a random x will not have a uniform histogram with this accuracy means, in other terminology, that the largest macro set $\Gamma_{\hat{\nu}}$ will not have the majority of the volume.

Third, if the size of the system is exorbitant, say its volume is greater than $10^{10^{10}}$ cubic meters (which is about $10^{10^{10}}$ times the volume of the known universe, which is 10^{80} cubic meters), while we keep the size of the cells Λ_j small on the macro scale, then the number of cells will be correspondingly large, and it is to be expected by chance alone

that a uniformly-randomly selected phase point in $\Gamma_{\rm mc}$ will possess a cell Λ_j somewhere in which a macroscopic observable M_j deviates significantly from its average value. As a consequence, the set where *every* M_j assumes its average value will not have most of the volume.

To obtain the estimate that $10^{10^{10}}$ cubic meters is the relevant volume, we subdivide the volume into m cells of (say) cubic millimeter size, consider the volume filled with air at room conditions, which has $n \approx 2.5 \times 10^{16}$ particles (i.e., N_2 molecules) per cubic millimeter, and ask whether the number of particles in any cell will be less than 0.999nor more than 1.001n. Since for a random phase point, the particles will be essentially uniformly distributed over the volume, the number N_i of particles in cell i has a binomial distribution with parameters nm and m^{-1} , which for large n and m is approximately Gaussian with mean n and variance n. The probability that $N_i < 0.999n$ or $N_i > 1.001n$ is of order $e^{-(0.001n)^2/2n} = e^{-n/2 \times 10^6}$, so for an appreciable probability that this happens for any cell anywhere, we need that $m \gtrsim e^{n/2 \times 10^6} \approx 10^{10^{10}}$.

This effect, that for exorbitantly large systems none of the Γ_{ν} is dominant, can be problematical when we want to take the thermodynamic limit and let the volume tend to infinity. It can easily be dealt with, either by increasing the cell size and the tolerances ΔM_j as we take the limit, or by defining Γ_{eq} differently as the set of those $x \in \Gamma_{mc}$ at which *most*, but not *all*, macro observables M_j assume their thermal equilibrium values.

8 The Boltzmann Equation

The expression "statistical mechanics," which was coined by Gibbs, fits particularly for the Boltzmann equation, one of the gems of the subject.⁴² This equation reads, in the version appropriate for the hard sphere gas without external forces,

$$\left(\frac{\partial}{\partial t} + \boldsymbol{v} \cdot \nabla_{\boldsymbol{q}}\right) f(\boldsymbol{q}, \boldsymbol{v}, t) = Q(\boldsymbol{q}, \boldsymbol{v}, t)$$
(8.1)

with the "collision term"

$$Q(\boldsymbol{q}, \boldsymbol{v}, t) = \lambda \int_{\mathbb{R}^3} d^3 \boldsymbol{v}_* \int_{\mathbb{S}^2} d^2 \boldsymbol{\omega} \, \mathbf{1}_{\boldsymbol{\omega} \cdot (\boldsymbol{v} - \boldsymbol{v}_*) > 0} \, \boldsymbol{\omega} \cdot (\boldsymbol{v} - \boldsymbol{v}_*) \times \left[f(\boldsymbol{q}, \boldsymbol{v}', t) \, f(\boldsymbol{q}, \boldsymbol{v}'_*, t) - f(\boldsymbol{q}, \boldsymbol{v}, t) \, f(\boldsymbol{q}, \boldsymbol{v}_*, t) \right], \quad (8.2)$$

a constant $\lambda > 0$, and the abbreviations

$$\boldsymbol{v}' = \boldsymbol{v} - [(\boldsymbol{v} - \boldsymbol{v}_*) \cdot \boldsymbol{\omega}]\boldsymbol{\omega}$$
(8.3)

$$\boldsymbol{v}'_* = \boldsymbol{v}_* + [(\boldsymbol{v} - \boldsymbol{v}_*) \cdot \boldsymbol{\omega}] \boldsymbol{\omega}$$
 (8.4)

The Boltzmann equation is considered for $\boldsymbol{v} \in \mathbb{R}^3$ and $\boldsymbol{q} \in \Lambda$ along with the boundary condition

$$f(\boldsymbol{q}, \boldsymbol{v}, t) = f(\boldsymbol{q}, \boldsymbol{v} - 2[\boldsymbol{v} \cdot \boldsymbol{n}]\boldsymbol{n}, t)$$
(8.5)

for $q \in \partial \Lambda$ with n = n(q) the outward unit normal vector to $\partial \Lambda$ at q (Λ is assumed to have piecewise smooth boundary).

The Boltzmann equation is a PDE (more precisely, integro-differential equation) intended for determining the time evolution of f as an autonomous macro-evolution. It is intended to apply to the hard sphere gas as described in Section 2.7 above in the *Boltzmann-Grad limit*⁴³

$$N \to \infty, \quad a \to 0, \quad 4Na^2 \to \lambda,$$
 (8.6)

where a is the radius of the spheres. Since in this limit the spheres get very small (for example, the volume occupied by the spheres $\frac{4}{3}\pi a^3 N$ tends to 0 in this limit), one speaks of a *dilute* or rarefiel gas.

The boundary condition (8.5) represents the specular reflection of spheres at the boundary: $\boldsymbol{v} - 2[\boldsymbol{v} \cdot \boldsymbol{n}]\boldsymbol{n}$ is the velocity of a particle that got reflected at the boundary with prior velocity \boldsymbol{v} ; cf. (2.31); identifying the phase points $(\boldsymbol{q}, \boldsymbol{v})$ and $(\boldsymbol{q}, \boldsymbol{v} - 2[\boldsymbol{v} \cdot \boldsymbol{n}]\boldsymbol{n})$ corresponds to the relation (8.5). The relation (8.3)–(8.4) between $(\boldsymbol{v}', \boldsymbol{v}'_*)$ and $(\boldsymbol{v}, \boldsymbol{v}_*)$ is exactly the one between the pre-collision and post-collision velocities, see (2.34).

⁴²L. Boltzmann: Weitere Studien über das Wärmegleichgewicht unter Gasmolekülen. Sitzungsberichte der Akademie der Wissenschaften Wien **66**: 275–370 (1872)

⁴³H. Grad: Principles of the Kinetic Theory of Gases. Pages 205–294 in S. Flügge (editor): *Handbuch der Physik, Vol. 12.* Berlin: Springer (1958)

8.1 Heuristic Derivation

In the absence of collisions, any density in $\Gamma_1 = \Lambda \times \mathbb{R}^3$ would be transported according to

$$\left(\frac{\partial}{\partial t} + \boldsymbol{v} \cdot \nabla_{\boldsymbol{q}}\right) f(\boldsymbol{q}, \boldsymbol{v}, t) = 0$$
(8.7)

with boundary condition (8.5) for specular reflection. The term $\boldsymbol{v} \cdot \nabla_{\boldsymbol{q}}$ is called the "streaming term." The evolution of f is of the form (8.1) with $Q(\boldsymbol{q}, \boldsymbol{v}) \Delta^3 \boldsymbol{q} \Delta^3 \boldsymbol{v}$ the change per time of the fraction of particles in $\Delta^3 \boldsymbol{q} \Delta^3 \boldsymbol{v}$ due to collisions. Here it is understood that $\Delta^3 \boldsymbol{q} \Delta^3 \boldsymbol{v}$ is large enough to contain many particles; the limit $\Delta^3 \boldsymbol{q} \Delta^3 \boldsymbol{v} \to 0$ is taken *after* the Boltzmann–Grad limit. In the following, we will write $d^3 \boldsymbol{q} d^3 \boldsymbol{v}$ for $\Delta^3 \boldsymbol{q} \Delta^3 \boldsymbol{v}$ and take it to be infinitesimal compared to the scale on which f varies. So

$$NQ(\boldsymbol{q},\boldsymbol{v}) d^3 \boldsymbol{q} d^3 \boldsymbol{v} = \text{rate of change in particle number in } d^3 \boldsymbol{q} d^3 \boldsymbol{v}.$$
 (8.8)

This change is of the form "gain $-\log s$," where "gain" is the number of particles that get scattered *into* $d^3 q d^3 v$ and "loss" *out of* $d^3 q d^3 v$. We know that the collisions $(v_1, v_2) = (v, v_*) \rightarrow (v', v'_*) = (v'_1, v'_2)$ are given by (8.3)–(8.4), and thus depend, apart from the incoming velocities (v, v_*) , only on the "collision parameter" $\omega = (q_2 - q_1)/2a$. As already considered in a homework exercise, we can easily determine the probability distribution of ω for two colliding particles with given v, v_* if we can assume that their exact (microscopic) positions in $d^3 q$ behave like they are random and independent. This assumption is the famous $Sto\betazahlansatz$ or hypothesis of molecular chaos. It implies that the distribution of $\omega \in \mathbb{S}^2$, given that a collision occurs, has density proportional to $1_{\omega \cdot (v-v_*)>0} \omega \cdot (v - v_*)$ relative to surface area $d^2 \omega$. The same kind of reasoning yields that the number \mathfrak{N} of collisions happening per dt to two spheres in $d^3 q$ with velocities in d^3v and d^3v_* and collision parameter in $d^2\omega$ is given by

$$\mathfrak{N} = 4N^2 a^2 \, \mathbf{1}_{\boldsymbol{\omega} \cdot (\boldsymbol{v} - \boldsymbol{v}_*) > 0} \, \boldsymbol{\omega} \cdot (\boldsymbol{v} - \boldsymbol{v}_*) \, f(\boldsymbol{q}, \boldsymbol{v}) \, f(\boldsymbol{q}, \boldsymbol{v}_*) \, d^3 \boldsymbol{q} \, d^3 \boldsymbol{v} \, d^3 \boldsymbol{v}_* \, d^2 \boldsymbol{\omega} \, dt \,. \tag{8.9}$$

That is because $N f(\boldsymbol{q}, \boldsymbol{v}) d^3 \boldsymbol{q} d^3 \boldsymbol{v}$ is the number of particles in $d^3 \boldsymbol{q} d^3 \boldsymbol{v}$; fix one such particle with exact location \boldsymbol{q}_1 . For another particle with velocity \boldsymbol{v}_* to hit the former in $d^2 \boldsymbol{\omega}$ within dt, its exact location \boldsymbol{q}_2 must lie in the 3-cylinder ("collision cylinder")

$$q_1 + 2a d^2 \omega + [0, dt] (v - v_*),$$
 (8.10)

and $\boldsymbol{\omega} \cdot (\boldsymbol{v} - \boldsymbol{v}_*)$ must be positive. This 3-cylinder has volume $dC = 4a^2 d^2 \boldsymbol{\omega} \boldsymbol{\omega} \cdot (\boldsymbol{v} - \boldsymbol{v}_*) dt$, so the number of particles in it with velocity in $d^3 \boldsymbol{v}_*$ is $N f(\boldsymbol{q}, \boldsymbol{v}_*) \mathbf{1}_{\boldsymbol{\omega} \cdot (\boldsymbol{v} - \boldsymbol{v}_*) > 0} dC d^3 \boldsymbol{v}_*$, provided we assume that this number is the same as in any other cylinder of the same volume, that is, if we make the assumption of molecular chaos. Putting these expressions together yields (8.9); this formula can itself be called the hypothesis of molecular chaos, as it is the only reference to this hypothesis that will be used in the following.

From (8.9) we obtain the number of losses by integrating together all possibilities for v_* and ω :

$$\log dt = 4N^2 a^2 dt d^3 \boldsymbol{q} d^3 \boldsymbol{v} \int_{\mathbb{R}^3} d^3 \boldsymbol{v}_* \int_{\mathbb{S}^2} d^2 \boldsymbol{\omega} \, \mathbf{1}_{\boldsymbol{\omega} \cdot (\boldsymbol{v} - \boldsymbol{v}_*) > 0} \, \boldsymbol{\omega} \cdot (\boldsymbol{v} - \boldsymbol{v}_*) \, f(\boldsymbol{q}, \boldsymbol{v}) \, f(\boldsymbol{q}, \boldsymbol{v}_*) \,. \tag{8.11}$$

We now turn to computing the number of gains and begin with a few preparations. Let $u' = (v', v'_*)$ be the post-collision velocities of a particle pair with pre-collision velocities $u = (v, v_*)$. For given ω , their relation (8.3)–(8.4) is of the form

$$u' = R_{\omega} u \,, \tag{8.12}$$

where $R_{\boldsymbol{\omega}}$ is a linear mapping $\mathbb{R}^6 \to \mathbb{R}^6$.

Proposition 3. R_{ω} has the following properties:

- (a) R_{ω} is orthogonal, $R_{\omega} \in O(6)$.
- (b) det $R_{\omega} = -1$
- (c) $R^2_{\omega} = I_6$
- (d) $R_{-\omega} = R_{\omega}$
- (e) $\boldsymbol{\omega} \cdot (\boldsymbol{v}' \boldsymbol{v}'_*) = -\boldsymbol{\omega} \cdot (\boldsymbol{v} \boldsymbol{v}_*).$

The proof is a homework exercise.

We are now ready to compute the number of gains. We need to find the number of collisions in $d^3 \boldsymbol{q}$ that end up with one particle in $d^3 \boldsymbol{v}$ (and the other with any velocity). The number of collisions in $d^3 \boldsymbol{q}$ during dt such that $u' \in C$ is, for any test set $C \subset \mathbb{R}^6$, equal to $1_{u' \in C} \mathfrak{N}$ integrated over $u = (\boldsymbol{v}, \boldsymbol{v}_*)$ and $\boldsymbol{\omega}$, i.e., by (8.9),

$$4N^2a^2d^3\boldsymbol{q}\,dt\int_{\mathbb{S}^2} d^2\boldsymbol{\omega}\int_{\mathbb{R}^6} d^6u\,\mathbf{1}_{\boldsymbol{\omega}\cdot(\boldsymbol{v}-\boldsymbol{v}_*)>0}\,\boldsymbol{\omega}\cdot(\boldsymbol{v}-\boldsymbol{v}_*)\,f(\boldsymbol{q},\boldsymbol{v})\,f(\boldsymbol{q},\boldsymbol{v}_*)\,\mathbf{1}_{R_{\boldsymbol{\omega}}u\in C}\,.$$
 (8.13)

Now we change variables in the *u*-integral, introducing $u' = R_{\omega}u$ as the integration variable. The expression then becomes

$$=4N^{2}a^{2}d^{3}\boldsymbol{q}\,dt\int_{\mathbb{S}^{2}}d^{2}\boldsymbol{\omega}\int_{\mathbb{R}^{6}}d^{6}u'\,\mathbf{1}_{\boldsymbol{\omega}\cdot(\boldsymbol{v}-\boldsymbol{v}_{*})>0}\,\boldsymbol{\omega}\cdot(\boldsymbol{v}-\boldsymbol{v}_{*})\,f(\boldsymbol{q},\boldsymbol{v})\,f(\boldsymbol{q},\boldsymbol{v}_{*})\,\mathbf{1}_{u'\in C}\,,\quad(8.14)$$

with every occurrence of components of u understood as $u = R_{\omega}^{-1}u' = R_{\omega}u'$; note that the Jacobian determinant is det $R_{\omega} = -1$. Now it is convenient to rename u' into u and write $u' = (v', v'_*)$ for $R_{\omega}u$ (called u before), yielding

$$=4N^{2}a^{2}d^{3}\boldsymbol{q}\,dt\int_{\mathbb{S}^{2}}d^{2}\boldsymbol{\omega}\int_{\mathbb{R}^{6}}d^{6}u\,\mathbf{1}_{\boldsymbol{\omega}\cdot(\boldsymbol{v}'-\boldsymbol{v}_{*}')>0}\,\boldsymbol{\omega}\cdot(\boldsymbol{v}'-\boldsymbol{v}_{*}')\,f(\boldsymbol{q},\boldsymbol{v}')\,f(\boldsymbol{q},\boldsymbol{v}_{*}')\,\mathbf{1}_{u\in C}\qquad(8.15)$$

$$= 4N^2 a^2 d^3 \boldsymbol{q} dt \int_{\mathbb{S}^2} d^2 \boldsymbol{\omega} \int_C d^6 u \, \mathbf{1}_{\boldsymbol{\omega} \cdot (\boldsymbol{v}' - \boldsymbol{v}'_*) > 0} \, \boldsymbol{\omega} \cdot (\boldsymbol{v}' - \boldsymbol{v}'_*) \, f(\boldsymbol{q}, \boldsymbol{v}') \, f(\boldsymbol{q}, \boldsymbol{v}'_*) \,. \tag{8.16}$$

By Proposition 3(e), this is

$$= -4N^2 a^2 d^3 \boldsymbol{q} dt \int_{\mathbb{S}^2} d^2 \boldsymbol{\omega} \int_C d^6 u \, \mathbf{1}_{\boldsymbol{\omega} \cdot (\boldsymbol{v} - \boldsymbol{v}_*) < 0} \, \boldsymbol{\omega} \cdot (\boldsymbol{v} - \boldsymbol{v}_*) \, f(\boldsymbol{q}, \boldsymbol{v}') \, f(\boldsymbol{q}, \boldsymbol{v}'_*) \,. \tag{8.17}$$

It is now convenient to rename $\omega \to -\omega$. This change of variables has

Jacobian determinant
$$= -1$$
. (8.18)

Here are three easy ways of seeing this: First, the mapping $\boldsymbol{q} \mapsto -\boldsymbol{q}$ in \mathbb{R}^3 has Jacobian determinant -1, and since in polar coordinates the r variable is not affected, the sign change must happen to $d^2\boldsymbol{\omega}$. Second, the antipode mapping $\boldsymbol{\omega} \mapsto -\boldsymbol{\omega}$ on \mathbb{S}^2 can be obtained by composing the reflection $z \to -z$ and the rotation through 180° about the z axis. Third, the antipode image of a right hand is a left hand.

We thus obtain that the quantity considered equals

$$=4N^{2}a^{2}d^{3}\boldsymbol{q}\,dt\int_{\mathbb{S}^{2}}d^{2}\boldsymbol{\omega}\int_{C}d^{6}u\,\mathbf{1}_{\boldsymbol{\omega}\cdot(\boldsymbol{v}-\boldsymbol{v}_{*})>0}\,\boldsymbol{\omega}\cdot(\boldsymbol{v}-\boldsymbol{v}_{*})\,f(\boldsymbol{q},\boldsymbol{v}')\,f(\boldsymbol{q},\boldsymbol{v}'_{*})\,,\qquad(8.19)$$

and this was the number of collisions in $d^3 q$ during dt such that the post-collision velocities $(\boldsymbol{v}, \boldsymbol{v}_*)$ lie in C. Now we are interested in $C = d^3 \boldsymbol{v} \times \mathbb{R}^3$, which yields the desired gain:

gain
$$dt = 4N^2 a^2 d^3 \boldsymbol{q} d^3 \boldsymbol{v} dt \int_{\mathbb{S}^2} d^2 \boldsymbol{\omega} \int_{\mathbb{R}^3} d^3 \boldsymbol{v}_* \, \mathbf{1}_{\boldsymbol{\omega} \cdot (\boldsymbol{v} - \boldsymbol{v}_*) > 0} \, \boldsymbol{\omega} \cdot (\boldsymbol{v} - \boldsymbol{v}_*) \, f(\boldsymbol{q}, \boldsymbol{v}') \, f(\boldsymbol{q}, \boldsymbol{v}'_*) \, .$$

(8.20)

Putting together (8.8), (8.11), and (8.20), we have that

$$Q(\boldsymbol{q}, \boldsymbol{v}) = \frac{\operatorname{gain} - \operatorname{loss}}{N \, d^3 \boldsymbol{q} \, d^3 \boldsymbol{v}}$$

$$= 4Na^2 \int_{\mathbb{R}^3} d^3 \boldsymbol{v}_* \int_{\mathbb{S}^2} d^2 \boldsymbol{\omega} \, \mathbf{1}_{\boldsymbol{\omega} \cdot (\boldsymbol{v} - \boldsymbol{v}_*) > 0} \, \boldsymbol{\omega} \cdot (\boldsymbol{v} - \boldsymbol{v}_*) \times$$

$$\left[f(\boldsymbol{q}, \boldsymbol{v}') \, f(\boldsymbol{q}, \boldsymbol{v}'_*) - f(\boldsymbol{q}, \boldsymbol{v}) \, f(\boldsymbol{q}, \boldsymbol{v}_*) \right], \qquad (8.22)$$

as claimed.

8.2 Mean Free Path

As a by-product, the above reasoning provides estimates of the time that a sphere spends in free flight between collisions, or the distance between collisions. When computing the number of losses, we found that for a given particle in $d^3 \boldsymbol{q} d^3 \boldsymbol{v}$, the number of particles hitting it during dt with velocity in $d^3 \boldsymbol{v}_*$ and collision parameter in $d^2 \boldsymbol{\omega}$ is $N f(\boldsymbol{q}, \boldsymbol{v}_*) \mathbf{1}_{\boldsymbol{\omega} \cdot (\boldsymbol{v} - \boldsymbol{v}_*) > 0} dC d^3 \boldsymbol{v}_*$ with $dC = 4a^2 d^2 \boldsymbol{\omega} \boldsymbol{\omega} \cdot (\boldsymbol{v} - \boldsymbol{v}_*) dt$. So the probability of a collision during dt is this quantity integrated over v_* and ω , which yields

$$4Na^{2} dt \int_{\mathbb{R}^{3}} d^{3}\boldsymbol{v}_{*} f(\boldsymbol{q}, \boldsymbol{v}_{*}) \int_{\mathbb{S}^{2}} d^{2}\boldsymbol{\omega} \, \mathbf{1}_{\boldsymbol{\omega} \cdot (\boldsymbol{v} - \boldsymbol{v}_{*}) > 0} \, \boldsymbol{\omega} \cdot (\boldsymbol{v} - \boldsymbol{v}_{*})$$

$$= 4Na^{2} dt \int_{\mathbb{R}^{3}} d^{3}\boldsymbol{v}_{*} f(\boldsymbol{q}, \boldsymbol{v}_{*}) |\boldsymbol{v} - \boldsymbol{v}_{*}| \int_{\mathbb{S}^{2}} d^{2}\boldsymbol{\omega} \, \mathbf{1}_{\omega_{z} > 0} \, \omega_{z}$$

$$(8.23)$$

$$=4Na^{2} dt \int_{\mathbb{R}^{3}} d^{3}\boldsymbol{v}_{*} f(\boldsymbol{q},\boldsymbol{v}_{*}) |\boldsymbol{v}-\boldsymbol{v}_{*}| 2\pi \int_{0}^{\pi/2} d\theta \sin\theta\cos\theta \qquad (8.24)$$

$$= 4\pi N a^2 dt \int_{\mathbb{R}^3} d^3 \boldsymbol{v}_* f(\boldsymbol{q}, \boldsymbol{v}_*) |\boldsymbol{v} - \boldsymbol{v}_*|.$$
(8.25)

As long as f does not change noticeably during the time of free flight, the mean free time τ is the reciprocal value of the collision rate,

$$\tau(\boldsymbol{q}, \boldsymbol{v}) = \left[4\pi N a^2 \int_{\mathbb{R}^3} d^3 \boldsymbol{v}_* f(\boldsymbol{q}, \boldsymbol{v}_*) |\boldsymbol{v} - \boldsymbol{v}_*|\right]^{-1}.$$
(8.26)

Often, the expressions "mean free time" and "mean free path" refer to the average over all particles and all collisions. Asymptotically in the Boltzmann–Grad limit, the mean free path ℓ can be computed easily as follows (under the hypothesis of molecular chaos). Think of a configuration of N spheres of radius 2a in a big cylinder around the x-axis with base area A and length L. Think of these spheres as fixed obstacles, and let a point particle move in the x-direction starting from a random point of the cylinder base; whenever it hits an obstacle, we replace it by a particle right behind the obstacle, as if it had passed through. The probability of hitting a particular obstacle is the visible area of the obstacle (i.e., its projection to the yz-plane) divided by A, or $4\pi a^2/A$. Note that this does not depend on the speed with which the point is moving. Thus, the expected number of obstacles hit while travelling the distance L is $4\pi Na^2/A$, so the expected number of collisions per distance is $4\pi Na^2/AL = 4\pi Na^2/V$. Due to the law of large numbers, if we have many point particles moving in the x-direction with initial positions uniform over the cylinder base, then the number of collisions per distance per particle is $4\pi Na^2/V$, so the mean free path is $V/4\pi Na^2$. Now any change in direction does not actually change the situation. Also, it does not matter whether the obstacles move. Furthermore, instead of a point colliding with obstacle of radius 2awe can assume that two spheres of radius a collide without changing the numbers. So the mean free path is^{44}

$$\ell = \frac{V}{\pi\lambda} \,. \tag{8.27}$$

The mean free time \bar{t} now depends on the velocity distribution. A rough estimate can be obtained for the Maxwellian distribution, for which a typical speed is given by

⁴⁴In fact, independently of f. To illustrate this point, suppose that 90% of all particles were in the left half and 10% in the right, so $z_L = 9z_R$ and, by (8.27), $\ell_L = \ell_R/9$. Then the average over all particles is $\ell = (N_L \ell_L + N_R \ell_R)/N = 1/4\pi a^2 z$ with z = N/V the average density.

 $v_{\rm rms} = \sqrt{\mathbb{E}(v^2)} = \sqrt{3kT/m}$ (as computed in a homework exercise; rms = root mean square). Thus, a typical free time is

$$\bar{t} = \frac{\ell}{v_{\rm rms}} = \left(\frac{m}{3kT}\right)^{1/2} \frac{V}{\pi\lambda} \,. \tag{8.28}$$

This quantity is often called the "mean free time."

8.3 Conservation Laws

We remark that if f_t obeys the Boltzmann equation, then

$$\int_{\Lambda} d^3 \boldsymbol{q} \int_{\mathbb{R}^3} d^3 \boldsymbol{v} f_t(\boldsymbol{q}, \boldsymbol{v})$$
(8.29)

and

$$\int_{\Lambda} d^3 \boldsymbol{q} \int_{\mathbb{R}^3} d^3 \boldsymbol{v} \, \boldsymbol{v}^2 \, f_t(\boldsymbol{q}, \boldsymbol{v}) \tag{8.30}$$

are time independent. This can be checked directly from the Boltzmann equation, but it is also physically clear as conservation laws for particle number and energy.

8.4 The H Theorem

The H functional is defined by

$$H(f) = \int_{\Lambda} d^3 \boldsymbol{q} \int_{\mathbb{R}^3} d^3 \boldsymbol{v} f(\boldsymbol{q}, \boldsymbol{v}) \log f(\boldsymbol{q}, \boldsymbol{v}), \qquad (8.31)$$

So s(f) = -k H(f) for the entropy s per particle according to (7.55). Boltzmann's H Theorem⁴⁵ asserts that if f_t is a solution of the Boltzmann equation then

$$\frac{dH(f_t)}{dt} \le 0. \tag{8.32}$$

Given what we know already, this relation is not surprising. We knew from (7.55) that the entropy of a given macro state f can be computed explicitly, we knew from the Boltzmann equation that f evolves autonomously, and we knew from Section 7.3.1 that in such a situation the entropy cannot decrease. Still, it is remarkable that this can be derived cleanly from the Boltzmann equation.

Another remark: Since non-decreasing entropy could permit that entropy is constant, it is of interest to characterize the cases in which equality holds in (8.32). This will be done in Section 8.5.

⁴⁵L. Boltzmann: Weitere Studien über das Wärmegleichgewicht unter Gasmolekülen. Sitzungsberichte der Akademie der Wissenschaften Wien **66**: 275–370 (1872)

Before we derive the H theorem, we present two auxiliary statements. As a shorthand notation, we write

$$f = f(q, v) f' = f(q, v') f_* = f(q, v_*) f'_* = f(q, v'_*),$$

and likewise with other functions of q and v.

Proposition 4. Fix $q \in \Lambda$, and let f(q, v) and $\phi(q, v)$ be functions such that the left-hand side of (8.33) exists. Then

$$\int_{\mathbb{R}^3} d^3 \boldsymbol{v} \, Q \, \phi = \frac{\lambda}{4} \int d^3 \boldsymbol{v} \int d^3 \boldsymbol{v}_* \int_{\mathbb{S}^2} d^2 \boldsymbol{\omega} \, \mathbf{1}_{\boldsymbol{\omega} \cdot (\boldsymbol{v} - \boldsymbol{v}_*) > 0} \, \boldsymbol{\omega} \cdot (\boldsymbol{v} - \boldsymbol{v}_*) \times (f' \, f'_* - f \, f_*) (\phi + \phi_* - \phi' - \phi'_*) \,. \tag{8.33}$$

Proof. By definition,

$$\int_{\mathbb{R}^3} d^3 \boldsymbol{v} \, Q \, \phi = \lambda \int d^3 \boldsymbol{v} \int d^3 \boldsymbol{v}_* \int_{\mathbb{S}^2} d^2 \boldsymbol{\omega} \, \mathbf{1}_{\boldsymbol{\omega} \cdot (\boldsymbol{v} - \boldsymbol{v}_*) > 0} \, \boldsymbol{\omega} \cdot (\boldsymbol{v} - \boldsymbol{v}_*) \left(f' \, f'_* - f \, f_* \right) \phi \,. \tag{8.34}$$

First, on the right-hand side rename the starred into unstarred variables and vice versa, and replace $\omega \to -\omega$; then also v' and v'_* change roles. By Proposition 3(d) and (8.18),

$$\int_{\mathbb{R}^3} d^3 \boldsymbol{v} \, Q \, \phi = \lambda \int d^3 \boldsymbol{v} \int d^3 \boldsymbol{v}_* \int_{\mathbb{S}^2} d^2 \boldsymbol{\omega} \, \mathbf{1}_{\boldsymbol{\omega} \cdot (\boldsymbol{v} - \boldsymbol{v}_*) > 0} \, \boldsymbol{\omega} \cdot (\boldsymbol{v} - \boldsymbol{v}_*) \left(f' \, f'_* - f \, f_* \right) \phi_* \,. \tag{8.35}$$

Second, start from (8.34) again and carry out a change of variables, replacing integration over $(\boldsymbol{v}, \boldsymbol{v}_*)$ by integration over the primed variables. In addition, replace $\boldsymbol{\omega} \to -\boldsymbol{\omega}$ again. Using det $R_{\boldsymbol{\omega}} = -1$, we obtain that

$$\int_{\mathbb{R}^3} d^3 \boldsymbol{v} \, Q \, \phi = -\lambda \int d^3 \boldsymbol{v}' \int d^3 \boldsymbol{v}'_* \int_{\mathbb{S}^2} d^2 \boldsymbol{\omega} \, \mathbf{1}_{\boldsymbol{\omega} \cdot (\boldsymbol{v} - \boldsymbol{v}_*) < 0} \, \boldsymbol{\omega} \cdot (\boldsymbol{v} - \boldsymbol{v}_*) \left(f' \, f'_* - f \, f_* \right) \phi \,. \tag{8.36}$$

Now rename primed into unprimed variables and vice versa, and use Proposition 3(d):

$$\int_{\mathbb{R}^3} d^3 \boldsymbol{v} \, Q \, \phi = \lambda \int d^3 \boldsymbol{v} \int d^3 \boldsymbol{v}_* \int_{\mathbb{S}^2} d^2 \boldsymbol{\omega} \, \mathbf{1}_{\boldsymbol{\omega} \cdot (\boldsymbol{v} - \boldsymbol{v}_*) > 0} \, \boldsymbol{\omega} \cdot (\boldsymbol{v} - \boldsymbol{v}_*) \left(f' \, f'_* - f \, f_* \right) \left(-\phi' \right). \tag{8.37}$$

Third, starting from (8.37), interchange the starred and unstarred variables (and $\omega \rightarrow -\omega$) to obtain:

$$\int_{\mathbb{R}^3} d^3 \boldsymbol{v} \, Q \, \phi = \lambda \int d^3 \boldsymbol{v} \int d^3 \boldsymbol{v}_* \int_{\mathbb{S}^2} d^2 \boldsymbol{\omega} \, \mathbf{1}_{\boldsymbol{\omega} \cdot (\boldsymbol{v} - \boldsymbol{v}_*) > 0} \, \boldsymbol{\omega} \cdot (\boldsymbol{v} - \boldsymbol{v}_*) \left(f' \, f'_* - f \, f_* \right) \left(-\phi'_* \right). \tag{8.38}$$

Now take the sum of (8.34), (8.35), (8.37), and (8.38), and divide by four; this yields (8.33).

Proposition 5 (Boltzmann inequality). If f(q, v) > 0 is such that the left-hand side exists, then

$$\int d^3 \boldsymbol{v} \, Q \, \log f \le 0 \,. \tag{8.39}$$

Proof. From (8.33) with $\phi = \log f$ (and a shorter notation for the integrals),

$$\int_{\mathbb{R}^3} d^3 \boldsymbol{v} Q \log f = \frac{\lambda}{4} \int d^3 \boldsymbol{v} d^3 \boldsymbol{v}_* d^2 \boldsymbol{\omega} \, \mathbf{1}_{\boldsymbol{\omega} \cdot (\boldsymbol{v} - \boldsymbol{v}_*) > 0} \, \boldsymbol{\omega} \cdot (\boldsymbol{v} - \boldsymbol{v}_*) (f' f'_* - f f_*) \, \log(f f_* / f' f'_*) \,.$$
(8.40)

For y, z > 0,

$$(z-y)\log(y/z) \le 0.$$
 (8.41)

To verify this, note that for y < z, z - y > 0 and $\log(y/z) < 0$; for y = z, $z - y = 0 = \log(y/z)$; and for y > z, z - y < 0 and $\log(y/z) > 0$. Now (8.39) follows.

Derivation of the H theorem. Start from the Boltzmann equation

$$\left(\frac{\partial}{\partial t} + \boldsymbol{v} \cdot \nabla_{\boldsymbol{q}}\right) f(\boldsymbol{q}, \boldsymbol{v}, t) = Q(\boldsymbol{q}, \boldsymbol{v}, t),$$

multiply both sides by $1 + \log f$, integrate over \boldsymbol{v} , and use that $\int d^3 \boldsymbol{v} Q = 0$ by (8.33) for $\phi = 1$. This leads to

$$\frac{\partial}{\partial t} \int d^3 \boldsymbol{v} \, f \log f + \nabla_{\boldsymbol{q}} \cdot \int d^3 \boldsymbol{v} \, \boldsymbol{v} \, f \log f = \int d^3 \boldsymbol{v} \, Q \, \log f \,. \tag{8.42}$$

By the Boltzmann inequality (8.39), the right-hand side is ≤ 0 . Now integrate over q: The right-hand side is ≤ 0 , the first term on the left yields dH/dt, and the second can be evaluated using the Gauss integral theorem

$$\int_{\Lambda} d^3 \boldsymbol{q} \, \nabla_{\boldsymbol{q}} \cdot \boldsymbol{J}(\boldsymbol{q}) = \int_{\partial \Lambda} d^2 \boldsymbol{q} \, \boldsymbol{n}(\boldsymbol{q}) \cdot \boldsymbol{J}(\boldsymbol{q}) \,, \tag{8.43}$$

 \mathbf{SO}

$$\operatorname{term}_{2} = \int d^{3}\boldsymbol{v} \, \int_{\partial \Lambda} d^{2}\boldsymbol{q} \, \boldsymbol{n}(\boldsymbol{q}) \cdot \boldsymbol{v} \, f \log f \,.$$
(8.44)

Now for every \boldsymbol{q} , $\boldsymbol{n}(\boldsymbol{q}) \cdot \boldsymbol{v} f \log f$ is an odd function of $\boldsymbol{n} \cdot \boldsymbol{v}$ because f is an even function of it by the boundary condition (8.5), $f(\boldsymbol{q}, \boldsymbol{v}) = f(\boldsymbol{q}, \boldsymbol{v} - 2[\boldsymbol{v} \cdot \boldsymbol{n}]\boldsymbol{n})$. Thus, changing the order of integration in (8.44), the \boldsymbol{v} -integral vanishes, so term 2 vanishes.

8.5 Maxwellians

A function $f(\boldsymbol{q}, \boldsymbol{v})$ that is a stationary solution of the Boltzmann equation will have time-independent $H(f_t)$. This fact leads our interest to the following extension of the H theorem.

Proposition 6. ⁴⁶ Suppose $f \in C^2(\mathbb{R}^6)$, f > 0. dH/dt = 0 iff f is a local Maxwellian,

$$f(\boldsymbol{q},\boldsymbol{v}) = n(\boldsymbol{q}) \left(\frac{\beta(\boldsymbol{q}) m}{2\pi}\right)^{3/2} \exp\left[-\beta(\boldsymbol{q}) \frac{m}{2} (\boldsymbol{v} - \boldsymbol{u}(\boldsymbol{q}))^2\right].$$
(8.45)

A local Maxwellian on $\Lambda \times \mathbb{R}^3$ satisfying the boundary condition (8.5) is stationary iff it is a global Maxwellian, i.e., n, β, \mathbf{u} are independent of \mathbf{q} , and $\mathbf{u} = 0$.

Proof. Since

$$\frac{dH}{dt} = \int d^3 \boldsymbol{q} \int d^3 \boldsymbol{v} \, Q \, \log f \tag{8.46}$$

and $\int d^3 \boldsymbol{v} Q \log f \leq 0, \, dH/dt = 0$ iff

$$\int d^3 \boldsymbol{v} \, Q \, \log f = 0 \tag{8.47}$$

for almost all q. (Since f is continuous, "almost all q" is equivalent to "all q.")

Part 1. We show that (8.47) holds iff f is a local Maxwellian.

Indeed, (8.47) means that equality holds in the Boltzmann inequality (8.39); since the Boltzmann inequality arose from (8.41), and equality holds in (8.41) iff y = z, equality holds in (8.39) iff

$$f'f'_* = ff_* \tag{8.48}$$

for almost all (equivalently, all) $\boldsymbol{v}, \boldsymbol{v}_*, \boldsymbol{\omega}$ with $\boldsymbol{\omega} \cdot (\boldsymbol{v} - \boldsymbol{v}_*) > 0$. The last condition can be dropped because it can be ensured by replacing $u \leftrightarrow u'$ if necessary. Writing $g = \log f$, (8.47) is equivalent to

$$g' + g'_* = g + g_* \tag{8.49}$$

whenever $u' = R_{\omega} u$ for some ω . There exists such an ω iff

$$v + v_* = v' + v'_*$$
 and $v^2 + v^2_* = v'^2 + v'^2_*$. (8.50)

Thus,

$$g(\boldsymbol{v} + \delta \boldsymbol{v}) + g(\boldsymbol{v}_* - \delta \boldsymbol{v}) = g(\boldsymbol{v}) + g(\boldsymbol{v}_*)$$
(8.51)

provided

$$(\boldsymbol{v} + \delta \boldsymbol{v})^2 + (\boldsymbol{v}_* - \delta \boldsymbol{v})^2 = \boldsymbol{v}^2 + \boldsymbol{v}_*^2.$$
(8.52)

⁴⁶L. Boltzmann: Über das Wärmegleichgewicht von Gasen, auf welche äussere Kräfte wirken. Sitzungsberichte der Akademie der Wissenschaften Wien **72**: 427–457 (1875)

L. Boltzmann: Über die Aufstellung und Integration der Gleichungen, welche die Molekularbewegungen in Gasen bestimmen. *Sitzungsberichte der Akademie der Wissenschaften Wien* **74**: 503–552 (1876)

Taking $\delta \boldsymbol{v}$ "infinitesimal,"

$$\delta \boldsymbol{v} \cdot \nabla g(\boldsymbol{v}) = \delta \boldsymbol{v} \cdot \nabla g(\boldsymbol{v}_*) \tag{8.53}$$

if

$$\delta \boldsymbol{v} \cdot \boldsymbol{v} = \delta \boldsymbol{v} \cdot \boldsymbol{v}_* \,. \tag{8.54}$$

This means that $\delta \boldsymbol{v} \cdot \nabla g(\boldsymbol{v})$ does not change as \boldsymbol{v} changes in a direction perpendicular to $\delta \boldsymbol{v}$, i.e.,

$$\sum_{i,j=1}^{3} \frac{\partial^2 g}{\partial v_i \partial v_j} \delta v_i \, \delta v'_j = 0 \text{ provided } \delta \boldsymbol{v} \cdot \delta \boldsymbol{v}' = 0.$$
(8.55)

Thus,

$$\frac{\partial^2 g}{\partial v_i \partial v_j} = h(\boldsymbol{v}) \,\delta_{ij} \,. \tag{8.56}$$

In particular, $\partial g/\partial v_i$ depends only on v_i , not on v_j for $j \neq i$. Writing

$$\frac{\partial g}{\partial v_i} = h_i(v_i) \,, \tag{8.57}$$

we conclude from (8.56) that

$$h'_{i}(v_{i}) = h'_{j}(v_{j}) \text{ for } i \neq j.$$
 (8.58)

Since the two sides are functions of different variables, all h'_i must equal a single constant, which we will denote by $-\beta m$. Then

$$\frac{\partial g}{\partial v_i} = -\beta m v_i + \gamma_i \tag{8.59}$$

 $(\gamma_i \text{ constant})$ and, finally,

$$g(\boldsymbol{v}) = -\beta \frac{m}{2} \boldsymbol{v}^2 + \boldsymbol{\gamma} \cdot \boldsymbol{v} + \alpha, \qquad (8.60)$$

which yields (8.45).

Part 2. Since a local Maxwellian satisfies (8.48), it has Q = 0. If it is stationary, it must have $\boldsymbol{v} \cdot \nabla_{\boldsymbol{q}} f = 0$ for all $\boldsymbol{q}, \boldsymbol{v}$; a calculation shows that then β must be constant, $\boldsymbol{u}(\boldsymbol{q}) = \boldsymbol{u}_0 + \boldsymbol{R} \times \boldsymbol{q}$ (with \times the cross product in \mathbb{R}^3 and $\boldsymbol{u}_0, \boldsymbol{R}$ constant vectors), and $n(\boldsymbol{q}) = n_0 \exp(\boldsymbol{R}^2 \boldsymbol{q}^2 - (\boldsymbol{R} \cdot \boldsymbol{q})^2)$. The boundary condition (8.5) then forces \boldsymbol{u} to vanish and $n(\boldsymbol{q})$ to be independent of \boldsymbol{q} . Conversely, that f is stationary.

In particular, Proposition 6 implies that the only stationary solutions of the Boltzmann equation are the global Maxwellians. This fits with the fact that the global Maxwellians (i.e., the Maxwell-Boltzmann distributions in the absence of external forces) are the thermal equilibrium macro states.

Note that the set of local Maxwellians is not closed under the Boltzmann equation: A local Maxwellian does not, in general, stay one. The uniqueness of the local Maxwellian as the solution of (8.48) has also been proved under weaker assumptions than C^2 , just continuous or even only measurable f^{47} .

⁴⁷See page 36 of C. Cercignani, R. Illner, and M. Pulvirenti: *The Mathematical Theory of Dilute Gases*. Berlin: Springer-Verlag (1994) for more detail and references.

Proposition 7. For a given f, let M be the Maxwellian with the same average energy as f, i.e.,

$$M(\boldsymbol{q}, \boldsymbol{v}) = c_1 e^{-c_2 \boldsymbol{v}^2} \tag{8.61}$$

where the constants c_1, c_2 are chosen so that

$$\int_{\Lambda} d^3 \boldsymbol{q} \int_{\mathbb{R}^3} d^3 \boldsymbol{v} \, M(\boldsymbol{q}, \boldsymbol{v}) = 1$$
(8.62)

and

$$\int_{\Lambda} d^3 \boldsymbol{q} \int_{\mathbb{R}^3} d^3 \boldsymbol{v} \, \boldsymbol{v}^2 \, M(\boldsymbol{q}, \boldsymbol{v}) = \int_{\Lambda} d^3 \boldsymbol{q} \int_{\mathbb{R}^3} d^3 \boldsymbol{v} \, \boldsymbol{v}^2 \, f(\boldsymbol{q}, \boldsymbol{v}) \,. \tag{8.63}$$

Then

$$H(f_t) \ge H(M) \tag{8.64}$$

for all t for which f_t exists.

Proof. Note first that

$$H(f_t) = \int dx f_t \log f_t = \int dx f_t \log \frac{f_t}{M} + \int dx f_t \log M.$$
(8.65)

Since the function $u \log u$ is convex (see Figure 11), we have that

$$\int dx f_t \log \frac{f_t}{M} = \int dx M \frac{f_t}{M} \log \frac{f_t}{M}$$
(8.66)

$$\geq u \log u \tag{8.67}$$

with $u = \int dx M \frac{f_t}{M} = 1$. But for $u = 1, u \log u = 0$. Thus,

$$H(f_t) \ge \int dx f_t \log M \tag{8.68}$$

$$= \log c_1 \int dx f_t - c_2 \int dx \, \boldsymbol{v}^2 f_t \tag{8.69}$$

$$= \log c_1 \int dx \, M - c_2 \int dx \, \boldsymbol{v}^2 \, M \tag{8.70}$$

$$= \int dx \, M \log M = H(M) \,. \tag{8.71}$$

Proposition 8. Let f and M be as in Proposition 7. If $H(f_t) \to H(M)$ as $t \to \infty$, then $||f_t - M||_{L^1} \to 0$ as $t \to \infty$.

Proof. Let the function $g: [0, \infty) \to [0, \infty)$ be

$$g(z) = \begin{cases} z & \text{if } 0 \le z \le 1\\ 1 & \text{if } z \ge 1 \end{cases}.$$
(8.72)

The following inequality is verified in a homework problem: There is a constant c > 0 independent of f and M such that

$$f\log f - f\log M + M - f \ge cg\left(\frac{|f-M|}{M}\right)|f-M|.$$
(8.73)

Integrating both sides gives (since $\int f = 1 = \int M$)

$$H(f) - H(M) = \int f \log f - \int M \log M$$
(8.74)

$$\stackrel{(8.70)}{=} \int f \log f - \int f \log M$$
 (8.75)

$$c \int g\left(\frac{|f-M|}{M}\right)|f-M| \tag{8.76}$$

$$= c \int_{L_t} |f - M| + c \int_{S_t} |f - M|^2 M^{-1}, \qquad (8.77)$$

where L_t and S_t are the sets where |f - M| is larger (smaller) than M. Since $H(f_t) \to H(M)$, both integrals tend to 0 as $t \to \infty$. The fact that the second integral tends to zero implies, by the Cauchy–Schwarz inequality for $|f - M|M^{-1/2}$ and $M^{1/2}$,

$$\int_{S_t} |f - M| \le \left[\int_{S_t} |f - M|^2 M^{-1} \right]^{1/2} \left[\int_{S_t} M \right]^{1/2} \to 0.$$
(8.78)

Hence,

$$\|f - M\|_{L^1} = \int_{L_t} |f - M| + \int_{S_t} |f - M| \to 0, \qquad (8.79)$$

as claimed.

Propositions 6, 7, and 8 together strongly suggest (and it is believed to be true) that solutions f_t tend to the corresponding global Maxwellian as $t \to \infty$. However, they do not prove it, and whether this is actually so is an open mathematical problem. A celebrated result by Laurent Desvillettes and Cédric Villani⁴⁸ gives a conditional answer: It guarantees the convergence to equilibrium and provides bounds on the speed of convergence provided that the solution exists globally in time and is sufficiently nice:⁴⁹

Theorem 17. Suppose that a certain solution $f_t(\boldsymbol{q}, \boldsymbol{v})$ of the Boltzmann equation (without external forces) exists for all $t \geq 0$, and assume that

(i) f_t is very regular (uniformly in time): all moments $\int_{\Gamma_1} d^3 \boldsymbol{q} \, d^3 \boldsymbol{v} \, f_t \, |\boldsymbol{v}|^k$ are finite and all derivatives (of any order) are bounded;

 $^{^{48}\}mathrm{L.}$ Desvillettes and C. Villani: On the trend to global equilibrium for spatially inhomogeneous kinetic systems: the Boltzmann equation. *Inventiones Mathematicae* **159**: 245–316 (2005)

⁴⁹Quoted from C. Villani: Convergence to Equilibrium: Entropy Production and Hypocoercivity (2004), available at http://cedricvillani.org/for-mathematicians/complete-list-of-publications/.

(ii) f_t stays away from 0: $f_t(\boldsymbol{q}, \boldsymbol{v}) \geq K e^{-A|\boldsymbol{v}|^n}$ for suitable constants K, A, n.

Then, with M the corresponding Maxwellian (as in Proposition 7), $||f_t - M||_{L^2} \to 0$ as $t \to \infty$, in fact with $||f_t - M||_{L^2}$ shrinking faster than t^{-k} for all k > 0; the same is true for all Sobolev norms and all moments of \boldsymbol{v} .

8.6 Existence of Solutions

Theorem 18. ⁵⁰ Let $\Gamma_1 = \Lambda \times \mathbb{R}^3$, where $\Lambda \subset \mathbb{R}^3$ is compact and has smooth boundary. Let the initial datum $f_0 : \Gamma_1 \to [0, \infty)$ for the Boltzmann equation

- be continuous,
- satisfy the boundary condition (8.5)
- be normalized, $\int_{\Gamma_1} dx_1 f_0(x_1) = 1$, and
- satisfy the bound

$$f_0(\boldsymbol{q}, \boldsymbol{v}) \le z \left(\frac{m\beta}{2\pi}\right)^{3/2} e^{-\beta m \boldsymbol{v}^2/2}$$
(8.80)

with some constants $z, \beta > 0$. (Note that the middle factor is just the normalizing factor of the Gaussian.)

Let \overline{t} be the heuristic mean free time as in (8.28) for density z = 1/V and inverse temperature β , i.e.,

$$\bar{t} = (m\beta/3)^{1/2} (\pi\lambda z)^{-1} \,. \tag{8.81}$$

Then the Boltzmann equation (8.1)–(8.4) with boundary condition (8.5) has a solution (in the sense of "mild solutions"⁵¹) f_t during the time interval $[0, t_0)$ with

$$t_0 = \frac{1}{5}\overline{t} \,. \tag{8.82}$$

The solution is unique, and $f_t \ge 0$.

Unfortunately, the time interval t_0 is very short. While the method of proof fails after t_0 , it does not suggest that the solution blows up, so it is quite possible that the solution exists globally, i.e., for all $t \ge 0$. It is known that in several special cases existence and uniqueness of the the solution hold globally:⁵² (i) If $f_0(\boldsymbol{q}, \boldsymbol{v})$ does not depend on \boldsymbol{q} (so f_t does not either). (ii) If f_0 is sufficiently close to a Maxwellian. (iii) If f_0 is sufficiently close to a function independent of \boldsymbol{q} (" f_0 has small gradients"). (iv) For a rare gas cloud in all space $\Lambda = \mathbb{R}^3$: If $f_0(\boldsymbol{q}, \boldsymbol{v}) \le b \exp(-\beta(\boldsymbol{q}^2 + \boldsymbol{v}^2))$ for some constants $b, \beta > 0$ with $b\lambda$ sufficiently small.

⁵⁰O. E. Lanford: On a Derivation of the Boltzmann Equation. Astérisque **40**: 117–137 (1976). Reprinted in J. L. Lebowitz and E. W. Montroll: Nonequilibrium Phenomena—The Boltzmann Equation, North-Holland (1983)

C. Cercignani, R. Illner, and M. Pulvirenti: *The Mathematical Theory of Dilute Gases*. Berlin: Springer-Verlag (1994)

⁵¹For the exact definition, see C. Cercignani, R. Illner, and M. Pulvirenti: *The Mathematical Theory* of *Dilute Gases*. Berlin: Springer-Verlag (1994).

⁵²C. Cercignani, R. Illner, and M. Pulvirenti: *The Mathematical Theory of Dilute Gases*. Berlin: Springer-Verlag (1994)

8.7 Rigorous Validity

We now describe Lanford's theorem on the rigorous validity of the Boltzmann equation.⁵³ It essentially asserts that for a very large number N of billiard balls of (very small) radius a with $4Na^2 = \lambda$ the constant in the Boltzmann equation, and for any reasonable density f_0 in Γ_1 , most phase points x with empirical distribution f_0 evolve in such a way that the empirical distribution of x(t) is close to f_t , where $t' \mapsto f_{t'}$ is the solution of the Boltzmann equation with initial datum f_0 . This is what is meant by saying that the Boltzmann equation is "valid."

More precisely, the theorem asserts that the Boltzmann equation is valid at least for not-too-large t: t can be up to $\frac{1}{5}\overline{t}$, where \overline{t} is (a lower bound of) the mean free time of f_0 . It is believed but not proven that the Boltzmann equation is valid for a much longer duration, maybe for all $t \ge 0$. The method of proof fails after $\frac{1}{5}\overline{t}$, but it does not give reason to think that the actual behavior changes at $\frac{1}{5}\overline{t}$. Empirical distributions are understood relative to a coarse graining (partition) of Γ_1 into cells A_i that are small but not too small. Here is a precise statement:

Theorem 19 (Lanford 1974). Let $\Gamma_1 = \Lambda \times \mathbb{R}^3$, where $\Lambda \subset \mathbb{R}^3$ is compact and has smooth boundary. Let the initial datum $f_0 : \Gamma_1 \to [0, \infty)$ for the Boltzmann equation

- be continuous,
- satisfy the boundary condition (8.5)
- be normalized, $\int_{\Gamma_1} dx_1 f_0(x_1) = 1$, and
- have compact support (i.e., vanish outside $\Lambda \times \Sigma$ for some compact $\Sigma \subset \mathbb{R}^3$).

Let $z, \beta > 0$ be constants such that f_0 satisfies the bound (8.80); such constants always exist because Λ and Σ are compact. We only make statements about the time interval $[0, t_0)$ with $t_0 = \frac{1}{5}\overline{t}$ and \overline{t} given by (8.81). Let $f_t(x_1)$ be the solution of the Boltzmann equation (8.1)–(8.4) with boundary condition (8.5) for $t \in [0, t_0)$ with initial datum f_0 .

For every N, set $a = a^{(N)}$ so that $4Na^2 = \lambda$, and let T^t be the flow map of hard spheres of radius a on Γ_1^N . Let $\Delta f^{(N)} > 0$ with $\Delta f^{(N)} \to 0$ as $N \to \infty$, but not too fast: $N \Delta f^{(N)} \to \infty$. Let $\mathscr{A}^{(N)} = \{A_i^{(N)} : i = 1 \dots r_N\}$ be a partition of $\Lambda \times \Sigma$ so that the cells shrink to zero but not too fast:

• $\max_{i \leq r_N}$ of the **q**-diameter of $A_i^{(N)}$ tends to 0 as $N \to \infty$;

⁵³O. E. Lanford: Time evolution of large classical systems. Pages 1–111 in Jürgen Moser (editor), *Dynamical Systems, Theory and Applications: Battelle Seattle 1974 Rencontres, Lecture Notes in Physics* vol. **38**. Berlin: Springer-Verlag (1975)

O. E. Lanford: On a Derivation of the Boltzmann Equation. Astérisque **40**: 117–137 (1976). Reprinted in J. L. Lebowitz and E. W. Montroll: Nonequilibrium Phenomena—The Boltzmann Equation, North-Holland (1983)

Aspects of the proof are also discussed in H. Spohn: Large Scale Dynamics of Interacting Particles. Berlin: Springer-Verlag (1991) and C. Cercignani, R. Illner, and M. Pulvirenti: The Mathematical Theory of Dilute Gases. Berlin: Springer-Verlag (1994)

- likewise for the *v*-diameter;
- $N \Delta f^{(N)} \inf_{i \leq r_N} \operatorname{vol}(A_i) \to \infty$
- $\max_{i \leq r_N} \operatorname{vol}(\partial_a A_i) / \operatorname{vol}(A_i) \to 0 \text{ as } N \to \infty, \text{ where } \partial_a A_i \text{ is the set of points within } \mathbf{q}$ -distance a from ∂A_i .

For any $x = (x_1, \ldots, x_N) \in \Gamma_1^N$ let $N_i(x)$ be the occupation number $\#\{1 \le j \le N : x_j \in A_i\}$. Set

$$\Gamma_{f_0}^{(N)} = \left\{ x \in \Gamma_1^N : \left| \frac{N_i(x)}{N} - \int_{A_i} dx_1 f_0(x_1) \right| \le \operatorname{vol}(A_i) \,\Delta f^{(N)} \right\},\tag{8.83}$$

and let $\mu^{(N)}$ be the normalized uniform measure over $\Gamma_{f_0}^{(N)}$,

$$\mu^{(N)}(\cdot) = \frac{\operatorname{vol}(\cdot \cap \Gamma_{f_0}^{(N)})}{\operatorname{vol}(\Gamma_{f_0}^{(N)})}.$$
(8.84)

Then for every $t \in [0, t_0)$, every $\varepsilon > 0$, and every $A \subseteq \Gamma_1$,

$$\mu^{(N)}\left\{x: \left|\frac{N_A(T^t x)}{N} - \int_A dx_1 f_t(x_1)\right| < \varepsilon\right\} \to 1 \quad as \ N \to \infty.$$
(8.85)

8.8 Irreversibility

Lanford's theorem has implications also for negative t: For most phase points in Γ_f , the Boltzmann equation also applies in the other time direction, so that entropy increases in both time directions! (See Figure 12.)





That is, for t < 0 the reverse Boltzmann equation (with $\lambda \to -\lambda$) applies. This can be seen by reversing all velocities in the phase point x = x(0),

$$x^{r} = (\boldsymbol{q}_{1}, -\boldsymbol{v}_{1}, \dots, \boldsymbol{q}_{N}, -\boldsymbol{v}_{N}), \qquad (8.86)$$

which maps (if the partition A_i is chosen suitably symmetric) Γ_f bijectively to Γ_{f^r} with

$$f^{r}(\boldsymbol{q}, \boldsymbol{v}) = f(\boldsymbol{q}, -\boldsymbol{v}). \tag{8.87}$$

If $t \mapsto f_t$ is a solution of the Boltzmann equation with constant λ , then $t \mapsto (f_{-t})^r$ is a solution of the Boltzmann equation with constant $-\lambda$. Theorem 19 implies that most phase points in Γ_{f^r} evolve according to the Boltzmann equation (so entropy increases), but the evolution of $T^t x^r$ is just $T^{-t} x$ with velocities reversed. We are now in a position to fully appreciate what I called Basic Fact #2 on page 2:

A closed real-world system that at time t_0 has macro-state ν appears macroscopically in the future, but not the past, of t_0 like a system that at time t_0 is in a typical micro-state compatible with ν .

A typical micro state evolves as depicted in Figure 12 with the entropy minimum at t_0 . What we observe in the real world looks like solutions of the Boltzmann equation, not of the reverse Boltzmann equation. We observe only increase of entropy, only the right branch in Figure 12, not the left. Why that this, we will discuss further in Section 9, but we can see here that Basic Fact #2 is a fact.

In this context, we can also formulate another variant of Loschmidt's time reversal paradox. Consider the following operations in parallel for a phase point x and its macro description f. We evolve $x \in \Gamma$ up to time t and f to f_t according to the Boltzmann equation; then we reverse the velocities, $x' = (T^t x)^r$ and $f'(q, v) = f_t(q, -v)$; then we evolve it again by t time units to obtain $T^t x'$ and f'_t . If x was typical in Γ_f , then f_t is the empirical distribution of $T^t x$, so x and f evolve in parallel. But x' and f' do not evolve in parallel: $T^t x'$ is, up to velocity reversal, the same as the x we started with, whereas f'_t is very different from f(q, -v): $s(f'_t) > s(f') = s(f_t) > s(f)$. That is because x' is not a typical point in $\Gamma_{f'}$, it violates the hypothesis of molecular chaos because the exact positions (and thus the exact collision parameters) are arranged in such a way that T^t will carry x' to $x \in \Gamma_f$, which is very exceptional behavior; after all, T^t will carry a typical point in $\Gamma_{f'}$.

You may wonder, if x' is an atypical point in $\Gamma_{f'}$, then $T^t x = (x')^r$ must be an atypical point in Γ_{f_t} (after all, most points $y \in \Gamma_{f_t}$ have $T^{-t}y \in \Gamma_{f'_t}^r$, but $y_0 = T^t x$ has $T^{-t}y_0 \in \Gamma_f$). But if $T^t x$ is an atypical point in Γ_{f_t} , then what justification do we have to believe that in the forward time direction, it will behave according to the Boltzmann equation? Why should we think that, e.g., $T^{2t}x \in \Gamma_{f_{2t}}$? Because Theorem 19 tells us so! At least as long as Theorem 19 is valid, for $t < t_0$, it guarantees that, for typical $x \in \Gamma_f$ and t up to t_0 , $T^t x$ will continue to behave thermodynamically (i.e., agree with the Boltzmann equation) although it is atypical in Γ_{f_t} ! But even beyond t_0 , it seems plausible that the Boltzmann equation remains valid: While $y_0 = T^t x$ has subtle correlations between the exact positions that ensure that $T^{-t}y_0$ has lower entropy, there is no reason to think that these correlations would make any difference for the future evolution of y_0 . It is believed that the Boltzmann equation remains valid, not forever but up to times of the order of recurrence times, when spontaneous entropy valleys should become significant so that the validity of the Boltzmann equation must find an end.

This brings us to Basic Fact #2 again, which tell us that y_0 , even though it is atypical in some way, behaves towards the future like a typical micro state $y \in \Gamma_{f_t}$. Basic Fact #2 can be regarded as a generalization of the prediction that heat will not flow from the cooler body to the hotter, or the prediction that a given macroscopic object will not spontaneously fly into the air although the laws of mechanics would allow that all the momenta of the thermal motion at some time all point upwards.⁵⁴

⁵⁴Here are three more references on irreversibility in statistical mechanics.

R. Penrose: The Emperor's New Mind. Oxford University Press (1989), chapter 7.

J. L. Lebowitz: From Time-symmetric Microscopic Dynamics to Time-asymmetric Macroscopic Behavior: An Overview. Pages 63–88 in G. Gallavotti , W. L. Reiter, J. Yngvason (editors): *Boltzmann's Legacy.* Zürich: European Mathematical Society (2008) http://arxiv.org/abs/0709.0724

P. Ehrenfest and T. Ehrenfest: Begriffliche Grundlagen der statistischen Auffassung in der Mechanik. In *Enzyklopädie der Mathematischen Wissenschaften*, Vol. IV-4, Art. 32 (1911). English translation by M.J. Moravcsik: *The Conceptual Foundations of the Statistical Approach in Mechanics*. Cornell University Press (1959)

9 The Thermodynamic Arrow of Time

An "arrow of time" means an irreversible phenomenon, or a difference between past and future. There are many arrows of time: The psychological arrow (we feel a direction of time), the arrow of causation (causes precede effects), the arrow of computer memory (which remembers yesterday's stock prices but not tomorrow's) or photographs (which show past configurations but not future ones), the arrow of aging of plants and animals, the arrow of electromagnetic radiation (the spherical waves related to an accelerated charge are outgoing, not ingoing), the arrow of black holes (there are no white holes, which would be the time reverse of black holes), and the arrow of the expansion of the universe. It has been argued convincingly that all of them, with two possible exceptions, are just consequences of the thermodynamic arrow of time (entropy increases).⁵⁵ The exceptions are the black holes and the expansion of the universe, which may or may not be related to the thermodynamic arrow. All the others necessarily point in the direction of entropy increase.

Let us inquire about the origin of the thermodynamic arrow. If low-entropy states are unlikely, then why are systems ever in such states? Because we prepare them that way. How can we? Because we have lower entropy still. Where does our low entropy come from? We eat low-entropy plants. Where does the plants' low entropy come from? From the sunlight. Low-entropy, high-energy photons arrive on Earth, highentropy, low-energy photons (correspondigly more of them) get radiated into space, so that energy does not accumulate but entropy gets lowered. Where does the low entropy of the sunlight come from? Two factors play a role: First, nuclear fusion is a process that increases entropy (although it requires a high activation energy), and second, the gravitational pull increases temperature while increasing entropy. That is, the ultimate reason why the sun works is that the primordial gas was spread-out (rather than clumped) and consisted mostly of hydrogen (rather than higher elements); both properties are features of low entropy. And how did that come about? Because the universe started out this way.⁵⁶

9.1 The Initial State of the Universe

Entropy is less-than-maximal today because it was very very low at the big bang. That connects with Basic Fact #3:

The real world as a whole (i.e., the universe) appears macroscopically like a system that at the big bang is in a typical micro state compatible with the universe's macro state at the big bang.

And that macro state had very low entropy. So the thermodynamic arrow of time has a cosmological origin! People have tried to explain this arrow from mechanics

⁵⁵See, e.g., S. W. Hawking: A Brief History of Time. London: Bantam (1988) or P. C. W. Davies: The Physics of Time Asymmetry. Berkeley: University of California Press (1974).

⁵⁶For a more detailed discussion of this chain, see chapter 7 of R. Penrose: *The Emperor's New Mind.* Oxford University Press (1989).

alone, or from the way theoreticians consider problems, but unsuccessfully. The further ingredient needed is a special state of the universe at the big bang. In the words of Richard Feynman:⁵⁷

Therefore I think it is necessary to add to the physical laws the hypothesis that in the past the universe was more ordered, in the technical sense, than it is today—I think this is the additional statement that is needed to make sense, and to make an understanding of the irreversibility.

The time it takes for the whole universe to reach thermal equilibrium from its lowentropy initial state is much longer than the 14 billion years it has had so far. And just like the Boltzmann equation, even if this is not proven, presumably holds for long times (up to the order of recurrence times), the initial low-entropy state should be enough to keep entropy increasing still today. That is why Basic Fact #2 is really a consequence of Basic Fact #3. Moreover, the initial low-entropy state should be enough to keep entropy increasing until the universe has reached thermal equilibrium. Then life will no longer be possible, and in fact nothing noteworthy will happen any more; this consequence was first noticed by Clausius, who called it the "heat death" of the universe.

Typicality has played a role in our considerations in several ways: As the basis of thermal equilibrium, as an explanation of equilibrium properties, and as an ingredient for the Boltzmann equation (or, more generally, thermodynamic behavior). But all consideration of typicality so far remained incomplete, as the actual phase point is surely enough not a typical one in its macro state. From the cosmological perspective, i.e., considering the whole universe starting at the big bang, the picture changes quite a bit and becomes very simple: Suppose that the initial macro state of the universe was Γ_{ν_0} , which has very low entropy; then a typical micro state $x \in \Gamma_{\nu_0}$ will behave thermodynamically (i.e., display a thermodynamic arrow of time) up to recurrence times, and thus will be consistent with our empirical evidence (as stated in Basic Fact #3). Moreover, once we fix the condition that $x(0) \in \Gamma_{\nu_0}$, typicality provides an *explanation* of the arrow of time: without any further conditions or assumptions, the arrow comes out for most $x(0) \in \Gamma_{\nu_0}$. The fact that x(0) would behave anti-thermodynamically for earlier times does not matter if there were no earlier times.

Here is Boltzmann (1898):⁵⁸

Wir wiesen nach, dass [H] in Folge der Durcheinanderbewegung der Gasmoleküle stets abnimmt. Die Einseitigkeit des Vorganges, welche hierin liegt, ist offenbar nicht in den für die Moleküle geltenden Bewegungsgleichungen begründet. Denn diese ändern sich nicht, wenn die Zeit ihr Vorzeichen wechselt. Diese Einseitigkeit liegt vielmehr einzig und allein in den Anfangsbedingungen. Dies ist aber nicht etwa so zu verstehen, als ob man für jeden Versuch wieder speciell annehmen müsste, dass die Anfangsbedingungen gerade bestimmte und nicht die entgegengesetzten, ebenso gut möglichen

⁵⁷Page 116 in R. P. Feynman: *The Character of Physical Law.* M.I.T. Press (1965)

⁵⁸ Vorlesungen über Gastheorie, Band 2. Leipzig: Barth (1898), §87

sind; sondern es genügt eine einheitliche Grundannahme über die anfängliche Beschaffenheit des mechanischen Weltbildes, aus welcher dann mit logischer Nothwendigkeit von selbst folgt, dass, wo immer Körper in Wechselwirkung treten, sich die richtigen Anfangsbedingungen vorfinden müssen.

Translation:⁵⁹

We proved that [H] continually decreases as a result of the motion of the gas molecules among each other. The one-sidedness of this process is clearly not based on the equations of motion of the molecules. For these do not change when the time changes its sign. This one-sidedness rather lies uniquely and solely in the initial conditions. This is not to be understood in the sense that for each experiment one must specially assume just certain initial conditions and not the opposite ones which are likewise possible; rather it is sufficient to have a uniform basic assumption about the initial properties of the mechanical picture of the world, from which it then follows with logical necessity that, [whenever bodies are] interacting, they must always be found in the correct initial conditions.

9.2 The Fluctuation Hypothesis

The question remains why the initial micro state should lie in this particular Γ_{ν_0} (the initial macro set of our universe), if that is such an "unlikely" state. Boltzmann tentatively suggested the following explanation: Suppose that, on the cosmological level, the time axis is \mathbb{R} and space is either \mathbb{R}^3 with infinitely many particles at finite density or some compact manifold with a really large volume and finite N; let us assume the latter. Suppose further that the dynamics is ergodic. Then almost every possible trajectory will have the property that the universe, after spending $10^{10^{10}}$ or more years in thermal equilibrium, will (sooner or later) deviate from equilibrium not only a little but also by an arbitrarily large amount, say by the entropy difference ΔS_0 between the entropy of our known universe 13 billion years ago and the entropy of universal thermal equilibrium. In fact, sooner or later the phase point will pass through Γ_{ν_0} , just "by chance" or "by fluctuation." At least, such fluctuations will form in some bounded regions ("bubbles"), for example of the size of the visible universe $(10^{10} \text{ light years})$. Then the entropy curve looks like Figure 12, with time units of perhaps 10^{11} years. Each of the two slopes of the curve corresponds to a space-time region that has an arrow of time, with the arrows of the two regions pointing in opposite directions (always in the direction of entropy increase, away from the time t_0 of minimum entropy). In each of the two regions, and in accordance with the arrow of time there, stars and galaxies will form, produce higher chemical elements, planets will form on which life may evolve and intelligent beings may exist. They will be unable to communicate with the other region (for example because the other region is always in the past, and you cannot send messages to the past) or any

⁵⁹By S. G. Brush, published as L. Boltzmann: *Lectures on Gas Theory*. Berkeley: University of California Press (1964)

other bubble (for example they are too far away in space and/or in time). In short, the world will look to these being like our world looks to us. That is the explanation: the source of the low entropy at t_0 was a very unlikely fluctuation, which despite its being unlikely must sometimes occur; this reasoning is called the *fluctuation hypothesis*.

The reasoning actually does not work, as pointed out particularly by Arthur Eddington (1931) and Richard Feynman (1965).⁶⁰ The reason is that also smaller fluctuations would occur that do not reach Γ_{ν_0} , have depth of less than the ΔS_0 considered before, have bubbles (i.e., islands within a sea of thermal equilibrium) of less than 10^{10} light years diameter, and have duration of less than 10^{11} years. For example, the fluctuation may comprise only the solar system, with just light days or light hours in diameter; let the lowest-entropy macro set it reaches be denoted by Γ_{ν_1} . Since the entropy difference ΔS_1 from equilibrium is much smaller than ΔS_0 , an ergodic trajectory would reach it much earlier and more frequently than Γ_{ν_0} . Let us write \mathscr{F}_0 for a fluctuation down to Γ_{ν_0} and \mathscr{F}_1 for one to Γ_{ν_1} . Suppose that Γ_{ν_1} is the present macro set of the solar system; then it contains all human beings along with their current brain states and memories. In \mathscr{F}_1 within the first second after the bottom, there are people who look like us and who have the same memories as we do, although they are fake memories. They are detailed and consistent memories of events that never happened—not to these people, at least. Their past has lasted only a second; what was before was not ordinary life but some reverse history (not necessarily the same as on the future branch). But to those people during the first second after the bottom, their world looks like ours to us.

Here are examples of even smaller relevant fluctuations. Instead of the whole solar system, the fluctuation could comprise only Earth, or only Tübingen, or only your body or, in fact, only your brain. Suppose the fluctuation reaches, as its entropy minimum, the macro set Γ_{ν_2} of your present brain state surrounded by matter in thermal equilibrium. Such a fluctuation \mathscr{F}_2 is called a "Boltzmann brain."⁶¹ Such trajectories can be obtained simply as the trajectory of a typical phase point in Γ_{ν_2} . There is a fraction of a second after the bottom during which everything seems normal to the unsuspecting Boltzmann brain, and then it dies quickly. (In the other time direction, before the bottom, it dies even more quickly because all macro velocities are reversed, so that the brain can never function properly.) But during this fraction of a second, the brain cannot distinguish whether it is in \mathscr{F}_2 or in \mathscr{F}_1 or in \mathscr{F}_0 .

And since \mathscr{F}_2 occurs much more frequently than \mathscr{F}_1 , which occurs much more frequently than \mathscr{F}_0 , most brains in fluctuations are actually in \mathscr{F}_2 (or \mathscr{F}_1), not in \mathscr{F}_0 . Thus, the fluctuation hypothesis implies the prediction that *you* should be in \mathscr{F}_2 , not in \mathscr{F}_0 .

⁶⁰A. S. Eddington: The End of the World: From the Standpoint of Mathematical Physics. *Nature* **127**: 447–453 (1931). Reprinted on page 406 in D. R. Danielson (editor): *The Book of the Cosmos: Imagining the Universe from Heraclitus to Hawking.* Cambridge, MA: Perseus (2000)

R. P. Feynman: The Character of Physical Law. M.I.T. Press (1965)

R. P. Feynman: *Lectures on Gravitation*. Edited by F. B. Morínigo, W. G. Wagner, and B. Hatfield. Westview Press (1995)

⁶¹The expression was coined, as far as I know, in A. Albrecht and L. Sorbo: Can the universe afford inflation? *Physical Review D* **70**: 063528 (2004) http://arxiv.org/abs/hep-th/0405270.

Let me dwell on this point for a moment. The general principle that is behind, which has been termed the "Copernican principle,"⁶² asserts that

we should be typical observers in a typical universe.
$$(9.1)$$

This principle can be understood as a rule for extracting predictions from a theory:

we should see what a typical observer (weighted with life span) in a typical universe sees. (9.2)

For example, if the theory does not involve the fluctuation hypothesis but says instead that time began at t = 0 with $x \in \Gamma_{\nu_0}$ (and particles move according to classical mechanics), then observers will see entropy increase. For another example, if not all observers see the same kind of behavior, then we should see what typical observers see. We are not in a typical place in the universe because a typical place does not support life, but we should expect to be in a place that is typical among those supporting life. Life requires a planet, in fact one that is neither too hot nor too cold.

Let us apply the Copernican principle to the fluctuation hypothesis. Although the life span of the Boltzmann brain in \mathscr{F}_2 is short, Boltzmann brains are so much more numerous that their total life span still far exceeds the total life span of the observers in fluctuations of the type \mathscr{F}_1 , which still far exceeds that of \mathscr{F}_0 . Thus, if the fluctuation hypothesis is right, then you should be a Boltzmann brain.

But we are not Boltzmann brains. How do we know? To begin with, we would trust our memories more than any physical theory. After all, any reason we may have in favor of a physical theory would come from experimental and theoretical results, of which we could not have reliable information if we could not trust our memories. But even according to the fluctuation hypothesis itself, we can test empirically whether we are Boltzmann brains: Boltzmann brains die quickly, and if you do not, then you are not one. Here are some variants of this reasoning: (i) Suppose the fluctuation is not just a brain but a "Boltzmann classroom." Then the people inside perhaps do not die immediately, but the classroom is surrounded by matter in thermal equilibrium (no other people, no trees, etc.), so we can just look outside or go outside and check. (ii) Although we assumed that the macro state of the Boltzmann brain is identical to your present brain state, we could relax that condition and allow any "normal" human brain state. Then the overwhelming majority of Boltzmann brains have inconsistent memories: If the memories were created by random combination of atoms, there is no reason why different memories should fit together to a coherent story. (iii) Similarly, if a "Boltzmann planet" with humans on it (but not necessarily in the present macro state of Earth) arose by fluctuation, then books should contain random sequences of letters (if they contain any letters at all) because nobody wrote them: they arose from a random combination of atoms. So if you open a book and see words, then you are not a Boltzmann brain. (iv) Likewise, Boltzmann planets would not have dinosaur bones in the ground because dinosaurs never existed anyway. (v) In a Boltzmann solar system,

⁶²J. R. Gott: Implications of the Copernican principle for our future prospects. *Nature* **363**: 315–319 (1993)

you would not see stars in the night sky (only Venus and the other planets) because there are no stars.

9.3 The Past Hypothesis

If the fluctuation hypothesis is out of the question, then what is the alternative? Here, Einstein's general theory of relativity makes a big difference. According to general relativity, we do not live in a Euclidean space with time axis \mathbb{R} ; rather, space-time is a manifold with a Lorentzian metric that can be curved. The simplest models of spacetime on a cosmological scale are the Friedmann-Lemaître-Robertson-Walker metrics. Among these models, those that are consistent with the observed expansion of the universe (primarily, with Hubble's law that distant galaxies are moving away from us at speeds proportional to the distance) have space-time singularities about 10^{10} years in the past from us. A space-time singularity is a boundary of the space-time manifold at which the metric becomes singular (i.e., diverges in some sense); the existence of a singularity suggests that space-time *ends* there. Thus, in the simplest cosmological models according to general relativity, time does not extend infinitely into the past but had a beginning about 10^{10} years ago. Whether that should be taken literally is not known, but it seems like a real possibility. It is consensus among experts that there was a time 13.7 billion years ago, the *big bang*, when the universe was much smaller and much hotter than today, but it is less clear whether the big bang was the beginning of time (i.e., a boundary of space-time).

Suppose it was. Then statements about the initial time can be formulated as statements about the boundary of space-time such as the following:

> The micro state of the universe at the singular boundary of space-time is a typical element of Γ_{ν_0} , where ν_0 has (9.3) very low entropy.

This statement has been termed the *past hypothesis*.⁶³ One option is to think of the past hypothesis as a fundamental law of nature. This would mean that there are two kinds of laws of nature: evolution laws and boundary laws. The evolution laws provide microscopic equations of motion, and the boundary laws put constraints on what could happen at the boundary of space-time, i.e., on the initial 3-surface. In this case, there may or may not exist a deeper explanation for why there is a boundary law, and why it says this particular thing.

If we want to think of (9.3) as a law of nature, then it seems that Γ_{ν_0} should be characterized in an explicit, sharp, and simple way. "Whatever the macro state of our universe was like 13.7 billion years ago" seems insufficient. Another difficulty with (9.3) is that space-time singularities are also expected to form inside black holes; that is, space-time may, in addition to its past boundary at the big bang, also have future boundaries, at least in some regions. At these future boundary surfaces, the micro state has no similarity with Γ_{ν_0} (it does not have low entropy); moreover, once the micro state

⁶³The expression was coined in D. Z. Albert: *Time and Chance*. Harvard University Press (2000).

at the past boundary has been chosen to be x, the deterministic evolution laws leave no room for further decisions about what the micro state on future boundaries should be. But the fundamental laws of nature should be time symmetric, so a precise version of the past hypothesis should not say that "on the past boundary, the micro state lies in Γ_{ν_0} "; it should say instead, "on one end of space-time, the micro state lies in Γ_{ν_0} ."

A proposed sharp formulation of the past hypothesis is Roger Penrose's Weyl curvature hypothesis (1979),⁶⁴ which asserts that:

At the singular boundary on one end of space-time, the Weyl curvature is 0. (9.4)

The curvature of a Lorentzian metric has two groups of components, the Ricci curvature and the Weyl curvature. In the Friedmann-Lemaître-Robertson-Walker metrics, the Weyl curvature vanishes at the big bang singularity, whereas in all known models of black holes, the Weyl curvature diverges at the singularity inside the black hole. Penrose has argued that, in the presence of gravity, "clumped" (high-entropy) states should in general have large Weyl curvature and uniform (low-entropy) distributions of matter should have small Weyl curvature. So it may be the case that typical universes satisfying the Weyl curvature hypothesis look very much like our universe, both in terms of the overall distribution of matter and in terms of the second law of thermodynamics.

However, Boltzmann brains can come back to haunt also a scenario with a past hypothesis. Suppose for example that time has a beginning at t = 0 but no end and extends to $t \to +\infty$. Forget about general relativity and suppose that space is some compact manifold. The entropy increases from $S(\nu_0)$ to S(eq), then remains at S(eq)for a long time; then fluctuations occur including, sooner or later, Boltzmann brains. If we wait sufficiently long, their number will exceed the number of ordinary observers (that came into existence through birth and evolution) by far, and their total life span will exceed that of ordinary observers by far. Thus, the theory predicts that you should be a Boltzmann brain.

What are the possible ways out? Here are some relevant considerations. (i) Some Friedmann-Lemaître-Robertson-Walker metrics have not only a beginning of time, but also an end, so the universe has a finite duration. If that duration is large but not too large, the Boltzmann brain problem may not come up. (ii) The expansion of the universe may make a difference. (iii) The situation needs to be re-assessed in quantum mechanics. Whether that will make Boltzmann brains less likely, depends on the precise version of quantum mechanics and on the expansion of the universe.⁶⁵

⁶⁴R. Penrose: Singularities and time-asymmetry. Pages 581–638 in S. Hawking, W. Israel (editors): General Relativity: An Einstein centenary survey. Cambridge University Press (1979)

⁶⁵S. Goldstein, W. Struyve, and R. Tumulka: The Bohmian Approach to the Problems of Cosmological Quantum Fluctuations. To appear in A. Ijjas and B. Loewer (editors), *Guide to the Philosophy of Cosmology*, Oxford University Press (2020) http://arxiv.org/abs/1508.01017

R. Tumulka: The Problem of Boltzmann Brains and How Bohmian Mechanics Helps Solve It. To appear in the *Proceedings of the 15th Marcel Grossmann Meeting on General Relativity (Rome 2018)*, World Scientific (2020) http://arxiv.org/abs/1812.01909

9.4 Without a Past Hypothesis?

An alternative proposal has been put forward by Sean Carroll (2004),⁶⁶ and I would like to briefly convey some elements of it. It is intended to explain the low-entropy macro-state of 13.7 billion years ago without an additional law; it builds on inflationary cosmology, but I will not go into that. It is time reversal invariant and assumes that time does not have a beginning, so that t extends back to $-\infty$, and "big bang" means just a certain space-time region. It further assumes that entropy is everywhere finite but unbounded on the energy surface, with the consequence that there is no thermal equilibrium macro state for the universe as a whole, and that the energy surface has infinite Liouville measure. As a consequence of *that*, the Poincaré recurrence theorem does not apply, and in fact recurrence does not occur. With an infinite measure, it becomes more tricky to define what is meant by "typical" behavior or the "overwhelming majority" of phase points, but it is not impossible. The proposal is set up in such a way that for the overwhelming majority of phase points x(0) on the energy surface, the entropy curve $t \mapsto S(x(t))$ is increasing (up to irrelevant minor entropy valleys) for $t > \tau$ for some constant τ depending on x(0), and decreasing for $t < \tau$, as depicted in Figure 13.



Figure 13: In Carroll's scenario, most histories of the universe have an entropy curve S(t) of this shape.

S. M. Carroll: From Eternity to Here. New York: Dutton (2010)

⁶⁶S. M. Carroll and J. Chen: Spontaneous Inflation and the Origin of the Arrow of Time. Preprint (2004) http://arxiv.org/abs/hep-th/0410270

S. M. Carroll and J. Chen: Does Inflation Provide Natural Initial Conditions for the Universe? General Relativity and Gravitation **37**: 1671–1674 (2005). Reprinted in International Journal of Modern Physics D **14**: 2335–2340 (2005). http://arxiv.org/abs/gr-qc/0505037

J. Barbour, T. Koslowski, and F. Mercati: A Gravitational Origin of the Arrows of Time. Preprint (2013) http://arxiv.org/abs/1310.5167

J. Barbour, T. Koslowski, and F. Mercati: Identification of a gravitational arrow of time. *Physical Review Letters* **113**: 181101 (2014) http://arxiv.org/abs/1409.0917

J. Barbour, T. Koslowski, and F. Mercati: Entropy and the Typicality of Universes. Preprint (2015) http://arxiv.org/abs/1507.06498

S. Goldstein, R. Tumulka, and N. Zanghi: Is the hypothesis about a low entropy initial state of the universe necessary for explaining the arrow of time? *Physical Review D* **94**: 023520 (2016) http://arxiv.org/abs/1602.05601

It follows that τ is the time of minimum entropy, and that there are two spacetime regions with opposite thermodynamic arrows of time, just as with the fluctuation hypothesis. However, these histories are quite different from fluctuations, partly because there is no thermal equilibrium. One way in which they are different is that Boltzmann brains do not occur (or very rarely, so they only form a small minority of observers). How does the proposal explain the low entropy? Essentially because every entropy value is low if arbitrarily high entropy values are possible.

Part II Quantum Statistical Mechanics

We will now discuss how to do statistical mechanics in the framework of quantum mechanics. Some aspects will be analogous to the classical case, others rather different. We begin with a brief summary of what quantum mechanics is.

10 Review of Quantum Mechanics

10.1 Fundamental Laws

There is no universal agreement of what quantum mechanics actually says, and very different proposals have been made as to how the quantum world works. Notable are Schrödinger's many-worlds theory, Everett's many-worlds theory, collapse theories (according to which the fundamental time evolution of the wave function is not unitary), and Bohmian mechanics. In addition, several incoherent or paradoxical proposals such as Bohr's concept of complementarity have been put forward. Finally, many authors have recommended to leave aside the question of how the world works and instead focus exclusively on rules for making predictions; a disadvantage of that approach is that these rules are difficult to formulate in a precise and complete way. For our mathematical purposes, we have a need for a precise formulation of quantum mechanics, and to this end, I will summarize the simplest one among the full theories, Bohmian mechanics. In Section 10.3, I will give a set of predictive rules without attempting full precision or completeness.

According to Bohmian mechanics, electrons and other elementary particles are material point particles moving in 3-dimensional space; as such, particle number *i* has position $Q_i(t) \in \mathbb{R}^3$ at time $t \in \mathbb{R}$. For a system of *N* particles, the configuration space is \mathbb{R}^{3N} . In addition, there exists a physical object that is mathematically represented by a function ψ on configuration space, called the *wave function*. For spinless particles, ψ is complex-valued; for *N* particles with spin $\frac{1}{2}$, ψ takes values in the spin space \mathbb{C}^{2^N} . The variables Q_i and ψ evolve with time according to the following two laws, Bohm's equation of motion

$$\frac{d\boldsymbol{Q}_i}{dt} = \frac{\hbar}{m_i} \operatorname{Im} \frac{\psi^* \nabla_i \psi}{\psi^* \psi} \left(\boldsymbol{Q}_1(t), \dots, \boldsymbol{Q}_N(t), t \right)$$
(10.1)

and the Schrödinger equation

$$i\hbar\frac{\partial\psi}{\partial t} = -\sum_{i=1}^{N} \frac{\hbar^2}{2m_i} \nabla_i^2 \psi + V\psi. \qquad (10.2)$$

Henceforth, we work in units in which $\hbar = 1$. In the case of spin,

$$\psi^* \phi = \sum_{s=1}^{2^N} \psi_s^* \phi_s \tag{10.3}$$

denotes the inner product between spinors; and V is the potential function, which can be real-valued or matrix-valued, for example the Coulomb potential

$$V(\boldsymbol{q}_1, \dots, \boldsymbol{q}_N) = \sum_{1 \le i < j \le N} \frac{e_i e_j}{|\boldsymbol{q}_i - \boldsymbol{q}_j|} \,. \tag{10.4}$$

We write \boldsymbol{q}_i for the variables in ψ and V in distinction from \boldsymbol{Q}_i , the actual position of particle i; e_i denotes the electric charge of particle i. Matrix-valued potentials occur when external magnetic fields act on particles with spin; these matrices are self-adjoint, $V^{\dagger} = V$, where V^{\dagger} denotes the adjoint (conjugate transpose) matrix.

Another fundamental law of Bohmian mechanics asserts that at any time t, the configuration $Q(t) = (\mathbf{Q}_1(t), \dots, \mathbf{Q}_N(t)) \in \mathbb{R}^{3N}$ is random with distribution density

$$\rho_t(q) = |\psi_t(q)|^2. \tag{10.5}$$

In the case with spin, $|\cdot|$ denotes the norm in spin space,

$$|\psi| = \sqrt{\psi^* \psi} \,. \tag{10.6}$$

The statement that Q(t) is random does not, of course, mean that it is independent for every t. On the contrary, the dependence could not be stronger as $Q(t_1)$ determines $Q(t_2)$, since the time evolution equations (10.1) and (10.2) are deterministic. In fact, (10.5) can be *postulated* only for one time, and then (10.1) and (10.2) determine ρ_t for every other time; it turns out ("equivariance theorem of $|\psi|^{2"}$) that it follows from (10.1) and (10.2) that (10.5) then holds for every t.

Another law concerns *identical* particles: For each species of particles, the wave function is either symmetric or anti-symmetric against permutation of particles of that species (*symmetrization postulate*):

$$\psi_{\dots s_i \dots s_j \dots} (\dots \boldsymbol{q}_i \dots \boldsymbol{q}_j \dots) = \gamma \, \psi_{\dots s_j \dots s_i \dots} (\dots \boldsymbol{q}_j \dots \boldsymbol{q}_i \dots) \tag{10.7}$$

with all other variables unchanged and $\gamma = \pm 1$. If $\gamma = 1$ then particles of that species are said to be *bosons*, if $\gamma = -1$ then *fermions*. The *spin-statistics law* asserts that every species with spin $0, 1, 2, \ldots$ is bosonic and every species with spin $\frac{1}{2}, \frac{3}{2}, \frac{5}{2}, \ldots$ is fermionic.

This completes the statement of the fundamental laws of the theory.

Remarks.

• Unordered configurations. Actually, the appropriate physical configuration space for N identical particles is ${}^{N}\mathbb{R}^{3}$ (unordered), not \mathbb{R}^{3N} (ordered). In fact, the permutation condition (10.7) ensures that initial ordered configurations that differ only by a permutation, $Q'_{0} = \sigma Q_{0}$, lead to ordered configurations at any t that differ only by the same permutation, $Q'_{t} = \sigma Q_{t}$. Put differently, (10.1) and (10.7) together define an equation of motion on ${}^{N}\mathbb{R}^{3}$, so we can consider unordered configurations Q_{t} . One moral from this situation is that for Q_{t} to be unordered, it is
not necessary that ψ is defined on ${}^{N}\mathbb{R}^{3}$. However, if we wish that ψ is defined on ${}^{N}\mathbb{R}^{3}$, that is not impossible, although it may seem so for fermionic wave functions. As Leinaas and Myrheim have pointed out,⁶⁷ fermionic wave functions can be regarded as cross-sections of a particular vector bundle over ${}^{N}\mathbb{R}^{3}$, the "fermionic line bundle." (A vector bundle over a manifold \mathcal{Q} is a collection of vector spaces E_{q} , one for each $q \in \mathcal{Q}$, and a topology and differentiable structure on the disjoint union of all E_{q} .) It has sometimes been claimed that quantum particles could not be identical if they had trajectories; Bohmian mechanics is a counter-example to this claim.

- Time reversal. Like each of our microscopic, mechanical theories, Bohmian mechanics is invariant under time reversal: If $t \mapsto (Q(t), \psi(t))$ is a solution of (10.1) and (10.2), then $t \mapsto (Q(-t), \psi^*(-t))$ is another one. (Note that conjugation of ψ reverses the velocities in (10.1).)
- Conditional wave function. The conditional wave function ψ_a of a subsystem a of $a \cup b$ with wave function $\psi(q_a, q_b)$ is defined to be

$$\psi_a(q_a) = \psi(q_a, Q_b) \tag{10.8}$$

with $Q = (Q_a, Q_b)$ the actual configuration. Since Q_b is random, so is ψ_a .

- *Limitations to control and knowledge*. This is a trait of Bohmian mechanics that is unfamiliar from classical theories. Here are two basic examples:
 - While the theory allows us to prepare a particle or system with a wave function ψ of our choice, it does not allow us to choose its position or configuration in addition to and independently of ψ . Rather, if we prepare ψ then the configuration will be random with distribution density $|\psi|^2$. This is a limitation to control.
 - If we know that a system has (conditional) wave function ψ , then we cannot know its configuration more accurately than the $|\psi|^2$ distribution allows. This is a limitation to knowledge.

These limitations are not additional postulates but follow from the laws stated earlier in this section.

To illustrate this, here is an outline of how these limitations arise (the first item follows from the second). Call the system a and its complement b. In a universe governed by Bohmian mechanics, there is a wave function Ψ of the universe, and (10.1) and (10.2) apply to Ψ . The configuration $Q = (Q_a, Q_b)$ is random with $|\Psi|^2$ distribution. The most information any information-processing system in b could have is to know Q_b and Ψ . Given Q_b , the conditional distribution of Q_a is

$$\rho(q_a|Q_b) = \mathcal{N} |\Psi(q_a, Q_b)|^2 = |\psi(q_a)|^2$$
(10.9)

⁶⁷J. Leinaas and J. Myrheim: On the theory of identical particles. *Il Nuovo Cimento* **37B**: 1–23 (1977)

with \mathcal{N} the normalizing factor and $\psi = \mathcal{N}^{1/2} \psi_a$ the conditional wave function of system a. If we have less information, then we will have to average this distribution over different values of Q_b (or Ψ).

10.2 Hilbert Space and Operators

The relevant set of wave functions is $L^2(\mathbb{R}^{3N}, \mathbb{C}^{\ell})$ of all square-integrable functions ψ : $\mathbb{R}^{3N} \to \mathbb{C}^{\ell}$ modulo changes on a null set. It forms a Hilbert space, i.e., a complex vector space \mathscr{H} with a sesqui-linear inner product $\langle -|-\rangle$ and that is complete in the norm $\|\psi\| = \sqrt{\langle \psi | \psi \rangle}$ (i.e., every Cauchy sequence converges). So does any $L^2(\Omega, \mathscr{F}, \mu, \mathbb{C}^{\ell})$, the space of square-integrable (relative to the measure μ) functions $\psi : \Omega \to \mathbb{C}^{\ell}$. The inner product in L^2 is

$$\langle \phi | \psi \rangle = \int_{\Omega} \mu(dq) \, \phi^*(q) \, \psi(q) \,. \tag{10.10}$$

For the unit sphere in \mathscr{H} I use the notation

$$\mathbb{S}(\mathscr{H}) = \{ \psi \in \mathscr{H} : \|\psi\| = 1 \}.$$
(10.11)

10.2.1 Time Evolution

The Schrödinger equation is of the form

$$i\frac{d\psi_t}{dt} = H\psi_t \tag{10.12}$$

with H called the Hamiltonian operator. The solution is of the form

$$\psi_t = U_t \psi_0 = e^{-iHt} \psi_0 \,. \tag{10.13}$$

The time evolution operators (propagators) U_t form a 1-parameter group,

$$U_s U_t = U_{s+t}, \quad U_0 = I,$$
 (10.14)

and are unitary, i.e., bijective $\mathscr{H} \to \mathscr{H}$ with

$$\langle U\phi|U\psi\rangle = \langle \phi|\psi\rangle. \tag{10.15}$$

Unitary operators are characterized by the property

$$U^{-1} = U^{\dagger} \,, \tag{10.16}$$

where S^{\dagger} means the adjoint of S, which is characterized by the property

$$\langle \phi | S^{\dagger} \psi \rangle = \langle S \phi | \psi \rangle \tag{10.17}$$

for all ϕ in the domain of S (which is \mathscr{H} for unitary operators but generally merely a dense subspace) and ψ in the domain of S^{\dagger} .⁶⁸ For example, Fourier transformation is a unitary operator on $\mathscr{H} = L^2(\mathbb{R}^d, \mathbb{C}^\ell)$. The Hamiltonian H is self-adjoint, i.e.,

$$H^{\dagger} = H \,. \tag{10.18}$$

It is generally assumed of quantum physical models that the evolution of the wave function is governed by (10.12) for some self-adjoint operator H. It then follows that e^{-iHt} exists and provides a unitary 1-parameter group. (Conversely, every strongly continuous⁶⁹ unitary 1-parameter group is of this form, a fact known as "Stone's theorem.")

10.2.2 Orthonormal Bases

An orthonormal basis (ONB) of a Hilbert space \mathscr{H} is a set B of vectors such that for all $\phi, \psi \in B$,

$$\langle \phi | \psi \rangle = \delta_{\phi\psi} = \begin{cases} 1 & \text{if } \phi = \psi \\ 0 & \text{if } \phi \neq \psi \end{cases},$$
(10.19)

and the finite linear combinations of vectors in B form a dense subspace of \mathscr{H} (so that the infinite linear combinations cover all of \mathscr{H}). Any two ONBs of \mathscr{H} have the same cardinality, the dimension dim \mathscr{H} of \mathscr{H} . Hilbert spaces can have finite, countable, or uncountable dimension; the latter case occurs rarely if ever in physics; $L^2(\mathbb{R}^d, \mathbb{C}^\ell)$ has countable dimension for every $d, \ell \geq 1$. A unitary isomorphism is a bijection $U : \mathscr{H}_1 \to$ \mathscr{H}_2 satisfying (10.15). Two Hilbert space are unitarily isomorphic iff they have the same dimension. For example, $\mathscr{H} = L^2(\mathbb{R}^d, \mathbb{C}^k)$ is unitarily isomorphic to the space ℓ^2 of square-summable complex sequences (which can be regarded as $\ell^2 = L^2(\mathbb{N}, \#, \mathbb{C})$ with # the counting measure). Such an isomorphism is, in fact, provided by any ONB $B = \{\phi_1, \phi_2, \ldots\}$ of \mathscr{H} by mapping any vector

$$\psi = \sum_{\alpha=1}^{\infty} c_{\alpha} \,\phi_{\alpha} \tag{10.20}$$

to the sequence (c_1, c_2, \ldots) of coefficients. A generalized ONB of a Hilbert space \mathscr{H} is a unitary isomorphism $\Phi : \mathscr{H} \to L^2(\Omega, \mu, \mathbb{C})$. The "basis vectors" $|\omega\rangle$ correspond to the elements ω of Ω but are not necessarily vectors in \mathscr{H} . For example, the "momentum basis" of $\mathscr{H} = L^2(\mathbb{R}^d, \mathbb{C})$ is the Fourier transformation with $\Omega = \mathbb{R}^d$ and $\mu =$ Lebesgue measure. The matrix representation of an operator A relative to an ONB $\{\phi_1, \phi_2, \ldots\}$ is the (dim \mathscr{H}) × (dim \mathscr{H})-matrix with entries

$$a_{\alpha\beta} = \langle \phi_{\alpha} | A \phi_{\beta} \rangle . \tag{10.21}$$

⁶⁸For the definition see, e.g., S. Teufel: Mathematische Physik II: Quantenmechanik, http://www.math.uni-tuebingen.de/arbeitsbereiche/ mathematische-methoden-der-naturwissenschaften/lehre/ss-2016/QuantMech/dateien/ copy7_of_Skript.pdf

⁶⁹I.e., $U_t \psi \to U_{t_0} \psi$ as $t \to t_0$ for every $\psi \in \mathscr{H}$.

10.2.3 Projections

Let \mathscr{K} be a closed subspace and $\mathscr{K}^{\perp} := \{\psi \in \mathscr{H} : \forall \phi \in \mathscr{K} : \langle \psi | \phi \rangle = 0\}$ the orthogonal complement of \mathscr{K} . Then every $\psi \in \mathscr{H}$ can be uniquely decomposed into $\psi = \psi_{||} + \psi_{\perp}$, where $\psi_{||} \in \mathscr{K}$ and $\psi_{\perp} \in \mathscr{K}^{\perp}$. The mapping $P\psi = \psi_{||}$ is the orthogonal projection to \mathscr{K} . It has the properties

$$P^2 = P \quad \text{and} \quad P^{\dagger} = P \,. \tag{10.22}$$

Conversely, every operator $P: \mathscr{H} \to \mathscr{H}$ with (10.22) is an orthogonal projection; it is common to briefly say "projection" instead of "orthogonal projection." The range (or image) of a projection is always a closed subspace; conversely, for every closed subspace \mathscr{K} there is a unique projection whose range is \mathscr{K} . Every vector in \mathscr{K} is an eigenvector with eigenvalue 1, every vector in \mathscr{K}^{\perp} an eigenvector with eigenvalue 0. An ONB of \mathscr{K} and one of \mathscr{K}^{\perp} will together form an ONB of \mathscr{H} consisting of eigenvectors; in particular, 0 and 1 are the only eigenvalues.

10.2.4 Haar Measure on the Unitary Group

The unitary operators on \mathscr{H} form a group $U(\mathscr{H})$, the unitary group. Given a fixed ONB, the unitary group is in a natural one-to-one correspondence with the ONBs (i.e., there is a unique unitary that will carry the fixed ONB to the selected ONB).

If dim $\mathscr{H} < \infty$, then there exists a uniform measure on $U(\mathscr{H})$ known as the Haar measure. While on \mathbb{R}^d , being uniform means being invariant under translations, being uniform on a group means being invariant under left multiplication with any group element. The Haar measure exists for every locally compact topological group and is unique up to a positive factor. If the group is compact (such as $U(\mathscr{H})$ for dim $\mathscr{H} < \infty$), then the Haar measure is finite and is also invariant under right multiplication. The Haar measure on $U(\mathscr{H})$ can be pictured as follows as the uniform distribution over ONBs. Select the first basis vector ϕ_1 uniformly on $\mathbb{S}(\mathscr{H})$, and let \mathscr{H}_1 be the orthogonal complement of ϕ_1 . Select ϕ_2 uniformly on $\mathbb{S}(\mathscr{H}_1)$, and let \mathscr{H}_2 be the orthogonal complement of $\{\phi_1, \phi_2\}$, etc..

10.2.5 The Spectral Theorem

The spectral theorem asserts the following. Suppose first that dim $\mathscr{H} < \infty$. Then every self-adjoint operator A possesses an ONB of eigenvectors. (Likewise, every unitary operator possesses an ONB of eigenvectors.) It follows that the matrix representation in this basis is diagonal. Since a diagonal matrix can be regarded as a multiplication operator, we can also say that in this ONB, A becomes a multiplication operator. Now consider infinite dimension. Then every self-adjoint operator A possesses a generalized ONB Φ in which it becomes a multiplication operator:

$$\Phi A \Phi^{-1} \psi(\omega) = f(\omega) \psi(\omega) \quad \text{for } \psi \in L^2(\Omega) \,. \tag{10.23}$$

In this situation one calls $|\omega\rangle$ a generalized eigenvector and $f(\omega)$ its generalized eigenvalue, and says that A gets diagonalized by Φ . For example, the negative Laplace

operator (free Hamiltonian) gets diagonalized by the momentum basis $|\mathbf{k}\rangle = e^{i\mathbf{k}\cdot\mathbf{q}}$ with $f(k) = \mathbf{k}^2$. "Eigenvectors" and "eigenvalues" simpliciter are $|\omega\rangle \in \mathscr{H}$ and their $f(\omega)$; so the free Hamiltonian does not have any eigenvalues. The set of all eigenvalues is called the "point spectrum," while the "spectrum" is roughly speaking the set of all generalized eigenvalues. Schrödinger Hamiltonians of systems in a compact 3-volume (either compact $\Lambda \subset \mathbb{R}^3$ with boundary conditions or compact manifolds without boundaries) with "reasonable" interactions have pure point spectrum and can thus be diagonalized by an ONB; moreover, each eigenspace has finite dimension, and the eigenvalues do not accumulate but form a sequence

$$E_1 \le E_2 \le E_3 \le \ldots \to \infty \,. \tag{10.24}$$

Another equivalent formulation of the spectral theorem refers to projection valued measures (PVMs). A PVM is a mapping P from a σ -algebra \mathscr{F} on Ω to the projection operators in \mathscr{H} that satisfies $P(\Omega) = I$ and is σ -additive (in the weak operator topology, or equivalently in the strong one⁷⁰):

$$P\left(\bigcup_{n=1}^{\infty} A_n\right) = \sum_{n=1}^{\infty} P(A_n)$$
(10.25)

whenever the sets $A_n \in \mathscr{F}$ are pairwise disjoint. More generally, a *positive-operator-valued measure (POVM)* is a mapping F from \mathscr{F} to the positive self-adjoint operators in \mathscr{H} (i.e., those with spectrum in $[0, \infty)$) that satisfies $F(\Omega) = I$ and is σ -additive. To express that the operator T is positive, one writes $T \geq 0$; note that in linear algebra, a positive operator is often called "positive semi-definite." Every POVM F on Ω acting on \mathscr{H} and every $\psi \in \mathbb{S}(\mathscr{H})$ define together a probability measure μ on Ω according to

$$\mu(\cdot) = \langle \psi | F(\cdot) | \psi \rangle. \tag{10.26}$$

The space $\mathscr{H} = L^2(\Omega, \mu, \mathbb{C}^{\ell})$ is automatically equipped with a "natural PVM" P_{nat} on Ω acting on \mathscr{H} : for every test set $\Delta \subseteq \Omega$,

$$P_{\rm nat}(\Delta) = 1_{\omega \in \Delta} \tag{10.27}$$

(i.e., the multiplication operator multiplying by the characteristic function of Δ) is the projection to the functions that vanish outside Δ .

Now the spectral theorem can be formulated as saying that for every self-adjoint operator A on (a dense subspace of) \mathscr{H} there is a PVM P on \mathbb{R} acting on \mathscr{H} such that $P(\Delta)$ is the projection to the spectral subspace of A for $\Delta \subseteq \mathbb{R}$ (i.e., the subspace spanned by the generalized eigenvectors with generalized eigenvalues in Δ), or $P(\Delta) = \Phi^{-1} \mathbf{1}_{\omega \in f^{-1}(\Delta)} \Phi$. Equivalently,

$$A = \int_{\mathbb{R}} P(d\lambda) \,\lambda \,. \tag{10.28}$$

⁷⁰To converge weakly means that $\sum_{n} \langle \psi | P(A_n) | \psi \rangle$ converges for every $\psi \in \mathscr{H}$. To converge strongly means that $\sum_{n} P(A_n) \psi$ converges in \mathscr{H} for every $\psi \in \mathscr{H}$.

If α is an eigenvalue of A, then $P(\{\alpha\})$ is the projection to the eigenspace. If several self-adjoint operators A_1, \ldots, A_n commute pairwise, then they can be diagonalized simultaneously: There is a PVM P on \mathbb{R}^n acting on \mathscr{H} such that

$$A_m = \int_{\mathbb{R}^n} P(d\boldsymbol{\lambda}) \,\lambda_m \quad \forall m = 1 \dots n \,. \tag{10.29}$$

For example, the position operators are simultaneously diagonalized by the natural PVM of $L^2(\mathbb{R}^{3N}, \mathbb{C}^{\ell})$.

An example of a POVM that is not a PVM is provided by $F(\cdot) = QP(\cdot)Q$ where P is a PVM and Q a projection unrelated to P; then F is a POVM acting on the range of Q.

An eigenvalue λ of an operator T is called *degenerate* if the dimension of the eigenspace is > 1. Generically, Hamiltonians are non-degenerate. In fact, in the n^2 -dimensional (real) space of self-adjoint $n \times n$ matrices, the matrices with a degenerate eigenvalue form a set of lower dimension.

A self-adjoint operator A is called unbounded if its spectrum is unbounded (e.g., this happens with the Laplacian). In that case, A is not a mapping $A : \mathcal{H} \to \mathcal{H}$ but rather $A : D \to \mathcal{H}$ with D a dense subspace of \mathcal{H} called the domain of A. However, $\exp(iHt)$ is bounded even if H is not, and $\exp(iHt)$ has domain \mathcal{H} .

10.2.6 Ergodic Components of the Unitary Evolution

Suppose that H has pure point spectrum. In the energy representation, i.e., in an ONB $\{|\alpha\rangle\}$ diagonalizing $H(H|\alpha\rangle = E_{\alpha}|\alpha\rangle)$, the unitary time evolution has the form

$$\psi_t = \sum_{\alpha} c_{\alpha} e^{-iE_{\alpha}t} |\alpha\rangle \tag{10.30}$$

with coefficients $c_{\alpha} = \langle \alpha | \psi \rangle$. In particular, the moduli of the coefficients $|\langle \alpha | \psi_t \rangle|$ are conserved. The surface \mathscr{T} in \mathscr{H} with fixed moduli $|c_n|$ and arbitrary phases is a torus a product of (finitely or infinitely many) circles. Every such surface \mathscr{T} is invariant. As discussed in one of the homework exercises for finite dimension, the dynamics on \mathscr{T} is ergodic iff the eigenvalues of H are rationally independent, a condition that is generically satisfied. In this case, the tori \mathscr{T} are the ergodic components of the unitary evolution in \mathscr{H} .

10.2.7 Tensor Product

The tensor product between two Hilbert spaces, $\mathcal{H}_a \otimes \mathcal{H}_b$ is the abstract operation that concretely looks like

$$L^{2}(\Omega_{a},\mu_{a},\mathbb{C})\otimes L^{2}(\Omega_{b},\mu_{b},\mathbb{C}) = L^{2}(\Omega_{a}\times\Omega_{b},\mu_{a}\times\mu_{b},\mathbb{C}).$$
(10.31)

Its elements are, instead of functions $\psi(x)$ and $\phi(y)$, functions $\Psi(x, y)$; the elements of $\mathscr{H}_a \otimes \mathbb{C}^n$ can be thought of as *n*-tuples of vectors from \mathscr{H}_a . The tensor product comes along with an operation between vectors: $\psi \otimes \phi$ is the element of $\mathscr{H}_a \otimes \mathscr{H}_b$ that corresponds to the function $\Psi(x, y) = \psi(x) \phi(y)$. The wave functions of a composite $a \cup b$ of two systems are element of $\mathscr{H}_a \otimes \mathscr{H}_b$. Not every element of $\mathscr{H}_a \otimes \mathscr{H}_b$ is a product $\psi \otimes \phi$; if the wave function is not a product, then *a* and *b* are said to be *entangled*. However, every element of $\mathscr{H}_a \otimes \mathscr{H}_b$ is an infinite linear combination of product elements. In fact, if $\{\psi_1, \psi_2, \ldots,\}$ is an ONB of \mathscr{H}_a and $\{\phi_1, \phi_2, \ldots\}$ is an ONB of \mathscr{H}_b , then $\{\psi_\alpha \otimes \phi_\beta : \alpha, \beta = 1, 2, \ldots\}$ is an ONB of $\mathscr{H}_a \otimes \mathscr{H}_b$.

For operators T_a on \mathcal{H}_a and T_b on \mathcal{H}_b , one can form an operator $T_a \otimes T_b$ on $\mathcal{H}_a \otimes \mathcal{H}_b$ that is determined by the property

$$(T_a \otimes T_b)(\psi \otimes \phi) = (T_a \psi) \otimes (T_b \phi).$$
(10.32)

Operators on $\mathbb{C}^m \otimes \mathbb{C}^n$ can be thought of as $n \times n$ matrices whose entries are $m \times m$ matrices, and for $T_a \otimes T_b$ these entries are multiples of each other.

Example. When (and only when) the systems a, b do not interact, the Hamiltonian is of the form

$$H = H_a \otimes I_b + I_a \otimes H_b \,, \tag{10.33}$$

and the propagator $U_t = e^{-iHt}$ is of the form

$$U_t = U_{a,t} \otimes U_{b,t} \tag{10.34}$$

with $U_{a/b,t} = e^{-iH_{a/b}t}$.

10.2.8 Trace

The trace of an operator is the sum of the diagonal entries of its matrix relative to an arbitrary ONB,

$$\operatorname{tr} T = \sum_{\alpha=1}^{\infty} \langle \phi_{\alpha} | T | \phi_{\alpha} \rangle .$$
 (10.35)

More precisely, for a bounded positive operator the trace is a number ≥ 0 or ∞ that turns out to be independent of the choice of ONB. For non-positive operators one proceeds as follows. The *trace class* of \mathscr{H} is the set of bounded operators T on \mathscr{H} such that the positive bounded operator $|T| = \sqrt{T^{\dagger}T}$ has finite trace. For operators in the trace class the series (10.35) converges absolutely and is independent of the ONB.

Partial trace: When T is an operator on $\mathscr{H}_a \otimes \mathscr{H}_b$ then its partial trace over \mathscr{H}_b , tr_bT, is an operator on \mathscr{H}_a . The partial trace is characterized by the property

$$\operatorname{tr}_b(T_a \otimes T_b) = \operatorname{tr}(T_b) T_a \tag{10.36}$$

and can be expressed explicitly in terms of an ONB $\{\phi_1^b, \phi_2^b, \ldots\}$ of \mathscr{H}_b as

$$\operatorname{tr}_{b} T = \sum_{\beta=1}^{\infty} \langle \phi_{\beta}^{b} | T | \phi_{\beta}^{b} \rangle, \qquad (10.37)$$

where the inner product is a partial inner product. It follows that

$$\operatorname{tr}(\operatorname{tr}_b(T)) = \operatorname{tr}(T). \tag{10.38}$$

10.3 Predictive Rules for an Idealized Experiment

Here are the rules for a certain type of experiment, called an *ideal quantum measurement*. (The name "measurement" is somewhat misleading because the experiment often generates a random outcome instead of making known a value that was well defined already before the experiment.) These rules can be derived from Bohmian mechanics for suitable experiments.

The set \mathscr{Z} of possible outcomes is finite (and usually regarded as a subset of \mathbb{R}); with every $z \in \mathscr{Z}$ is associated a subspace \mathscr{H}_z of \mathscr{H} such that $\mathscr{H}_{z'} \perp \mathscr{H}_z$ for $z' \neq z$ and

$$\mathscr{H} = \bigoplus_{z} \mathscr{H}_{z} \,. \tag{10.39}$$

Let P_z denote the projection to \mathscr{H}_z . The experiment is idealized as having duration 0. If it is carried out on a system with wave function $\psi \in \mathbb{S}(\mathscr{H})$, then the probability of obtaining the outcome z is

$$\mathbb{P}(Z=z) = \langle \psi | P_z | \psi \rangle = \| P_z \psi \|^2.$$
(10.40)

If the actual outcome was z, then the wave function ψ' immediately after the experiment is the "collapsed" wave function

$$\psi' = \frac{P_z \psi}{\|P_z \psi\|} \,. \tag{10.41}$$

If $\mathscr{Z} \subset \mathbb{R}$, then the self-adjoint operator

$$A = \sum_{z \in \mathscr{Z}} z P_z \tag{10.42}$$

is often called the *observable* "measured" in the experiment; note that the P_z form a PVM on \mathscr{Z} , and (10.42) is the spectral decomposition of A.

10.4 The Main Theorem about POVMs

The main theorem about POVMs asserts that for every experiment in quantum mechanics that can be carried out on a system S with arbitrary wave function $\psi \in \mathbb{S}(\mathcal{H})$, there is a POVM F on the space \mathscr{Z} of the possible outcomes of the experiment such that F is acting on \mathscr{H} and for every $\psi \in \mathbb{S}(\mathscr{H})$, the probability distribution of the random outcome Z is given by

$$\mathbb{P}(Z \in \Delta) = \langle \psi | F(\Delta) | \psi \rangle \tag{10.43}$$

for every test set $\Delta \subseteq \mathscr{Z}$.

Derivation from Bohmian mechanics. We write $\Psi(x, y)$ for the joint wave function of S(with configuration variable $x \in \mathcal{Q}_S = \mathbb{R}^{3N_S}$) and the experimental apparatus A (with configuration variable $y \in \mathcal{Q}_A = \mathbb{R}^{3N_A}$). At the beginning of the experiment (t = 0), since S and A are independent, $\Psi_0(x, y) = \psi(x) \phi(y)$. Of course, $\Psi_t = U_t \Psi_0$ will in general no longer factorize for t > 0.

Suppose first that the experiment has a fixed duration T. The outcome Z must somehow be displayed by the apparatus, so it will be some function of Y_T , $Z = \zeta(Y_T)$; ζ is called the calibration function. Since $(X_t, Y_t) \sim |\Psi_t(x, y)|^2$, and writing $P(\cdot)$ for the natural PVM on $L^2(\mathcal{Q}_S \times \mathcal{Q}_A)$, we have that

$$\mathbb{P}(Z \in \Delta) = \mathbb{P}(Y_T \in \zeta^{-1}(\Delta))$$
(10.44)

$$= \int_{\mathcal{Q}_S} dx \int_{\zeta^{-1}(\Delta)} dy \, |\Psi_T(x,y)|^2 \tag{10.45}$$

$$= \langle \Psi_T | P \big(\mathcal{Q}_S \times \zeta^{-1}(\Delta) \big) | \Psi_T \rangle_{S \cup A}$$
(10.46)

$$= \langle \psi \otimes \phi | U_T^{\dagger} P \big(\mathcal{Q}_S \times \zeta^{-1}(\Delta) \big) U_T | \psi \otimes \phi \rangle_{S \cup A}$$
(10.47)

$$= \langle \psi | F(\Delta) | \psi \rangle_S \tag{10.48}$$

with

$$F(\Delta) = \langle \phi | U_T^{\dagger} P \big(\mathcal{Q}_S \times \zeta^{-1}(\Delta) \big) U_T | \phi \rangle_A$$
(10.49)

(which is an operator because of the *partial* inner product). It remains to verify that $F(\cdot)$ is a POVM. It is a general fact that for self-adjoint operator R, $R_S = \langle \phi | R | \phi \rangle_A$ is also self-adjoint, essentially because

$$\langle \chi | R_S^{\dagger} \psi \rangle_S = \langle R_S \chi | \psi \rangle_S \tag{10.50}$$

$$= \langle R\chi \otimes \phi | \psi \otimes \phi \rangle_{S \cup A} \tag{10.51}$$

$$= \langle \chi \otimes \phi | R | \psi \otimes \phi \rangle \tag{10.52}$$

$$= \langle \chi | R_S | \psi \rangle \,. \tag{10.53}$$

For positive R, R_S is also positive because a self-adjoint operator K is positive if $\langle \psi | K | \psi \rangle \geq 0$ for all ψ , and $\langle \psi | R_S | \psi \rangle_S = \langle \psi \otimes \phi | R | \psi \otimes \phi \rangle_{S \cup A} \geq 0$. (By the way F is in general not a PVM: while $U^{\dagger}PU$ is a projection when P is, R_S is in general not a projection when R is.)

For $\Delta = \mathscr{Z}$, $\zeta^{-1}(\Delta) = \mathcal{Q}_A$ (some outcome must occur; if necessary, we need to designate a certain outcome to mean that the experiment could not be completed for example because the apparatus broke). Thus, $P(\mathcal{Q}_A \times \zeta^{-1}(\mathscr{Z})) = I$ and $F(\mathscr{Z}) = I$. Additivity in Δ follows from the following facts: (i) If Δ_n are mutually disjoint then so are the $\zeta^{-1}(\Delta_n)$ and their products with \mathcal{Q}_S . (ii) P is additive. (iii) F is linear in P.

If the duration T is random (e.g., if the experiment involves a detector waiting to register a particle), then we may include in the apparatus a device that records the outcome and the time T at which the experiment was complete. Suppose that at a late time τ , we terminate the experiment and read out the recording device with result $Z_{\tau} \in (\mathscr{Z} \times [0, \tau]) \cup \{\infty\}$; here, we set $Z_{\tau} = \infty$ if the experiment was not over at τ , and $Z_{\tau} = (Z, T)$ otherwise. We know that the distribution of Z_{τ} is $\langle \psi | F_{\tau}(\cdot) | \psi \rangle$ for some POVM F_{τ} . Since it is known at any time whether the experiment is over yet, $F_{\tau_2}(\Delta) = F_{\tau_1}(\Delta)$ for $\tau_1 < \tau_2$ and $\Delta \subseteq \mathscr{Z} \times [0, \tau_1]$. Letting $\tau \to \infty$, $F_{\tau}(\Delta) \to F_{\infty}(\Delta)$ for every $\Delta \subseteq \mathscr{Z} \times [0, t]$ and thus also for every $\Delta \subseteq \mathscr{Z} \times [0, \infty)$ (in the strong sense $F_{\tau}(\Delta)\psi \to F_{\infty}(\Delta)\psi$ for every $\psi \in \mathscr{H}$). The marginal $F(\Delta) = F_{\infty}(\Delta \times [0, \infty))$ is the desired POVM.⁷¹

Definition 10. Two experiments (that can be carried out on arbitrary wave functions $\psi \in \mathbb{S}(\mathscr{H})$) are equivalent in law iff for every $\psi \in \mathbb{S}(\mathscr{H})$, they have the same distribution of the outcome. Thus, they are equivalent in law iff they have the same POVM. A corresponding equivalence class of experiments is called an *observable*.

If \mathscr{E}_1 and \mathscr{E}_2 are equivalent in law and a particular run of \mathscr{E}_1 has yielded the outcome z_1 , it cannot be concluded that \mathscr{E}_2 would have yielded z_1 as well. The counterfactual question, "what would z_2 have been if we had run \mathscr{E}_2 ?" cannot be tested empirically, but it can be analyzed in Bohmian mechanics; there, one sometimes finds $z_2 \neq z_1$ (for the same Q_S and ψ in both experiments, but different Q_A and ϕ). That is why the term "observable" can be rather misleading: It is intended to suggest "observable quantity," but an observable is not even a well-defined quantity to begin with (as the outcome Z depends on \mathcal{Q}_A and ϕ), it is a class of experiments with equal probability distributions.

10.5 Density Operators

Consider a random wave function Ψ with probability distribution μ on (the Borel σ -algebra of) $\mathbb{S}(\mathcal{H})$. Then, for any experiment,

$$\mathbb{P}(Z \in \Delta) = \int_{\mathbb{S}(\mathscr{H})} \mu(d\psi) \langle \psi | F(\Delta) | \psi \rangle$$
(10.54)

$$= \int_{\mathbb{S}(\mathscr{H})} \mu(d\psi) \operatorname{tr}\left(|\psi\rangle\langle\psi|F(\Delta)\right)$$
(10.55)

$$= \operatorname{tr}\left(\rho_{\mu} F(\Delta)\right) \tag{10.56}$$

with

$$\rho_{\mu} = \int_{\mathbb{S}(\mathscr{H})} \mu(d\psi) |\psi\rangle\langle\psi| \qquad (10.57)$$

called the *density operator* or *density matrix* of μ . As a consequence, no experiment can distinguish between two distributions μ_1, μ_2 that have the same density operator (a limitation to knowledge that applies not only in Bohmian mechanics but every version of quantum mechanics). If sufficiently many POVMs can actually be realized through suitable experiments, then every density operator represents an *empirical equivalence class* of distributions μ .

Density operators have the properties

⁷¹The main theorem about POVMs even remains true if $\mathbb{P}(T = \infty) > 0$ and Z assumes a particular value z_{∞} in that case. Then $0 \neq F_{\infty}\{\infty\} = \lim_{\tau \to \infty} F_{\tau}\{\infty\} = I - F_{\infty}(\mathscr{Z} \times [0, \infty))$ and $F\{z_{\infty}\} = F_{\infty}\{\infty\}$.

- ρ is self-adjoint;
- $\rho \ge 0$ (positive operator);
- tr $\rho = 1$ (in particular, ρ lies in the trace class).

Conversely, every ρ with these properties arises as ρ_{μ} for some μ . (For example, one can show that every ρ with these properties has pure point spectrum and can thus be diagonalized by an ONB $\{\phi_1, \phi_2, \ldots\}, \rho = \sum_{\alpha} p_{\alpha} |\phi_{\alpha}\rangle \langle \phi_{\alpha}|$ with p_{α} the eigenvalues of ρ ; note $p_{\alpha} \geq 0$ and $\sum_{\alpha} p_{\alpha} = 1$. Then $\mu = \sum_{\alpha} p_{\alpha} \delta_{\phi_{\alpha}}$ has $\rho_{\mu} = \rho$.)

Density operators are often called states or quantum states. They are called pure iff

$$\rho = |\psi\rangle\langle\psi| \tag{10.58}$$

(a 1-dimensional projection) for some $\psi \in \mathbb{S}(\mathscr{H})$ and *mixed* otherwise. A natural norm on density operators is the *trace norm*

$$\|T\|_{\rm tr} = {\rm tr}\,\sqrt{T^{\dagger}T} \tag{10.59}$$

Let me briefly outline the reason. Suppose we seek to distinguish two nearby density operators ρ_1, ρ_2 ; an experiment with POVM F will yield

$$\mathbb{P}_1(Z \in \Delta) - \mathbb{P}_2(Z \in \Delta) = \operatorname{tr}\left((\rho_1 - \rho_2)F(\Delta)\right), \qquad (10.60)$$

and we will want to choose $F(\Delta)$ so as to maximize the difference. Diagonalize $T = \rho_1 - \rho_2 = \sum_{\alpha} \tau_{\alpha} |\phi_{\alpha}\rangle \langle \phi_{\alpha}|$; an optimal choice is $F(\Delta) = \sum_{\alpha:\tau_{\alpha}>0} |\phi_{\alpha}\rangle \langle \phi_{\alpha}|$, so $F(\Delta^c) = I - F(\Delta) = \sum_{\alpha:\tau_{\alpha}\leq0} |\phi_{\alpha}\rangle \langle \phi_{\alpha}|$. Since $\sum_{\alpha} \tau_{\alpha} = 0$, we have that

$$\operatorname{tr}(TF(\Delta)) = \sum_{\alpha:\tau_{\alpha}>0} \tau_{\alpha} = \frac{1}{2} \sum_{\alpha} |\tau_{\alpha}| = \frac{1}{2} ||T||_{\operatorname{tr}}, \qquad (10.61)$$

so $\frac{1}{2} \| \rho_1 - \rho_2 \|_{tr}$ represents the maximal difference of probabilities for any experiment.

Time evolution. As every ψ evolves to $\psi_t = e^{-iHt}\psi$, a probability distribution μ evolves to $T^t_*\mu = \mu \circ e^{iHt}$, and the density matrix ρ to

$$\rho_t = e^{-iHt} \rho e^{iHt} \,, \tag{10.62}$$

which is the solution to the von Neumann equation

$$\frac{d\rho_t}{dt} = -i[H,\rho]. \tag{10.63}$$

Now consider a composite system $a \cup b$ with Hilbert space $\mathscr{H} = \mathscr{H}_a \otimes \mathscr{H}_b$. If we can only do experiments on a (no interaction between the apparatus and b, or between

a and b), then their POVMs are of the form $F_a(\Delta) \otimes I_b$, as follows from the proof of the main theorem about POVMs. As a consequence,

$$\mathbb{P}(Z \in \Delta) = \langle \psi | F_a(\Delta) \otimes I_b | \psi \rangle = \operatorname{tr}(\rho_a F_a(\Delta))$$
(10.64)

with

$$\rho_a = \operatorname{tr}_b |\psi\rangle\langle\psi|\,,\qquad(10.65)$$

called the *reduced density operator* of a. Thus, a density operator can arise in two ways: Either as a statistical density operator because the wave function is random, or as a reduced density operator because the system is entangled with another system. A reduced density matrix evolves according to the von Neumann equation (10.63) with Hreplaced by H_a if there is no interaction between a and b, $H_{a\cup b} = H_a \otimes I_b + I_a \otimes H_b$; in general, however, ρ_a does not have an autonomous time evolution.

10.6 Existence of Density Operators

Proposition 9. Let \mathscr{H} be a Hilbert space. Then every probability measure μ on (the Borel σ -algebra of) $\mathbb{S}(\mathscr{H})$ possesses a density matrix

$$\rho_{\mu} = \int_{\mathbb{S}(\mathscr{H})} \mu(d\psi) |\psi\rangle \langle\psi|, \qquad (10.66)$$

where the integral is understood in the weak sense, i.e., there is an operator $\rho_{\mu} : \mathcal{H} \to \mathcal{H}$ such that for every $\phi, \chi \in \mathcal{H}$,

$$\langle \phi | \rho_{\mu} | \chi \rangle = \int_{\mathbb{S}(\mathscr{H})} \mu(d\psi) \langle \phi | \psi \rangle \langle \psi | \chi \rangle .$$
(10.67)

Proof. By the Cauchy–Schwarz inequality,

$$\left| \langle \phi | \psi \rangle \langle \psi | \chi \rangle \right| \le \| \phi \| \| \chi \|, \qquad (10.68)$$

so the integrand on the right-hand side of (10.67) is a bounded function, and thus in $L^1(\mu)$, so the integral exists for every ϕ and χ . Moreover, as a function of ϕ and χ it is a sesqui-linear form $\beta(\phi, \psi)$; since it is $\leq \|\phi\| \|\chi\|$, one says β is a *bounded* sesquilinear form. Every bounded sesqui-linear form is of the form $\beta(\phi, \chi) = \langle \phi | S | \chi \rangle$ for some bounded operator $S = \rho_{\mu}$.

(That is a consequence of the Riesz representation theorem, which states that every bounded linear functional $\psi \mapsto L(\psi)$ is of the form $L(\psi) = \langle \omega | \psi \rangle$ for some $\omega \in \mathscr{H}$. Here we use the conjugate version, that an anti-linear $L(\phi) = \beta(\phi, \chi)$ is of the form $L(\phi) = \langle \phi | \omega \rangle$ for some $\omega \in \mathscr{H}$; since L depends linearly on χ , so does ω , so $\omega = S\chi$.) \Box

10.7 Recurrence

A recurrence theorem holds for the unitary evolution for both pure and mixed states in finite- and infinite-dimensional \mathscr{H} :

Proposition 10. Suppose that *H* has pure point spectrum. For any ρ_0 , any $\varepsilon > 0$, and any T > 0, there is t > T such that

$$\|\rho_t - \rho_0\|_{\rm tr} < \varepsilon \,. \tag{10.69}$$

Proof. If the Hilbert space is finite-dimensional, then there is t > T such that

$$\|e^{-iHt} - I\| < \varepsilon, \qquad (10.70)$$

where $\|\cdot\|$ is the operator norm (largest absolute eigenvalue). This follows for example from the Poincaré recurrence theorem applied to the unitary group with flow given by the left multiplication by $\exp(-iHt)$ and measure given by the Haar measure, which is finite and invariant under the flow. Since for the operator norm, $\|ST\| \leq \|S\| \|T\|$, we have for any density matrix ρ_0 that

$$\left\| e^{-iHt} \rho_0 e^{iHt} - \rho_0 \right\| \le \left\| e^{-iHt} \rho_0 e^{iHt} - e^{-iHt} \rho_0 \right\| + \left\| e^{-iHt} \rho_0 - \rho_0 \right\|$$
(10.71)

$$\leq \|\rho_0 e^{iHt} - \rho_0\| + \|e^{-iHt}\rho_0 - \rho_0\| \tag{10.72}$$

$$\leq \|e^{iHt} - I\| \|\rho_0\| + \|e^{-iHt} - I\| \|\rho_0\| \tag{10.73}$$

$$< 2\varepsilon \|\rho_0\| \le 2\varepsilon \,. \tag{10.74}$$

Since norms are equivalent in finite dimension, an adjustment of ε by some constant factor (dependent on dim \mathscr{H}) yields (10.69).

If \mathscr{H} is infinite-dimensional, then (10.70) may fail but (10.69) still holds, as we show now. For $\rho_0 = \sum_{\alpha=1}^{\infty} p_\alpha |\psi_\alpha\rangle \langle\psi_\alpha|$ with ONB $\{\psi_\alpha\}$ choose r so large that $\sum_{\alpha=r+1}^{\infty} p_\alpha < \varepsilon$ and set $\rho'_0 = \sum_{\alpha=1}^r p_\alpha |\psi_\alpha\rangle \langle\psi_\alpha|$. Then $\|\rho'_0 - \rho_0\|_{\mathrm{tr}} < \varepsilon$; that is, we have approximated ρ_0 by an operator of finite rank. Now each vector $\psi_\alpha \in \mathscr{H}$ can be approximated in the Hilbert space norm by ψ''_α that is a linear combination of finitely many energy eigenvectors, even with $\|\psi''_\alpha\| = 1$; say, $\|\psi''_\alpha - \psi_\alpha\| < \varepsilon/2r$ for all $\alpha = 1, \ldots, r$. Set $\rho''_0 = \sum_{\alpha=1}^r p_\alpha |\psi''_\alpha\rangle \langle\psi''_\alpha|$, which is concentrated on the space spanned by certain finitely many energy eigenvectors. Since for any $\phi, \chi \in \mathbb{S}(\mathscr{H})$,

$$\left\| |\phi\rangle\langle\phi| - |\chi\rangle\langle\chi| \right\|_{\rm tr} = 2\sqrt{1 - \left|\langle\phi|\chi\rangle\right|^2} \le 2\|\phi - \chi\| \tag{10.75}$$

and $\sum_{\alpha=1}^{r} p_{\alpha} \leq 1$, we have that $\|\rho_{0}'' - \rho_{0}'\| < \varepsilon$. From the first half of this proof we know that there is t > T with $\|\rho_{t}'' - \rho_{0}''\| < \varepsilon$. Distances between density matrices are constant under unitary evolution, $\|\rho_{t}'' - \rho_{0}'\| = \|\rho_{0}'' - \rho_{0}'\|$ etc., so $\|\rho_{t} - \rho_{0}\| < 5\varepsilon$.

We remark that also a reduced density matrix ρ_a (which does not have an autonomous time evolution) will return to near its initial value if the full density matrix $\rho_{a\cup b}$ does so, which will happen for $H_{a\cup b}$ with pure point spectrum.

An example of a unitary evolution without recurrence is the free Schrödinger evolution (without potential) in \mathbb{R}^3 . There, everything propagates away to spatial infinity without returning. Note that the free Hamiltonian (i.e., the negative Laplace operator) has continuous spectrum.

11 Thermodynamic Ensembles

In quantum mechanics, the thermodynamic ensembles correspond to certain density matrices or to certain probability distributions of wave functions.

11.1 The Micro-Canonical Ensemble

The quantum analog of an energy surface Γ_E would be an energy eigenspace. However, whereas in classical mechanics every phase point lies on Γ_E for some E, only very special wave functions lie in an energy eigenspace. It is therefore more appropriate to consider an *energy shell*, i.e., an energy interval

$$I_{\rm mc} = (E - \Delta E, E] \tag{11.1}$$

whose length ΔE is often taken to be the macroscopic resolution of energy or, at any rate, to be small on the macroscopic scale and large on the microscopic scale; the latter means that $I_{\rm mc}$ contains many eigenvalues of H (in realistic examples, of order $10^{10^{10}}$ eigenvalues). To this interval there corresponds a subspace $\mathscr{H}_{\rm mc}$ of \mathscr{H} , the spectral subspace of H associated with $I_{\rm mc}$; it is called the *micro-canonical subspace* or also the *energy shell*. If H has pure point spectrum, then $\mathscr{H}_{\rm mc}$ is the subspace spanned by the eigenvectors of H with eigenvalues in $I_{\rm mc}$.

We henceforth assume that H has pure point spectrum, that there are only finitely many eigenvalues below any given value, and that every eigenvalue E_{α} has finite multiplicity m_{α} (as would be the case for a system enclosed in a finite volume Λ). Then dim \mathscr{H}_{mc} will be finite; realistic values are of order $10^{10^{10}}$.

The obvious measure on the wave functions in the energy shell is the (normalized) uniform distribution over $S(\mathscr{H}_{mc})$, denoted by u_{mc} in the following. The corresponding density matrix is

$$\rho_{\rm mc} = \frac{1}{d_{\rm mc}} P_{\rm mc} = \frac{1}{d_{\rm mc}} \mathbf{1}_{I_{\rm mc}}(H)$$
(11.2)

with

$$d_{\rm mc} = \dim \mathscr{H}_{\rm mc} = \operatorname{tr} P_{\rm mc} \tag{11.3}$$

and $P_{\rm mc}$ the projection to $\mathscr{H}_{\rm mc}$. Both the measure $u_{\rm mc}$ and the density matrix $\rho_{\rm mc}$ go by the name of "the micro-canonical ensemble."

11.2 Density of States

It is of interest how many energy eigenvalues lie in suitable intervals. Let $\gamma(E)$ be the dimension of the spectral subspace of $(-\infty, E]$, i.e.,

$$\gamma(E) = \operatorname{tr} 1_{(-\infty, E]}(H) = \sum_{\alpha: E_{\alpha} \le E} m_{\alpha} \,. \tag{11.4}$$

Although γ is clearly a step function (piecewise constant), it will usually look smooth on the macroscopic scale. Let $\tilde{\gamma}$ be a smooth version of γ ; the function

$$\Omega(E) = \frac{d\tilde{\gamma}(E)}{dE} \tag{11.5}$$

is called the *density of states*. In this context, let me give away already that also in the quantum case we will find the thermal equilibrium entropy to be

$$S(E, V, N) = k \log \Omega(E), \qquad (11.6)$$

analogously to the classical case.

Example. The ideal Bose gas: Consider N identical bosons of spin 0 in a container $\Lambda \subset \mathbb{R}^3$. For simplicity of the calculation, let us take Λ to be a cube $[0, L]^3$. We compute the density of states and the equilibrium entropy function.

The Hamiltonian is, up to a factor, the Laplacian in 3N dimensions,

$$H = -\frac{1}{2m}\Delta\,,\tag{11.7}$$

with Dirichlet boundary conditions,

$$\psi(q) = 0 \quad \text{whenever } q_i = 0 \text{ or } q_i = L \text{ for } i = 1 \dots 3N. \tag{11.8}$$

More precisely, the domain of the Hamiltonian H consists of functions (from the second Sobolev space) that satisfy the boundary conditions, and on this domain H acts like (11.7). Dirichlet boundary conditions arise naturally if we think of the Hamiltonian as the negative Laplacian plus the external potential

$$V_1(\boldsymbol{q}) = \begin{cases} 0 & \text{for } \boldsymbol{q} \in \Lambda \\ \infty & \text{for } \boldsymbol{q} \notin \Lambda , \end{cases}$$
(11.9)

and of V_1 as the limit of potentials that move from 0 to ∞ in a smooth way; large values of the potential will push down the values of the eigenfunctions (all of which lie in the domain) near $\partial \Lambda$, and in fact the values of all functions in the domain near $\partial \Lambda$, with the consequence of value 0 on $\partial \Lambda$ in the limit.

The Hamiltonian in 1 dimension (i.e., -1/2m times the second derivative on an interval with Dirichlet boundary conditions) has non-degenerate eigenvalues⁷²

$$E_n = \frac{\pi^2}{2mL^2} n^2 \tag{11.10}$$

and eigenfunctions

$$\varphi_n(q) = \left(\frac{2}{L}\right)^{1/2} \sin(n\frac{\pi}{L}q) \tag{11.11}$$

⁷²For example, this calculation is done on page 78 in C. Cohen-Tannoudji, B. Diu, and F. Laloë: *Quantum Mechanics. Vol. 1.* Translated from the French by S. R. Hemley, N. Ostrowsky, and D. Ostrowsky. Paris: Hermann and John Wiley & Sons (1977).

with $n \in \mathbb{N}$; the φ_n form an ONB. Now consider 3N dimensions, but let us leave aside the bosonic symmetrization for a moment. Then the Hamiltonian H on $\mathscr{H} = L^2([0, L]^{3N})$ has an ONB of eigenfunctions that are products of the 1d eigenfunctions,

$$\varphi_n(q) = \left(\frac{2}{L}\right)^{3N/2} \prod_{i=1}^N \prod_{a=1}^3 \sin(n_{i,a} \frac{\pi}{L} q_{i,a})$$
(11.12)

where $n = (n_{1,1}, ..., n_{N,3}) \in \mathbb{N}^{3N}$ and $q = (q_{1,1}, ..., q_{N,3}) \in [0, L]^{3N}$, and eigenvalues

$$E_n = \sum_{i=1}^N \sum_{a=1}^3 \frac{\pi^2}{2mL^2} n_{i,a}^2 = \frac{\pi^2}{2mL^2} ||n||^2.$$
(11.13)

Degeneracies occur between n's with equal $||n||^2$; this happens for permutations of the components of n when they are different, but also due to relations such as

$$7^2 + 4^2 = 8^2 + 1^2. (11.14)$$

Now consider the subspace \mathscr{H}_+ of permutation-symmetric (bosonic) wave functions, and let P_+ be the projection to \mathscr{H}_+ . Explicitly,

$$P_{+}\psi(\boldsymbol{q}_{1},\ldots,\boldsymbol{q}_{N}) = \frac{1}{N!} \sum_{\sigma \in S_{N}} \psi(\boldsymbol{q}_{\sigma(1)},\ldots,\boldsymbol{q}_{\sigma(N)}). \qquad (11.15)$$

For comparison, the projection to the anti-symmetric (fermionic) wave functions can be written analogously as

$$P_{-}\psi(\boldsymbol{q}_{1},\ldots,\boldsymbol{q}_{N}) = \frac{1}{N!} \sum_{\sigma \in S_{N}} (-1)^{\sigma} \psi(\boldsymbol{q}_{\sigma(1)},\ldots,\boldsymbol{q}_{\sigma(N)}), \qquad (11.16)$$

where $(-1)^{\sigma}$ means the sign of σ .

Claim: With suitable normalization factors $c_n > 0$, $\{c_n P_+ \varphi_n : n \in \mathbb{N}^{3N}\}$ is an ONB of \mathscr{H}_+ consisting of eigenvectors of H.

Proof. Since H is permutation-symmetric, P_+ commutes with H, and $P_+\varphi_n$ thus is another eigenfunction with the same eigenvalue as φ_n ,

$$HP_+\varphi_n = P_+H\varphi_n = P_+E_n\varphi_n = E_nP_+\varphi_n.$$
(11.17)

Writing $n = (\mathbf{n}_1, \ldots, \mathbf{n}_N)$ with $\mathbf{n}_i = (n_{i,1}, n_{i,2}, n_{i,3})$, we obtain that $P_+\varphi_n = P_+\varphi_{n'}$ iff n' is a permutation of n in the sense $(\mathbf{n}'_1, \ldots, \mathbf{n}'_N) = (\mathbf{n}_{\sigma(1)}, \ldots, \mathbf{n}_{\sigma(N)})$, or $n' = \sigma n$ for short. So, there are repetitions in the list of $c_n P_+\varphi_n$ as n runs through \mathbb{N}^{3N} , and it would suffice to use one representative n from each permutation class "n modulo S_N " (considering only permutations σ of the N particles, not of the 3N components). Moreover, always $P_+\varphi_n \neq 0$, and if $P_+\varphi_{n'} \neq P_+\varphi_n$ then $P_+\varphi_{n'} \perp P_+\varphi_n$ because then each term in $P_+\varphi_n = N!^{-1} \sum_{\sigma} \varphi_{\sigma n}$ is orthogonal to every term in $P_+\varphi_{n'}$. The $P_+\varphi_n$ span all of \mathscr{H}_+ because the φ_n span all of \mathscr{H} . This completes the proof of the claim.

By the way, whenever n is such that all n_i are mutually distinct, then $\sigma n \neq n$ for all σ , all summands in (11.15) are mutually orthogonal, and thus

$$c_n = \sqrt{N!} \tag{11.18}$$

because whenever χ_1, \ldots, χ_r are mutually orthogonal then $\|\chi_1 + \ldots + \chi_r\|^2 = \|\chi_1\|^2 + \ldots + \|\chi_r\|^2$ (Pythagoras).

So, in order to count (approximately) the eigenvalues up to E we need to determine (approximately) the number of n's modulo σ with $E_n \leq E$. Again, let us leave σ aside for a moment and ask first about the number of n's with $E_n \leq E$. They are the lattice points in the positive quadrant in the 3N-ball of radius $R = \sqrt{2mEL/\pi}$. This suggests that for large E, their number is approximately equal to the volume of the intersection of the positive quadrant with the ball of radius R; the approximation should be good when $\overline{e} = E/N$ is much larger than the ground state energy per particle

$$e_0 = \frac{3\pi^2}{2mL^2} \,. \tag{11.19}$$

The 3N-ball has volume

$$\mathcal{V}_{3N} = \frac{\pi^{3N/2}}{(3N/2)!} R^{3N} \tag{11.20}$$

(with the factorial of a non-integer x understood as $\Gamma(1+x)$). Since it has 2^{3N} quadrants of equal size, we get that

$$\#\{n: E_n \le E\} \approx \frac{\mathcal{V}_{3N}}{2^{3N}} = \frac{1}{(3N/2)!} \left(\frac{mEL^2}{2\pi}\right)^{3N/2} \approx \left(\frac{mEL^2e}{3\pi N}\right)^{3N/2}$$
(11.21)

using $k! \approx k^k e^{-k}$. For sufficiently large E, most n have no σ with $\sigma n = n$, so most permutation classes have N! elements, so we need to divide the last number by N!,

$$\gamma(E) \approx \frac{1}{N!} \left(\frac{mEL^2e}{3\pi N}\right)^{3N/2} \approx \left(\frac{mEL^2e^{5/3}}{3\pi N^{5/3}}\right)^{3N/2}.$$
 (11.22)

We take the last expression as $\tilde{\gamma}(E)$. Taking the derivative, we obtain that

$$\Omega(E) = \frac{3N}{2} \left(\frac{mEL^2 e^{5/3}}{3\pi N^{5/3}}\right)^{3N/2-1}$$
(11.23)

or, neglecting factors of order $N^{\text{const.}}$ and writing $V = L^3$,

$$\Omega(E) \approx \left(\frac{me^{5/3}}{3\pi} \frac{E}{N}\right)^{3N/2} \left(\frac{V}{N}\right)^N.$$
(11.24)

If we had not set $\hbar = 1$, we would have obtained a further factor of \hbar^2 after 3π in the denominator. Equation (11.6) then yields, with the notation $h = 2\pi\hbar$,

$$S(E, V, N) = kN \left[\frac{3}{2} \log \frac{E}{N} + \log \frac{V}{N} + \frac{3}{2} \log \frac{4\pi m}{3} + \frac{5}{2} - 3 \log h \right].$$
(11.25)

This is the same expression as in the classical case (as computed in a homework exercise), except for the constant $-3 \log h$. In this regime of large E, the same expression for S(E, V, N) is obtained for the Fermi gas.

One should expect three types of corrections to the calculation above. First, a "permutation correction" from the fact that the assumption $n_i \neq n_j$ for most n can only be expected to hold when $\overline{e} \gg e_0$. Second, a "sphere correction" from the fact that the number of lattice points in a 3N-ball of radius R can only be expected to be close to its volume when $R \gg 1$. And third, a "plane correction" from the fact that in our count we have included lattice points for which some component vanishes, $n_{i,a} = 0$, whereas we need to count only those with all $n_{i,a} \neq 0$.

Example. Distribution of eigenvalues in $I_{\rm mc}$. Since the density of states $\Omega(E)$ increases very quickly, like $E^{3N/2}$, most eigenvalues in $I_{\rm mc} = (E - \Delta E, E]$ actually lie close to the right end E. To estimate how close, we consider the probability distribution on the energy axis with density $\propto E^{\alpha}$ between 0 and $E_0 > 0$ (and 0 outside) and compute the expectation value. We find that the density is

$$\rho(E) = 1_{0 < E < E_0} (\alpha + 1) E_0^{-\alpha - 1} E^{\alpha} , \qquad (11.26)$$

and the expectation is

$$\langle E \rangle = \int_0^{E_0} dE \, E \, \rho(E) = \frac{\alpha + 1}{\alpha + 2} E_0 \,.$$
 (11.27)

Renaming E_0 into E and using $\alpha = (3N - 1)/2$, we find that the average energy eigenvalue below E lies at

$$\left(1 - \frac{2}{3N+3}\right)E,$$
 (11.28)

which suggests that most eigenvalues are only of order E/N below E. In practice, ΔE will be much larger than E/N; as a consequence, it does not matter much how large ΔE is: the number of eigenvalues in $I_{\rm mc}$ will remain essentially the same if we make ΔE twice as large or half as large. That is why one often takes

$$I_{\rm mc} = (-\infty, E] \tag{11.29}$$

instead of (11.1): It does not matter to add just a few more outlier eigenvalues. \Box

11.3 The Canonical Density Operator

The canonical density operator is defined to be

$$\rho_{\rm can} = \frac{1}{Z} e^{-\beta H} \tag{11.30}$$

with $Z = \operatorname{tr} \exp(-\beta H)$ and inverse temperature $\beta > 0$. (No confusion should arise from using the same name β for the inverse temperature and an index labeling basis vectors.) For this operator to exist, one needs that the E_{α} tend to ∞ quickly enough so that

$$\sum_{\alpha} m_{\alpha} \exp(-\beta E_{\alpha}) < \infty \,. \tag{11.31}$$

In classical mechanics, the canonical ensemble arises as the marginal of the microcanonical ensemble for a small subsystem, and a corresponding statement holds here: Suppose that $\mathscr{H} = \mathscr{H}_a \otimes \mathscr{H}_b$, that system b is much larger than a, and that the interaction between a and b is negligible, $H = H_a \otimes I_b + I_a \otimes H_b$. Then

$$\operatorname{tr}_b \rho_{\mathrm{mc}} \approx \rho_{\mathrm{can}} \tag{11.32}$$

for a suitable choice of $\beta = \beta(E)$.

Here is a derivation of this statement under the assumption that b has the density of states of an ideal gas. Let $I_{\rm mc} := (E - \Delta E, E]$. For simplicity, suppose further that for $i = a, b, H_i$ is non-degenerate; we write (with slight abuse of notation by relying on the name of the index)

$$H_a = \sum_{\alpha} E_{\alpha} |\alpha\rangle \langle \alpha| \tag{11.33}$$

$$H_b = \sum_{\beta} E_{\beta} |\beta\rangle \langle\beta|. \qquad (11.34)$$

Let ρ_a be the reduced density matrix of $\rho_{\rm mc}$ for a,

$$\rho_a = \operatorname{tr}_b \rho_{\mathrm{mc}} \,. \tag{11.35}$$

Then

$$\rho_{\rm mc} = \mathscr{N}_N \sum_{\alpha,\beta} \mathbb{1}_{E_\alpha + E_\beta \in I_{\rm mc}} |\alpha\rangle \langle \alpha| \otimes |\beta\rangle \langle \beta| \,. \tag{11.36}$$

with normalizing factor \mathcal{N}_N . Thus, using (11.24),

$$\rho_a = \mathscr{N}_N \sum_{\alpha} \# \left\{ \beta : E_\beta \in I_{\rm mc} - E_\alpha \right\} |\alpha\rangle \langle \alpha| \tag{11.37}$$

$$\approx \mathcal{N}_N \sum_{\alpha} \Omega(E - E_{\alpha}) |\alpha\rangle \langle \alpha|$$
(11.38)

$$\approx \tilde{\mathcal{N}}_{N} \sum_{\alpha} \left(\frac{E - E_{\alpha}}{N}\right)^{3N/2} |\alpha\rangle\langle\alpha|$$
(11.39)

$$=\tilde{\mathcal{N}}_{N} \bar{e}^{3N/2} \sum_{\alpha} \left(1 - \frac{E_{\alpha}}{N\bar{e}}\right)^{3N/2} |\alpha\rangle \langle \alpha|$$
(11.40)

$$\stackrel{N \to \infty}{\longrightarrow} \frac{1}{Z} \sum_{\alpha} \exp\left(-\frac{3E_{\alpha}}{2\overline{e}}\right) |\alpha\rangle\langle\alpha|, \qquad (11.41)$$

which is (11.30) with $\beta = 3/2\overline{e}$ (which corresponds to the familiar relation $\overline{e} = \frac{3}{2}kT$). We mention in passing that ρ_{can} comes out also if b is not an ideal gas, just with a possibly different dependence $\beta(\overline{e})$.

Also in the quantum-mechanical context there is a phenomenon of equivalence of ensembles, meaning roughly that $\rho_{\rm mc}$ and $\rho_{\rm can}$ are very similar, provided we are comparing suitable pairs of E and β . Since $\rho_{\rm mc}$ and $\rho_{\rm can}$ are both diagonal in the energy representation, this similarity boils down for many purposes to the similarity between the corresponding probability distributions over the energy axis (with m_{α} the multiplicity of E_{α}),

$$\frac{1}{d_{\rm mc}} \sum_{\alpha: E_{\alpha} \in I_{\rm mc}} m_{\alpha} \,\delta_{E_{\alpha}} \tag{11.42}$$

and

$$\frac{1}{Z} \sum_{\alpha} m_{\alpha} e^{-\beta E_{\alpha}} \,\delta_{E_{\alpha}} \,. \tag{11.43}$$

11.4 The Heisenberg Model

The Heisenberg model⁷³ is a quantum-mechanical version of the Ising model. It assumes that one atom is placed at each location i of a finite lattice $\Lambda \subset \mathbb{Z}^d$ with $N = \#\Lambda$ sites, and that each atom can be modeled as a particle with spin $\frac{1}{2}$ (and fixed location). The Hilbert space is thus

$$\mathscr{H} = (\mathbb{C}^2)^{\otimes N}, \qquad (11.44)$$

and the Hamiltonian is taken to be

$$H = -J \sum_{\boldsymbol{i}, \boldsymbol{j}: |\boldsymbol{i}-\boldsymbol{j}|=1} \boldsymbol{\sigma}_{\boldsymbol{i}} \cdot \boldsymbol{\sigma}_{\boldsymbol{j}}, \qquad (11.45)$$

where σ_i is the triple of Pauli spin matrices

$$\sigma^x = \begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix}, \quad \sigma^y = \begin{pmatrix} 0 & -i \\ i & 0 \end{pmatrix}, \quad \sigma^z = \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix}, \quad (11.46)$$

acting on the spin at site i. Just as the Ising model is considered with a canonical probability distribution, the Heisenberg model is considered with a canonical density matrix $Z^{-1}e^{-\beta H}$. However, in contrast to the Ising model, the Heisenberg model possesses a time evolution: the unitary evolution e^{-iHt} in \mathcal{H} .

(Note that no symmetrization or anti-symmetrization is required here because a permutation of the particles would correspond to exchanging their locations along with their spins. If we use their locations to label the particles, then permutation symmetry is automatically dealt with. Thus, all of the 2^N dimensions of \mathscr{H} represent physically possible states.)

⁷³W. Heisenberg: Zur Theorie des Ferromagnetismus. Zeitschrift für Physik **49**: 619–636 (1928)

11.5 Canonical Typicality

Canonical typicality is the following fact⁷⁴: For most pure states ψ from an energy shell \mathscr{H}_{mc} of a large system, the reduced density matrix of a small subsystem s is approximately canonical (with a suitable β),

$$\rho_s^{\psi} \approx \rho_{\rm can} \,, \tag{11.47}$$

provided the interaction between s and its complement $s^c = b$ is weak. Here, $\rho_s^{\psi} = \operatorname{tr}_b |\psi\rangle\langle\psi|$. The degree of approximation will be the better the larger the "large" environment b (called the *heat bath*). We will give a precise formulation below.

Let us compare this to the statement about $\rho_{\rm can}$ from the previous section: $\rho_{\rm can} \approx {\rm tr}_b \rho_{\rm mc}$. The right-hand side is just the average of the reduced density matrix:

$$\int_{\mathbb{S}(\mathscr{H}_{\mathrm{mc}})} u_{\mathrm{mc}}(d\psi) \,\rho_s^{\psi} = \int_{\mathbb{S}(\mathscr{H}_{\mathrm{mc}})} u_{\mathrm{mc}}(d\psi) \,\mathrm{tr}_b \,|\psi\rangle\langle\psi| \tag{11.48}$$

$$= \operatorname{tr}_{b} \int_{\mathbb{S}(\mathscr{H}_{\mathrm{mc}})} u_{\mathrm{mc}}(d\psi) |\psi\rangle\langle\psi| \qquad (11.49)$$

$$= \operatorname{tr}_b \rho_{\mathrm{mc}} \,. \tag{11.50}$$

That is, the statement in the previous section was that the marginal of micro-canonical is canonical, and canonical typicality is the stronger statement that not only on average, but even for most ψ is ρ_s^{ψ} canonical.

Let us contrast this with the situation in classical mechanics. The closest analog of the canonical density matrix is the canonical distribution over phase space, and correspondingly for micro-canonical. Again, the marginal of micro-canonical is canonical. But the analog of a pure state ψ would then be a phase point X of the composite $s \cup b$, and the "reduced state" for s of X would be again a "pure state" X_s , the list of the positions and momenta of all particles belonging to s. One can say that in classical mechanics, the reduced state of a pure state is always pure, whereas in quantum mechanics the reduced state of a pure state can be mixed. In fact, ρ_s^{ψ} is pure iff ψ factorizes, $\psi = \psi_s \otimes \psi_b$; thus, ρ_s^{ψ} is mixed whenever s is *entangled* with b in ψ . (In fact, in order to quantify the strength of the entanglement in ψ one often quantifies the extent to which ρ_s^{ψ} is mixed.) To sum up, canonical typicality has no analog in classical mechanics.

Let us move toward a mathematical formulation of canonical typicality. The size of a system can be quantified particularly easily in the Heisenberg model (or similar ones):

⁷⁴This was discovered by several groups independently: J. Gemmer, G. Mahler, and M. Michel: *Quantum Thermodynamics: Emergence of Thermodynamic Behavior within Composite Quantum Systems.* Lecture Notes in Physics **657**. Berlin: Springer (2004)

S. Popescu, A. J. Short, and A. Winter: Entanglement and the foundation of statistical mechanics. *Nature Physics* **21(11)**: 754–758 (2006)

S. Goldstein, J.L. Lebowitz, R. Tumulka, and N. Zanghi: Canonical Typicality. *Physical Review Letters* **96**: 050403 (2006) http://arxiv.org/abs/cond-mat/0511091

Preliminary considerations in this direction can already be found in E. Schrödinger: *Statistical Thermodynamics.* Second Edition, Cambridge University Press (1952)

Some of the proofs we give follow A. Sugita: On the Basis of Quantum Statistical Mechanics. *Nonlinear Phenomena in Complex Systems* **10**: 192–195 (2007) http://arxiv.org/abs/cond-mat/0602625

Suppose the subsystem s corresponds to a particular region in space; then the size of s can be expressed through the number N_s of lattice sites belonging to it (proportional to the volume of the region, if the lattice used is regular), and the Hilbert space \mathscr{H}_s of s has dimension $d_s = 2^{N_s}$. This suggests characterizing "largeness" by conditions on the dimensions. Here is a mathematical formulation of canonical typicality:

Theorem 20. Let \mathscr{H}_s and \mathscr{H}_b be Hilbert spaces of dimension d_s and d_b , $\mathscr{H} = \mathscr{H}_s \otimes \mathscr{H}_b$, $\mathscr{H}_{\mathrm{mc}}$ be any subspace of \mathscr{H} of dimension d_{mc} , ρ_{mc} be $1/d_{\mathrm{mc}}$ times the projection to $\mathscr{H}_{\mathrm{mc}}$, and u_{mc} the uniform distribution on $\mathbb{S}(\mathscr{H}_{\mathrm{mc}})$. Then for any $\varepsilon > 0$,

$$u_{\rm mc}\left\{\psi\in\mathbb{S}(\mathscr{H}_{\rm mc}):\left\|\rho_s^{\psi}-\operatorname{tr}_b\rho_{\rm mc}\right\|_{\rm tr}<\varepsilon\right\}\geq 1-\frac{d_s^4}{\varepsilon^2 d_{\rm mc}}\,.$$
(11.51)

We know that in relevant cases, $tr_b \rho_{\rm mc} = \rho_{\rm can}$. For the right-hand side to be close to 1, we need that d_s is small compared to $d_{\rm mc}$. For example, if we want the right-hand side to be greater than $1 - 10^{-12}$ and take $\varepsilon = 10^{-12}$, then we need that

$$d_s < 10^{-9} d_{\rm mc}^{1/4} \,. \tag{11.52}$$

To get a rough idea of what that means in practice, consider a Heisenberg model with N sites, so dim $\mathscr{H} = 2^N$; suppose further that the energy shell arises from partitioning the energy axis into $10^{60} = 2^{200}$ intervals, so that perhaps, roughly, $d_{\rm mc} = 2^{N-200}$. Then (11.52) becomes $2^{N_s} = d_s < 2^{-30}2^{N/4-50} = 2^{N/4-80}$ or $N_s < N/4 - 80$. That is, if N is a macroscopic number (> 10^{20}), then s can comprise up to a quarter of all lattice sites.

Let us turn to the proof of Theorem 20. As tools, we need the following two lemmas.

Lemma 3. Let $\Psi \sim u_{\rm mc}$. For any operator $A : \mathscr{H} \to \mathscr{H}$,

$$\mathbb{E} \langle \Psi | A | \Psi \rangle = \operatorname{tr}(\rho_{\mathrm{mc}} A) \tag{11.53}$$

and

$$\operatorname{Var}\langle\Psi|A|\Psi\rangle \le \frac{V_A(\rho_{\mathrm{mc}})}{d_{\mathrm{mc}}+1},$$
(11.54)

where the quantity V_A is defined by

$$V_A(\rho) = \operatorname{tr}\left[\left(A - \operatorname{tr}(\rho A)\right)^{\dagger} \left(A - \operatorname{tr}(\rho A)\right)\rho\right]$$
(11.55)

$$= \operatorname{tr}(\rho A^{\dagger} A) - \left| \operatorname{tr}(\rho A) \right|^{2}, \qquad (11.56)$$

and the variance of a complex random variable (as A is not required to be self-adjoint) is understood as

$$\operatorname{Var} X = \mathbb{E}[(X - \mathbb{E}X)^*(X - \mathbb{E}X)] = \mathbb{E}(X^*X) - \mathbb{E}(X^*)\mathbb{E}(X).$$
(11.57)

Proof. Since $\langle \Psi | A | \Psi \rangle = \operatorname{tr}(A | \Psi \rangle \langle \Psi |)$, we have that

$$\mathbb{E} \langle \Psi | A | \Psi \rangle = \mathbb{E} \operatorname{tr}(A | \Psi \rangle \langle \Psi |) = \operatorname{tr}\left(A \mathbb{E} | \Psi \rangle \langle \Psi |\right) = \operatorname{tr}(A\rho_{\mathrm{mc}}).$$
(11.58)

We now turn to the variance. Suppose first that $\mathscr{H}_{\mathrm{mc}} = \mathscr{H}$, so Ψ is uniform in $\mathbb{S}(\mathscr{H})$. Let $d = \dim \mathscr{H}$, let $\{|m\rangle : m = 1, \ldots, d\}$ be an ONB of \mathscr{H} , $\Psi = \sum_m \Psi_m |m\rangle$, and $A_{m\ell} = \langle m | A | \ell \rangle$. Then

$$X := \langle \Psi | A | \Psi \rangle = \sum_{m,\ell=1}^{d} \Psi_m^* A_{m\ell} \Psi_\ell$$
(11.59)

and

$$\mathbb{E}(X^*X) = \mathbb{E}\sum_{\ell,m,\ell',m'} \Psi_m A^*_{m\ell} \Psi^*_{\ell} \Psi^*_{m'} A_{m'\ell'} \Psi_{\ell'}$$
(11.60)

$$= \sum_{\ell,m,\ell',m'} A_{m\ell}^* A_{m'\ell'} \mathbb{E} \, \Psi_m \Psi_\ell^* \Psi_{m'}^* \Psi_{\ell'} \,, \qquad (11.61)$$

so we need the fourth moments of Ψ . They are computed in a homework exercise:

$$\mathbb{E}\left(|\Psi_{\ell}|^{2} |\Psi_{m}|^{2}\right) = \frac{1+\delta_{\ell m}}{d(d+1)}, \qquad (11.62)$$

while all other fourth moments vanish. Thus,

$$\mathbb{E}(X^*X) = \sum_{\ell,m} |A_{m\ell}|^2 \frac{1+\delta_{\ell m}}{d(d+1)} + \sum_{m,m'} A^*_{mm} A_{m'm'} \frac{1+\delta_{mm'}}{d(d+1)} - \sum_m |A_{mm}|^2 \frac{2}{d(d+1)}$$
$$= \frac{1}{d(d+1)} \left[\sum_{\ell,m} |A_{m\ell}|^2 + \sum_{\ell,m} A^*_{mm} A_{\ell\ell} \right]$$
(11.63)

Now $\mathbb{E}X = \operatorname{tr} A/d$, so

Var
$$X = \frac{1}{d(d+1)} \sum_{\ell,m} |A_{m\ell}|^2 - \frac{1}{d^2(d+1)} |\operatorname{tr} A|^2$$
. (11.64)

Since $V_A(I/d) = \operatorname{tr}(A^*A)/d - |\operatorname{tr} A|^2/d^2$,

$$\frac{V_A(I/d)}{d+1} = \text{Var}\,X\,.$$
(11.65)

The statement for other \mathscr{H}_{mc} follows by replacing $A \to P_{mc}AP_{mc}$, which yields

$$\operatorname{Var}\langle\Psi|A\Psi\rangle = \frac{V_{P_{\mathrm{mc}}AP_{\mathrm{mc}}}(\rho_{\mathrm{mc}})}{d_{\mathrm{mc}}+1},\qquad(11.66)$$

and noting that $V_{P_{\rm mc}AP_{\rm mc}}(\rho_{\rm mc}) \leq V_A(\rho_{\rm mc})$ because $\operatorname{tr}(\rho_{mc}P_{\rm mc}AP_{\rm mc}) = \operatorname{tr}(\rho_{\rm mc}A)$ and thus, with the abbreviations $B := A - \operatorname{tr}(\rho_{\rm mc}A)I$ and $P := P_{\rm mc}$,

$$V_{PAP}(\rho_{\rm mc}) = \operatorname{tr} \left[PB^{\dagger} PBP \rho_{\rm mc} \right]$$
(11.67)

$$= \operatorname{tr} \left[P B \rho_{\mathrm{mc}} B^{\dagger} \right] \tag{11.68}$$

$$\leq \operatorname{tr}\left[B\rho_{\mathrm{mc}}B^{\dagger}\right] = V_A(\rho_{\mathrm{mc}}), \qquad (11.69)$$

as $B\rho_{\rm mc}B^{\dagger} \ge 0$.

Lemma 4. For operators $M : \mathscr{H} \to \mathscr{H}$,

$$\|M\|_{\rm tr} \le \sqrt{\dim \mathscr{H}} \|M\|_2 \tag{11.70}$$

with $||M||_2$ the Hilbert-Schmidt norm

$$||M||_2 = \sqrt{\operatorname{tr}(M^{\dagger}M)}.$$
 (11.71)

Proof. $A = M^{\dagger}M$ is self-adjoint and can be diagonalized, $A = \sum_{n} a_{n} |n\rangle \langle n|$ for some ONB $\{|n\rangle\}$. Then $||M||_{tr} = \sum_{n} \sqrt{a_{n}}$ and $||M||_{2} = \sqrt{\sum_{n} a_{n}}$. Since the $\sqrt{}$ function is concave,

$$\sum_{n} \frac{1}{\dim \mathscr{H}} \sqrt{a_n} \le \sqrt{\sum_{n} \frac{1}{\dim \mathscr{H}}} a_n \tag{11.72}$$

(Jensen's inequality). Multiply by dim \mathscr{H} to obtain (11.70).

Proof of Theorem 20. Since Chebyshev's inequality

$$\mathbb{P}\Big(|X - \mathbb{E}X|^2 \ge \eta^2\Big) \le \frac{\mathbb{E}(|X - \mathbb{E}X|^2)}{\eta^2}$$
(11.73)

is valid also for complex-valued X (it follows in this form from the Markov inequality $\mathbb{P}(Y \ge a) \le \mathbb{E}Y/a$ for $Y = |X - \mathbb{E}X|^2$ and $a = \eta^2$), it follows from Lemma 3 that for any operator A and any $\eta > 0$,

$$u_{\rm mc}\left\{\psi\in\mathbb{S}(\mathscr{H}_{\rm mc}):\left|\langle\psi|A|\psi\rangle-\operatorname{tr}(A\rho_{\rm mc})\right|<\eta\right\}\geq1-\frac{V_A}{\eta^2(d_{\rm mc}+1)}.$$
(11.74)

Now let $\mathscr{H} = \mathscr{H}_s \otimes \mathscr{H}_b$, and let $\{|\ell\rangle_s : \ell = 1, \ldots, d_s\}$ be an ONB of \mathscr{H}_s . For

$$A_{\ell m} = \left[|\ell\rangle_{ss} \langle m| \right] \otimes I_b \,, \tag{11.75}$$

we have that $\langle \psi | A_{\ell m} | \psi \rangle = {}_{s} \langle m | \rho_{s}^{\psi} | \ell \rangle_{s}$ and $\operatorname{tr}(A_{\ell m} \rho_{\mathrm{mc}}) = {}_{s} \langle m | \operatorname{tr}_{b} \rho_{\mathrm{mc}} | \ell \rangle_{s}$. By Lemma 4, we have that

$$\left\|\rho_s^{\psi} - \operatorname{tr}_b \rho_{\mathrm{mc}}\right\|_{\mathrm{tr}}^2 \le d_s \sum_{\ell,m=1}^{d_s} \left| \langle m | \rho_s^{\psi} - \operatorname{tr}_b \rho_{\mathrm{mc}} | \ell \rangle \right|^2 \tag{11.76}$$

$$= d_s \sum_{\ell,m=1}^{d_s} \left| \langle \psi | A_{\ell m} | \psi \rangle - \operatorname{tr}(A_{\ell m} \rho_{\mathrm{mc}}) \right|^2$$
(11.77)

$$\leq d_s^3 \max_{\ell,m} \left| \langle \psi | A_{\ell m} | \psi \rangle - \operatorname{tr}(A_{\ell m} \rho_{\mathrm{mc}}) \right|^2, \qquad (11.78)$$

and thus

$$u_{\rm mc} \Big\{ \psi : \| \rho_s^{\psi} - \operatorname{tr}_b \rho_{\rm mc} \|_{\rm tr} < d_s^{3/2} \eta \Big\}$$

= $u_{\rm mc} \Big\{ \psi : \| \rho_s^{\psi} - \operatorname{tr}_b \rho_{\rm mc} \|_{\rm tr}^2 < d_s^3 \eta^2 \Big\}$ (11.79)

$$\geq u_{\rm mc} \left\{ \psi : d_s^3 \max_{\ell,m} \left| \langle \psi | A_{\ell m} | \psi \rangle - \operatorname{tr}(A_{\ell m} \rho_{\rm mc}) \right|^2 < d_s^3 \eta^2 \right\}$$
(11.80)

$$= u_{\rm mc} \bigcap_{\ell,m} \left\{ \psi : \left| \langle \psi | A_{\ell m} | \psi \rangle - \operatorname{tr}(A_{\ell m} \rho_{\rm mc}) \right|^2 < \eta^2 \right\}$$
(11.81)

$$\stackrel{(11.74)}{\geq} 1 - \sum_{\ell m} \frac{V_{A_{\ell m}}}{\eta^2 (d_{\rm mc} + 1)} \tag{11.82}$$

$$\geq 1 - \frac{\sum_{\ell m} V_{A_{\ell m}}}{\eta^2 d_{\rm mc}} \tag{11.83}$$

or, setting $\varepsilon = d_s^{3/2} \eta$,

$$u_{\rm mc}\left\{\psi\in\mathbb{S}(\mathscr{H}_{\rm mc}):\left\|\rho_s^{\psi}-\operatorname{tr}_b\rho_{\rm mc}\right\|_{\rm tr}<\varepsilon\right\}\geq 1-\frac{d_s^3\sum_{\ell m}V_{A_{\ell m}}}{\varepsilon^2 d_{\rm mc}}\,.$$
(11.84)

To compute $\sum_{\ell m} V_{A_{\ell m}}$, note that

$$V_{A_{\ell m}} = \operatorname{tr} \left[\rho_{mc} A_{\ell m}^{\dagger} A_{\ell m} \right] - \left| \operatorname{tr} (\rho_{mc} A_{\ell m}) \right|^2$$
(11.85)

$$= \langle m | \operatorname{tr}_{b} \rho_{\mathrm{mc}} | m \rangle - |\langle m | \operatorname{tr}_{b} \rho_{\mathrm{mc}} | \ell \rangle|^{2}, \qquad (11.86)$$

 \mathbf{SO}

$$\sum_{\ell m} V_{A_{\ell m}} = d_s - \operatorname{tr}\left((\operatorname{tr}_b \rho_{\mathrm{mc}})^{\dagger} (\operatorname{tr}_b \rho_{\mathrm{mc}}) \right) \le d_s \,. \tag{11.87}$$

This yields, in total, (11.51).

Here are some further comments about Theorem 20.

- First, it can be understood as saying that ρ^ψ_s is nearly constant as a function of ψ (for most ψ, it is near its average, which by (11.50) is tr_b ρ_{mc}). While we know that in many relevant cases, tr_b ρ_{mc} ≈ ρ_{can}, this relation was based on the assumptions that b is much larger than s, and that the interaction between s and b is negligible. But by now we are also considering cases in which s is almost one quarter the size of s∪b, so b is only 3 times as big; this situation, as well as the interaction between s and b may lead to deviations (corrections) of tr_b ρ_{mc} from ρ_{can}; in that case, it is tr_b ρ_{mc} (and not ρ_{can}) that occurs as the typical reduced state.
- What if $d_s = \infty$? Specifically, if we are considering, instead of the Heisenberg model, particles with position degrees of freedom, say particles in a region $\Lambda =$

 $\Lambda_s \cup \Lambda_b \subset \mathbb{R}^3$, then both \mathscr{H}_s and \mathscr{H}_b have infinite dimension, although \mathscr{H}_{mc} has finite dimension, provided that Λ is bounded. So, what if $d_s = \infty$? Then Theorem 20 would seem to be useless, but things are not so bad. Effectively, only finitely many dimensions of \mathscr{H}_s are relevant to \mathscr{H}_{mc} : Let $\mathscr{\tilde{H}}_s$ be the span of the eigenvectors of $\operatorname{tr}_b \rho_{mc}$ with the largest *n* eigenvalues; take *n* large enough so that the sum of these eigenvalues is close to 1. Then $\mathscr{\tilde{H}}_s$ and an analogously constructed $\mathscr{\tilde{H}}_b$ can play the roles of \mathscr{H}_s and \mathscr{H}_b in the above reasoning.

• Popescu, Short, and Winter⁷⁵ have found a sharper estimate than Theorem 20:

Theorem 21. Let \mathscr{H}_s and \mathscr{H}_b be Hilbert spaces of dimension d_s and d_b , $\mathscr{H} = \mathscr{H}_s \otimes \mathscr{H}_b$, and \mathscr{H}_{mc} be any subspace of \mathscr{H} of dimension d_{mc} . Then for any $\tilde{\varepsilon} > 0$,

$$u_{\rm mc}\left\{\psi\in\mathbb{S}(\mathscr{H}_{\rm mc}):\left\|\rho_s^{\psi}-\operatorname{tr}_b\rho_{\rm mc}\right\|_{\rm tr}<\tilde{\varepsilon}+\frac{d_s}{\sqrt{d_{\rm mc}}}\right\}\geq 1-4\exp\left(-\frac{d_{\rm mc}\tilde{\varepsilon}^2}{18\pi^3}\right).$$
(11.88)

In their proof (which I will not present here), there are two sources of error, one contributing $\tilde{\varepsilon}$ and the other $d_s/\sqrt{d_{\rm mc}}$. To appreciate the strength of this estimate, note that already for N = 300, using our previous guess $d_{\rm mc} = 2^{N-200} = 2^{100} = 10^{30}$ and $\tilde{\varepsilon} = 10^{-12}$, we find the right-hand side to be $\approx 1 - 10^{780}$. The estimate will be most useful if $d_s/\sqrt{d_{\rm mc}}$ is roughly of the same size as $\tilde{\varepsilon}$, so we need that

$$d_s \ll d_{\rm mc}^{1/2}$$
 (11.89)

This means an improvement over (11.52), which required $d_s \ll d_{\rm mc}^{1/4}$, because of the larger exponent. It means that s can be, rather than a quarter, up to half the size of the whole system $s \cup b!$ One can show⁷⁶ that 1/2 is the best possible fraction, i.e., that canonical typicality cannot hold in general if s is greater than b.

11.6 The GAP Measure

The mapping from probability measures on $\mathbb{S}(\mathscr{H})$ to density matrices, $\mu \mapsto \rho_{\mu}$, is many-to-one. For example, for dim $\mathscr{H} = d < \infty$, $\rho_u = I/d$, and for any ONB $\{|n\rangle\}$, the uniform distribution over this basis, $\mu = d^{-1} \sum_n \delta_{|n\rangle}$, has $\rho_{\mu} = I/d$ as well. It is therefore not obvious that there should be a measure on $\mathbb{S}(\mathscr{H})$ that represents the canonical ensemble, but that is actually the case. It has to do with the concept of the conditional wave function (10.8), which is defined in Bohmian mechanics by inserting the actual configuration of b into $\psi \in \mathscr{H}_{\delta} \otimes \mathscr{H}_{b}$. More abstractly, for any given generalized

⁷⁵S. Popescu, A. J. Short, and A. Winter: Entanglement and the foundation of statistical mechanics. *Nature Physics* **21(11)**: 754–758 (2006)

⁷⁶S. Goldstein, D. A. Huse, J. L. Lebowitz, and R. Tumulka: Macroscopic and Microscopic Thermal Equilibrium. Annalen der Physik **529**: 1600301 (2017) http://arxiv.org/abs/1610.02312

ONB $B = \{|q_b\rangle\}$ of \mathscr{H}_b we can define the conditional wave function as the random vector $\psi_s \in \mathscr{H}_s$ given by

$$\psi_s = \langle Q_b | \psi \rangle_b \,, \tag{11.90}$$

where $\langle -|-\rangle_b$ means the partial inner product over \mathscr{H}_b , and $|Q_b\rangle$ is a random element of *B* chosen with the obvious probability distribution in terms of ψ , i.e., the appropriate version of the $|\psi|^2$ distribution:

$$\mathbb{P}(Q_b \in \Delta) = \int_{\Delta} dq_b \, \|\langle q_b | \psi \rangle_b \|_s^2 = \langle \psi | I_s \otimes P_{\text{nat}}(\Delta) | \psi \rangle \,. \tag{11.91}$$

This definition also makes sense in case dim $\mathcal{H}_b = d_b < \infty$ (on which we will focus in the following) and then amounts to

$$\mathbb{P}(Q_b = q_b) = \|\langle q_b | \psi \rangle_b \|_s^2.$$
(11.92)

Moreover, it will be convenient to include a normalization factor in the definition of the conditional wave function ψ_s . Then ψ_s is a random vector in $\mathbb{S}(\mathscr{H}_s)$, and we can ask what its distribution is. In general, this distribution depends on ψ and B, but it turns out that in the framework of canonical typicality, this distribution is universal, i.e., depends only on H_s and the inverse temperature β of s:

There is a probability distribution $GAP(H_s, \beta)$ on $\mathbb{S}(\mathscr{H}_s)$ such that if b is large then for most ONBs of \mathscr{H}_b and most ψ in $\mathbb{S}(\mathscr{H}_{mc}), \psi_s$ (11.93) is approximately $GAP(H_s, \beta)$ -distributed for suitable $\beta = \beta(E)$.

Thus, $GAP(H_s, \beta)$ is a distribution over wave functions that can be regarded as the canonical ensemble in quantum mechanics. Its density matrix is ρ_{can} . In fact, for every density matrix ρ on a Hilbert space \mathscr{H} there is a probability measure $GAP(\rho)$ on $S(\mathscr{H})$, and $GAP(H_s, \beta) = GAP(\rho_{can})$ on \mathscr{H}_s . $GAP(\rho)$ was first introduced by Jozsa, Robb, and Wootters⁷⁷ under the name *Scrooge measure*⁷⁸ as the most spread-out probability measure on $S(\mathscr{H})$ with density matrix ρ . The GAP measure can also be constructed on infinite-dimensional Hilbert spaces, but we will need it only in finite dimension. The acronym "GAP" indicates how it can be constructed:

G: Starting from a density matrix ρ , form first the Gaussian measure on \mathscr{H} with mean zero and covariance matrix ρ , $G(\rho)$. On a complex vector space, the Gaussian measure means the following. One says that X is a complex Gaussian random variable with mean $\mu \in \mathbb{C}$ and variance $\sigma^2 \geq 0$ if Re X and Im X are independent real Gaussian random variables with means Re μ and Im μ and equal variances $\sigma^2/2$; the variance is then given by Var $X = \mathbb{E}[|X - \mathbb{E}X|^2] = \sigma^2$. A random

⁷⁷R. Jozsa, D. Robb, and W. K. Wootters: Lower bound for accessible information in quantum mechanics. *Physical Review A* **49**: 668-677 (1994)

 $^{^{78}}$ Named after Ebenezer Scrooge, a fictional character in Charles Dickens' novella *A Christmas Carol* (1843) whose most salient trait is that of being stingy. Jozsa et al. had in mind that this measure "is particularly stingy with its information."

vector $\Psi \in \mathscr{H}$ is said to be Gaussian iff for every $\phi \in \mathscr{H}$, the complex random variabe $\langle \phi | \Psi \rangle$ is Gaussian. One can show⁷⁹ that a Gaussian measure is uniquely determined by its mean and its covariance operator

$$C = \mathbb{E}|\Psi - \mathbb{E}\Psi\rangle\langle\Psi - \mathbb{E}\Psi|.$$
(11.94)

The covariance operator is self-adjoint and positive. In finite dimension, $\mathscr{H} = \mathbb{C}^d$, $G(\rho)$ has probability density function

$$f(\psi) = \frac{1}{\pi^d \det \rho} \exp\left(-\langle \psi | \rho^{-1} | \psi \rangle\right), \qquad (11.95)$$

provided ρ has full rank. The components of $\Psi \sim G$ relative to an eigenbasis of ρ are independent complex Gaussian random variables whose variances are the eigenvalues of ρ .

A: is for "adjust": re-weight the measure by the density function $\psi \mapsto \|\psi\|^2$ (a function $\mathscr{H} \to \mathbb{R}$). That is, writing $G = G(\rho)$,

$$GA(\Delta) = \int_{\Delta} G(d\psi) \, \|\psi\|^2 \,. \tag{11.96}$$

Note that GA is normalized because, for $\Psi \sim G$,

$$GA(\mathscr{H}) = \int_{\mathscr{H}} G(d\psi) \, \|\psi\|^2 = \mathbb{E} \|\Psi\|^2 = \operatorname{tr} \rho = 1.$$
 (11.97)

P: means "project to the unit sphere," $P(\psi) = \psi/||\psi||$. That is, GAP is the distribution of $\Psi^{GAP} = P(\Psi^{GA})$, or

$$GAP(\Delta) = GA(\mathbb{R}_+\Delta),$$
 (11.98)

for any test set $\Delta \subseteq \mathbb{S}(\mathscr{H})$.

The combination adjust-and-project has the property that it leaves the density matrix unchanged: Given a measure μ on $\mathbb{S}(\mathscr{H})$ with $\mathbb{E}_{\mu} \|\Psi\|^2 = 1$, then μAP is a probability measure on $\mathbb{S}(\mathscr{H})$ with density matrix

$$\rho_{\mu AP} = \int_{\mathscr{H}} \mu A(d\psi) |P(\psi)\rangle \langle P(\psi)| = \int_{\mathscr{H}} \|\psi\|^2 \, \mu(d\psi) \, \frac{|\psi\rangle \langle \psi|}{\|\psi\|^2} = \int_{\mathscr{H}} \mu(d\psi) \, |\psi\rangle \langle \psi| = \rho_{\mu} \,.$$
(11.99)

Since $G(\rho)$ has mean zero, $\rho_{G(\rho)} = C_{G(\rho)} = \rho$, so

$$\rho_{GAP(\rho)} = \rho \,. \tag{11.100}$$

⁷⁹Yu. V. Prohorov: Convergence of Random Processes and Limit Theorems in Probability Theory. Theory of Probability and Its Applications 1: 157–214 (1956)

(In fact, $GAP(\rho)$ also has mean zero because it is invariant under the antipode mapping $\psi \mapsto -\psi$.)

The measure $G(\rho)$ can be understood as follows. Let $\{\phi_i\}$ be an ONB of eigenvectors of ρ and p_i the corresponding eigenvalues,

$$\rho = \sum_{i} p_{i} |\phi_{i}\rangle \langle \phi_{i}| \,. \tag{11.101}$$

Let Z_i be independent complex Gaussian random variables with variance

$$\mathbb{E}|Z_i|^2 = p_i \,. \tag{11.102}$$

Then $G(\rho)$ is the distribution of

$$\Psi^G = \sum_i Z_i \,\phi_i \,. \tag{11.103}$$

If zero is an eigenvalue of ρ , then this definition still makes sense. We denote by $\operatorname{support}(\rho)$ the positive spectral subspace of ρ (i.e., the orthogonal complement of the kernel). Then $G(\rho)$ is concentrated on $\operatorname{support}(\rho)$ and is absolutely continuous in that subspace. It follows that $GAP(\rho)$ is concentrated on $\mathbb{S}(\operatorname{support}(\rho))$ and absolutely continuous there.

If ρ is proportional to a projection, $\rho = d_R^{-1} P_R$ with P_R the projection to a subspace $\mathscr{H}_R \subseteq \mathscr{H}$ and $d_R = \dim \mathscr{H}_R$, then $GAP(\rho)$ is the uniform distribution on $\mathbb{S}(\mathscr{H}_R)$.

An alternative, equivalent definition of $GAP(\rho)$ is

$$GAP(\rho) = uDAP(\rho), \qquad (11.104)$$

which is adjust-and-project applied to the " ρ -distorted uniform" measure $uD(\rho)$ defined to be the distribution of

$$\Psi^{uD(\rho)} = d^{1/2} \rho^{1/2} \Psi^u , \qquad (11.105)$$

where Ψ^u is uniformly distributed on $\mathbb{S}(\mathscr{H})$. It is easy to see that $uD(\rho)$ has density matrix ρ :

$$\mathbb{E}|\Psi^{uD(\rho)}\rangle\langle\Psi^{uD(\rho)}| = d\,\rho^{1/2}\mathbb{E}|\Psi^{u}\rangle\langle\Psi^{u}|\rho^{1/2} = \rho^{1/2}I\rho^{1/2} = \rho\,.$$
(11.106)

We omit the proof of (11.104).⁸⁰

Proposition 11. For given $\psi \in \mathbb{S}(\mathscr{H}_s \otimes \mathscr{H}_b)$ and $B \in ONB(\mathscr{H}_b)$, let ψ_s be the (normalized) conditional wave function. The density matrix associated with its distribution is ρ_s^{ψ} ,

$$\mathbb{E}|\psi_s\rangle\langle\psi_s| = \rho_s^{\psi}.$$
 (11.107)

⁸⁰It is given in S. Goldstein, J. L. Lebowitz, C. Mastrodonato, R. Tumulka, and N. Zanghì: Universal Probability Distribution for the Wave Function of a Quantum System Entangled with Its Environment. *Communications in Mathematical Physics* **342**: 965–988 (2016) http://arxiv.org/abs/1104.5482

The proof is a homework exercise.

Let $\mu_s^{\psi,B}$ denote the distribution of the conditional wave function ψ_s . The probability that $\psi_s \in \Delta \subseteq \mathbb{S}(\mathscr{H}_s)$ is

$$\mu_s^{\psi,B}(\Delta) = \mathbb{P}(\psi_s \in \Delta) = \sum_{q_b} \left\| \langle q_b | \psi \rangle \right\|^2 \delta_{\langle q_b | \psi \rangle / \| \langle q_b | \psi \rangle \|}(\Delta)$$
(11.108)

$$= \sum_{q_b} \left\| \langle q_b | \psi \rangle \right\|^2 \mathbf{1}_{\Delta} \left(\frac{\langle q_b | \psi \rangle}{\| \langle q_b | \psi \rangle \|} \right).$$
(11.109)

The following Proposition provides a link between $\mu_s^{\psi,B}$ and the *GAP* measures; it asserts that when $\mu_s^{\psi,B}$ gets averaged over all orthonormal bases *B* of \mathscr{H}_b , the resulting distribution on $\mathbb{S}(\mathscr{H}_s)$ is a *GAP* distribution. Let $ONB(\mathscr{H}_b)$ be the set of orthonormal bases of \mathscr{H}_b , and let u_{ONB} be the uniform probability measure on $ONB(\mathscr{H}_b)$, corresponding to the Haar measure on the unitary group $U(\mathscr{H}_b)$. Fix $\mathscr{H}_s, \mathscr{H}_b$, and ψ , and regard $\mu_s^{\psi,B}$ as a function of $B \in ONB(\mathscr{H}_b)$.

Proposition 12. For $B \sim u_{ONB}$,

$$\mathbb{E}\,\mu_s^{\psi,B} = GAP(\rho_s^\psi)\,.\tag{11.110}$$

We omit the proof.⁸¹ The following theorem asserts that the distribution of ψ_s is not only on average, but in fact for most bases *B* close to GAP. We use the notation

$$\mu(f) = \int \mu(dx) f(x)$$
 (11.111)

for the average of the function f under the probability measure μ . We express closeness between two measures μ, ν by means of upper bounds on $|\mu(f) - \nu(f)|$; different classes of test functions f then correspond to different notions of closeness.

Theorem 22 (Typicality of the GAP measure). Assume $1 \le d_s \le d_b < \infty$ and $d_b \ge 4$. For every $\varepsilon > 0$, every $\psi \in \mathbb{S}(\mathscr{H}_s \otimes \mathscr{H}_b)$, and every bounded measurable test function $f : \mathbb{S}(\mathscr{H}_s) \to \mathbb{R}$,

$$u_{ONB}\left\{B: \left|\mu_s^{\psi,B}(f) - GAP(\rho_s^{\psi})(f)\right| < \varepsilon \, \|f\|_{\infty}\right\} \ge 1 - \frac{4}{\varepsilon^2 d_b}.$$
(11.112)

I will give an outline of the proof. It makes use of the following fact of linear algebra, known as the *Schmidt decomposition* or *singular value decomposition*⁸²:

⁸¹It is given in S. Goldstein, J. L. Lebowitz, C. Mastrodonato, R. Tumulka, and N. Zanghì: Universal Probability Distribution for the Wave Function of a Quantum System Entangled with Its Environment. *Communications in Mathematical Physics* **342**: 965–988 (2016) http://arxiv.org/abs/1104.5482

⁸²It was found by Eugenio Beltrami in 1873, independently by Camille Jordan in 1874, independently by James Joseph Sylvester in 1889, and further developed by Erhard Schmidt in 1907.

Proposition 13. For every $\psi \in \mathscr{H}_s \otimes \mathscr{H}_b$ there exist ONBs $(\chi_1, \ldots, \chi_{d_s})$ of \mathscr{H}_s and $(\phi_1, \ldots, \phi_{d_b})$ of \mathscr{H}_b such that

$$\psi = \sum_{i} \sigma_i \, \chi_i \otimes \phi_i \tag{11.113}$$

with real $\sigma_i \geq 0$. (The values that occur as σ_i and their multiplicities are, in fact, uniquely determined by ψ .)

Equivalently, every complex $n \times m$ matrix M can be written in the form

$$M = U\Sigma V^{\dagger}, \qquad (11.114)$$

where U is unitary in \mathbb{C}^n , V is unitary in \mathbb{C}^m , and Σ is an $n \times m$ matrix that is diagonal (with additional zero rows or columns if $n \neq m$) and non-negative entries σ_{α} (the "singular values" of M) on the diagonal.

The proof is a homework exercise. If M is self-adjoint $n \times n$, then one can even demand U = V, but a general $n \times n$ matrix is not diagonalizable (only those are for which the self-adjoint and the skew-adjoint part commute—and can therefore be simultaneously diagonalized). So the singular-value decomposition is a different, weaker sense of "diagonalization."

For Theorem 22 it also plays a role that the vectors of a random ONB in high dimension are almost independent. For example, if we choose two unit vectors ϕ, χ exactly independently (with uniform distribution) then their inner product $\langle \phi | \chi \rangle$ has expectation 0 and variance 1/d, as follows from symmetry considerations.⁸³ That is, $|\langle \phi | \chi \rangle|$ will typically be small like $1/\sqrt{d}$, so ϕ and χ are almost orthogonal. So it does not come as a surprise when the following lemma (proof omitted)⁸⁴ expresses a converse statement—a sense in which two exactly orthogonal random vectors are almost independent: the correlation coefficient of any L^2 test function g of them is small like 1/d.

Lemma 5. Let $d \ge 4$, and let $\{B_1, \ldots, B_d\}$ be a random ONB of \mathbb{C}^d . Then, for every test function $g \in L^2(\mathbb{S}(\mathbb{C}^d), u, \mathbb{R})$,

$$\left| \operatorname{Cov}(g(B_1), g(B_2)) \right| \le \frac{1}{d-1} \operatorname{Var}(g(B_1)).$$
 (11.115)

Through usual law-of-large-numbers kind of reasoning based on Chebyshev's inequality, one obtains from Lemma 5 the following lemma, which asserts roughly that in high dimension d, the members B_1, \ldots, B_d of an orthonormal basis are rather uniformly distributed over the unit sphere—so uniformly, in fact, that $\frac{1}{d} \sum_{j=1}^d g(B_j)$ is a good approximation to $\int_{\mathbb{S}} u(d\psi) g(\psi)$.

⁸³Indeed, invariance under $\phi \mapsto -\phi$ implies zero expectation. Concerning the variance, think of ϕ as already chosen and consider χ in an ONB containing ϕ ; then the desired variance is nothing but the variance of the first component of χ , or $\mathbb{E}|\chi_1|^2$. But $1 = \|\chi\|^2 = \sum_i |\chi_i|^2$, and taking expectations yields $1 = \mathbb{E} \sum_i |\chi_i|^2 = d \mathbb{E}|\chi_1|^2$, as claimed.

⁸⁴It is proved as Theorem 2 in S. Goldstein, J. L. Lebowitz, R. Tumulka, and N. Zanghì: Any Orthonormal Basis in High Dimension is Uniformly Distributed over the Sphere. *Annales de l'Institut Henri Poincaré (B) Probabilités et Statistiques* **53**: 701–717 (2017) http://arxiv.org/abs/1406.2576

Lemma 6. Let $\varepsilon > 0, \delta > 0, d \in \mathbb{N}$ with $d \ge 4$ and $d \ge 2\delta^{-1}\varepsilon^{-2}$, and let $B \sim u_{ONB(\mathbb{C}^d)}$. Then, for every test function $g \in L^2(\mathbb{S}(\mathbb{C}^d), u, \mathbb{R})$,

$$\mathbb{P}\left(\left|\frac{1}{d}\sum_{j=1}^{d}g(B_j) - \mathbb{E}g\right| \le \varepsilon\sqrt{\operatorname{Var}g}\right) \ge 1 - \delta, \qquad (11.116)$$

with $\mathbb{E}g = \mathbb{E}g(B_1)$ and $\operatorname{Var} g = \operatorname{Var} g(B_1)$.

Proof of Theorem 22. Fix ε , \mathscr{H}_s , \mathscr{H}_b , ψ , and f. Let the function g be defined, for any $\phi \in \mathbb{S}(\mathscr{H}_b)$, by

$$g(\phi) = d_b \left\| \langle \phi | \psi \rangle \right\|^2 f\left(P(\langle \phi | \psi \rangle) \right).$$
(11.117)

Then, for any $B \in ONB(\mathscr{H}_b)$,

$$\mu_s^{\psi,B}(f) = \frac{1}{d_b} \sum_{j=1}^{d_b} g(B_j) , \qquad (11.118)$$

cf. (11.109). Now regard B as random, $B \sim u_{ONB}$. By Proposition 12,

$$GAP(\rho_s^{\psi})(f) = \mathbb{E}\mu_s^{\psi,B}(f) = \mathbb{E}\frac{1}{d_b}\sum_{j=1}^{d_b} g(B_j) = \mathbb{E}g.$$
(11.119)

We now show that

$$\operatorname{Var} g \le 2 \, \|f\|_{\infty}^2 \,. \tag{11.120}$$

Indeed, writing X for a uniformly distributed random point on $\mathbb{S}(\mathscr{H}_b)$, and $Y = \langle X | \psi \rangle_b \in \mathscr{H}_s$, we have that

$$\operatorname{Var} g = \mathbb{E}\left[g(X)^2\right] - \left(\mathbb{E}[g(X)]\right)^2 \tag{11.121}$$

$$\leq \mathbb{E}\big[g(X)^2\big] \tag{11.122}$$

$$= \mathbb{E}\left[d_b^2 \, \|Y\|^4 \, f\left(P(Y)\right)^2\right]$$
(11.123)

$$\leq d_b^2 \, \|f\|_{\infty}^2 \, \mathbb{E}\Big[\|Y\|^4\Big] \,. \tag{11.124}$$

We now estimate $\mathbb{E}||Y||^4$. As a tool, let

$$\psi = \sum_{i=1}^{d_s} \sqrt{p_i} \,\chi_i \otimes \phi_i \tag{11.125}$$

be the Schmidt decomposition (Proposition 13) of ψ , where $(\chi_1, \ldots, \chi_{d_s}) \in ONB(\mathscr{H}_s)$, $(\phi_1, \ldots, \phi_{d_b}) \in ONB(\mathscr{H}_b)$, and $\rho_s^{\psi} = \sum_i p_i |\chi_i\rangle \langle \chi_i |$. Note that $\sum_{i=1}^{d_s} p_i = 1$. Let

$$p^2 := \sum_{i=1}^{d_s} p_i^2 \tag{11.126}$$

and note that $0 < p^2 \leq 1$. Then

$$\mathbb{E} \|Y\|^4 = \mathbb{E} \left\| \langle X|\psi \rangle \right\|^4 \tag{11.127}$$

$$= \mathbb{E}\left[\left(\sum_{i=1}^{d_s} p_i \left|\langle X|\phi_i\rangle\right|^2\right)^2\right]$$
(11.128)

$$= \mathbb{E}\left[\sum_{i,j=1}^{d_s} p_i p_j \left| \langle X | \phi_i \rangle \right|^2 \left| \langle X | \phi_j \rangle \right|^2 \right]$$
(11.129)

$$=\sum_{i=1}^{d_s} p_i^2 \mathbb{E} |\langle X|\phi_i\rangle|^4 + \sum_{\substack{i,j=1\\i\neq j}}^{d_s} p_i p_j \mathbb{E} \left[|\langle X|\phi_i\rangle|^2 |\langle X|\phi_j\rangle|^2 \right]$$
(11.130)

$$=\sum_{i=1}^{d_s} p_i^2 \mathbb{E} |\langle X|\phi_1\rangle|^4 + \sum_{\substack{i,j=1\\i\neq j}}^{d_s} p_i p_j \mathbb{E} \left[|\langle X|\phi_1\rangle|^2 |\langle X|\phi_2\rangle|^2 \right]$$
(11.131)

[because the distribution of X is invariant under unitaries]

$$= p^{2} \mathbb{E} |\langle X|\phi_{1}\rangle|^{4} + (1-p^{2}) \mathbb{E} \left[|\langle X|\phi_{1}\rangle|^{2} |\langle X|\phi_{2}\rangle|^{2} \right]$$
(11.132)

$$= p^{2} \mathbb{E}|X_{1}|^{4} + (1 - p^{2}) \mathbb{E}\left[|X_{1}|^{2} |X_{2}|^{2}\right]$$
(11.133)

$$=\frac{2p^2}{d_b(d_b+1)} + \frac{1-p^2}{d_b(d_b+1)} \le \frac{2}{d_b^2}$$
(11.134)

by (11.62). This, together with (11.124), proves (11.120).

Now, in Lemma 6, replace d by d_b (so $\mathbb{C}^d = \mathscr{H}_b$), replace δ by $4\varepsilon^{-2}d_b^{-1}$, and ε by $\varepsilon/\sqrt{2}$. Then, the condition $d \ge 2\delta^{-1}\varepsilon^{-2}$ gets replaced by

$$d_b \ge 2(\varepsilon/\sqrt{2})^{-2} (4\varepsilon^{-2} d_b^{-1})^{-1}, \qquad (11.135)$$

which is satisfied because the right-hand side simplifies to d_b , and the condition $d \ge 4$ is satisfied as well. Inserting (11.118) and (11.119), Lemma 6 asserts that

$$\mathbb{P}\left(\left|\mu_s^{\psi,B}(f) - GAP(\rho_s^{\psi})(f)\right| \le \frac{\varepsilon}{\sqrt{2}}\sqrt{\operatorname{Var} g}\right) \ge 1 - \frac{4}{\varepsilon^2 d_b}.$$
(11.136)

From this and (11.120), we obtain (11.112), the relation we wanted to prove.

By putting together Theorem 22 about the typicality of the GAP measure and Theorem 20 about canonical typicality and adding a bit of further work, one can draw the following conclusion⁸⁵ as a precise version of the statement (11.93):

⁸⁵S. Goldstein, J. L. Lebowitz, C. Mastrodonato, R. Tumulka, and N. Zanghì: Universal Probability Distribution for the Wave Function of a Quantum System Entangled with Its Environment. *Communications in Mathematical Physics* **342**: 965–988 (2016) http://arxiv.org/abs/1104.5482

Theorem 23. For every $\varepsilon, \delta > 0$ and every continuous function $f : \mathbb{S}(\mathscr{H}_s) \to \mathbb{R}$, there is a number $D_{\mathrm{mc}} = D_{\mathrm{mc}}(\varepsilon, \delta, d_s, f) > 0$ such that for every $d_{\mathrm{mc}} > D_{\mathrm{mc}}$ and $\mathscr{H}_{\mathrm{mc}} \subseteq \mathscr{H}_s \otimes \mathscr{H}_b$ with dim $\mathscr{H}_{\mathrm{mc}} = d_{\mathrm{mc}}$,

$$u_R \times u_{ONB} \Big\{ \big(\psi, B\big) \in \mathbb{S}(\mathscr{H}_{\mathrm{mc}}) \times ONB(\mathscr{H}_b) : \\ \left| \mu_s^{\psi, B}(f) - GAP(\mathrm{tr}_b \,\rho_{\mathrm{mc}})(f) \right| < \varepsilon \Big\} \ge 1 - \delta . \quad (11.137)$$

12 Macro States, Macro Variables, Thermal Equilibrium, and Entropy

12.1 Overview

The quantum analog to the partition

$$\Gamma_{\rm mc} = \bigcup_{\nu} \Gamma_{\nu} \tag{12.1}$$

of the classical energy shell into macro sets is a decomposition

$$\mathscr{H}_{\rm mc} = \bigoplus_{\nu} \mathscr{H}_{\nu} \tag{12.2}$$

of the quantum energy shell \mathscr{H}_{mc} into subspaces \mathscr{H}_{ν} that I will call macro spaces. The \oplus symbol means orthogonal sum. It follows that the $d_{\nu} = \dim \mathscr{H}_{\nu}$ obey

$$\sum_{\nu} d_{\nu} = d_{\rm mc} \,. \tag{12.3}$$

We write \mathscr{D} for the collection $\{\mathscr{H}_{\nu}\}$ of macro spaces. The idea is that the description of a "macroscopic look" of the system (i.e., of a macro state) corresponds to one of the \mathscr{H}_{ν} . It seems natural that different macro states should be orthogonal to each other. I will discuss some examples below.

The entropy of a macro state ν is then defined by the fundamental entropy formula

$$S(\nu) = k \log \dim \mathscr{H}_{\nu} \tag{12.4}$$

in analogy to the classical relation $S(\nu) = k \log \operatorname{vol}(\Gamma_{\nu})$. The quantity (12.4) is sometimes called the *quantum Boltzmann entropy*. It is striking that the ambiguity in the classical definition due to the arbitrary unit of volume, which had the consequence that the classical entropy is defined only up to addition of an arbitrary constant, is absent in the quantum case.

Usually, the thermal equilibrium macro state $\mathscr{H}_{\nu} = \mathscr{H}_{eq}$ is one that has the overwhelming majority of dimensions in \mathscr{H}_{mc} ,

$$\frac{\dim \mathscr{H}_{eq}}{\dim \mathscr{H}_{mc}} = 1 - \varepsilon \tag{12.5}$$

with $0 < \varepsilon \ll 1$. This situation is analogous to Γ_{eq} having the overwhelming majority of volume in classical mechanics. As a consequence,

$$S(\text{eq}) \approx k \log \dim \mathscr{H}_{\text{mc}}$$
 (12.6)

This is in basic agreement with the formula for equilibrium entropy

$$S(E, V, N) \approx k \log \Omega(E)$$
 (12.7)
mentioned earlier in (11.6), with $\Omega(E)$ the density of states. More precisely,

$$S(\text{eq}) \approx k \log[\gamma(E) - \gamma(E - \Delta E)]$$
 (12.8)

with $d\gamma/dE = \Omega(E)$, but due to the very quick growth of $\Omega(E)$ and $\gamma(E)$, it often does not matter much whether one subtracts $\gamma(E - \Delta E)$, whether one uses Ω or γ , or how big ΔE is.

12.2 Macro Observables

John von Neumann (1903–1957) motivated the orthogonal decomposition (12.2) in a 1929 paper⁸⁶ as follows. He suggested considering a family of self-adjoint operators M_1, \ldots, M_K representing the *macro observables*. Because of their macroscopic nature, they should have the following properties:

1. They commute pairwise:

$$[M_i, M_j] = 0. (12.9)$$

(The notation [A, B] means AB - BA and is called the commutator of A and B.)

- 2. Each M_i is highly degenerate, with dimensions of its eigenspaces of order 10^N or greater. In comparison, the number K of macro observables should not be excessively large (not like 10^N).
- 3. The eigenvalues of M_j are separated by distances representing the macroscopic resolution of measurement. For example, as a reasonable model we could assume that the eigenvalues lie in $\Delta M_j \mathbb{Z}$, where ΔM_j is the macroscopic resolution of M_j .

Then define the \mathscr{H}_{ν} as the joint eigenspaces of all M_j . That is, let $\nu := (m_1, \ldots, m_K)$ be a list of eigenvalues m_j of M_j , and

$$\mathscr{H}_{\nu} := \bigcap_{j=1}^{K} \mathscr{H}_{M_j, m_j} , \qquad (12.10)$$

where \mathscr{H}_{M_j,m_j} denotes the eigenspace of M_j with eigenvalue m_j . The \mathscr{H}_{ν} are mutually orthogonal. Since the M_j commute pairwise, they can be simultaneously diagonalized, so $\oplus_{\nu}\mathscr{H}_{\nu}$ is the whole Hilbert space. It is expected that most $\mathscr{H}_{\nu} \neq \{0\}$ have huge dimension. (Any \mathscr{H}_{ν} with dimension 0 should simply be deleted from the list \mathscr{D} of macro spaces.)

⁸⁶J. von Neumann: Beweis des Ergodensatzes und des *H*-Theorems in der neuen Mechanik. *Zeitschrift für Physik* **57**: 30–70 (1929). English translation in *European Physical Journal H* **35**: 201–237 (2010) http://arxiv.org/abs/1003.2133. The title ("Proof of the ergodic theorem and the *H* theorem in quantum mechanics") is rather misleading, as his main result in that paper is neither an analog of ergodicity nor one of Boltzmann's *H* theorem. Rather, it expresses a new property, "normal typicality," that I will discuss in a later section.

The statement that one of the \mathscr{H}_{ν} is dominant, i.e., has the overwhelming majority of dimensions, then means that all of the macro observables M_j are nearly constant in \mathscr{H}_{mc} : most eigenvalues (with multiplicity) of M_j are equal, and only few differ.

To make the properties 1–3 plausible, von Neumann argued that, for example, when we measure the position and momentum of a macroscopic body (consisting, say, of Nparticles of mass m) in (say) the x direction, then the quantum observables we measure are actually not its center-of-mass position operator

$$Q = \frac{1}{N} \sum_{i=1}^{N} Q_i$$
 (12.11)

and its center-of-mass momentum operator

$$P = \sum_{i=1}^{N} P_i \,, \tag{12.12}$$

for several reasons, including that Q and P do not commute, so they cannot be simultaneously measured, and that measuring either Q or P would require infinite precision. Rather, von Neumann argued, we actually measure two different observables \tilde{Q} and \tilde{P} that are close to Q and P, that have spectrum in $\Delta Q \mathbb{Z}$ and $\Delta P \mathbb{Z}$, and that commute, $[\tilde{Q}, \tilde{P}] = 0$. That is possible, von Neumann argued further, because if N is large then Q and P have small commutator compared to typical eigenvalues of Q and P:

$$[Q, P] = \left[\frac{1}{N}\sum_{i}Q_{i}, \sum_{j}P_{j}\right]$$
(12.13)

$$= \frac{1}{N} \sum_{ij} \left[Q_i, P_j \right] \tag{12.14}$$

$$=\frac{1}{N}\sum_{ij}i\hbar\delta_{ij} \tag{12.15}$$

$$=i\hbar\,,\qquad(12.16)$$

 \mathbf{SO}

$$\left\| [Q,P] \right\| \ll qp \tag{12.17}$$

for typical eigenvalues q and p of Q and P, provided that typical position coordinates and velocities, as well as m, are of order 1 (so that q = O(1) and p = O(N)). (The norm here is the operator norm.)

As another example of small commutators, consider a Heisenberg model of N spins, and consider the total spin (total magnetization) in the z direction,

$$S^{z} = \sum_{i=1}^{N} \sigma_{i}^{z} , \qquad (12.18)$$

and likewise S^x and S^y for other directions in 3-space. From the commutation relation of the Pauli matrices,

$$[\sigma^x, \sigma^y] = 2i\sigma^z \text{ (and cyclic permutation of } xyz)$$
(12.19)

we obtain that

$$[S^x, S^y] = \sum_{ij} [\sigma_i^x, \sigma_j^y] = 2i \sum_{ij} \delta_{ij} \sigma_i^z = 2i \sum_i \sigma_i^z, \qquad (12.20)$$

 \mathbf{SO}

$$\left\| [S^x, S^y] \right\| \le 2N \ll N^2 = s^x s^y,$$
 (12.21)

as the largest eigenvalues s^x of S^x are of order N (since the eigenvalues of σ^x are ± 1).

So the following picture arises. Natural candidates for macro observables can be obtained by partitioning the system's volume Λ into cells Δ_i (say, cubic millimeters) that represent the macroscopic resolution of space and considering, for each cell, the particle number operator (i.e., multiplication by the function $N_i(q) = \#\{j = 1, \ldots, N :$ $q_j \in \Delta_i\}$), the energy in Δ_i (possibly neglecting interaction terms with neighboring cells), the momentum in Δ_i in the x, y, z direction, and/or the total magnetization of Δ_i in the x, y, z directions. These operators A_1, \ldots, A_K are expected to have small commutators and need to be modified in two ways: first, to make them commute exactly ("rounding"), and second by coarse-graining them with macroscopic resolution ΔM_j (say, replacing every eigenvalue by the nearest integer multiple of ΔM_j). The result of these modifications will be the operators M_1, \ldots, M_K .

This brings us to the math question whether it is actually possible to find, for almost commuting operators A_1, \ldots, A_K (i.e., with small commutators), commuting operators $\tilde{A}_1, \ldots, \tilde{A}_K$ that approximate A_1, \ldots, A_K . I report here three results about this. The natural sense of closeness here is provided by the operator norm, for example because we want the eigenvalues of \tilde{A}_j to be close to the eigenvalues of A_j . So in the following $\|\cdot\|$ will always be the operator norm. The first result is a positive one for K = 2:

Proposition 14 (Huaxin Lin 1995). ⁸⁷ For every $\varepsilon > 0$ there is $\delta > 0$ such that for all d and any two self-adjoint $d \times d$ matrices A, B with $||A|| \leq 1$, $||B|| \leq 1$, and $||[A, B]|| \leq \delta$, there are two self-adjoint $d \times d$ matrices \tilde{A}, \tilde{B} with $[\tilde{A}, \tilde{B}] = 0$ and $||A - \tilde{A}|| \leq \varepsilon$ and $||B - \tilde{B}|| \leq \varepsilon$.

However, for K = 3, commuting $\tilde{A}_1, \ldots, \tilde{A}_K$ need not exist in general:

Proposition 15. ⁸⁸ For every $d \in \mathbb{N}$ there are three self-adjoint $d \times d$ matrices A_1, A_2, A_3 with the following properties: $||A_j|| = 1$, $||[A_i, A_j]|| \leq 3/d$ for all $i, j \in \{1, 2, 3\}$, and for

⁸⁷H. Lin: Almost commuting self-adjoint matrices and applications. Pages 193–233 in Operator algebras and their applications (Waterloo, ON, 1994/1995), volume 13 of Fields Institute Communications Providence, RI: American Mathematical Society (1997)

⁸⁸This particular result was proven in M. B. Hastings and T. A. Loring: Almost Commuting Matrices, Localized Wannier Functions, and the Quantum Hall Effect. *Journal of Mathematical Physics* **51**: 015214 (2010) http://arxiv.org/abs/0910.5490

A very similar example was already given in different form in M. D. Choi: Almost commuting matrices need not be nearly commuting. *Proceedings of the American Mathematical Society* **102(3)**: 529–533 (1988)

any pairwise commuting A_1, A_2, A_3 ,

$$||A_1 - \tilde{A}_1|| + ||A_2 - \tilde{A}_2|| + ||A_3 - \tilde{A}_3|| \ge \sqrt{1 - 8/d}.$$
 (12.22)

Explicitly, A_1, A_2, A_3 are just the d-dimensional generalization of the three Pauli matrices times 2/(d-1), i.e., they are the three spin operators $\sigma_s^x, \sigma_s^y, \sigma_s^z$ for a spin-s particle $(s = \frac{1}{2}, 1, \frac{3}{2}, 2, \frac{5}{2}, \ldots \text{ and } d = 2s + 1)$ times a factor 1/s:

$$A_{1} = \frac{1}{2s} \begin{pmatrix} 0 & c_{1} & & & \\ c_{1} & 0 & c_{2} & & \\ c_{2} & \ddots & \ddots & \\ & \ddots & \ddots & c_{d-2} & & \\ & & c_{d-2} & 0 & c_{d-1} \\ & & & c_{d-1} & 0 \end{pmatrix}$$

$$A_{2} = \frac{i}{2s} \begin{pmatrix} 0 & -c_{1} & & & \\ c_{1} & 0 & -c_{2} & & \\ c_{2} & \ddots & \ddots & \\ & c_{2} & \ddots & \ddots & \\ & & c_{d-2} & 0 & -c_{d-1} \\ & & & c_{d-1} & 0 \end{pmatrix}$$

$$A_{3} = \frac{1}{s} \begin{pmatrix} s & s-1 & & & \\ s-2 & & & \\ & s-2 & & \\ & & & -s+1 & \\ & & & -s+1 & \\ & & & & -s \end{pmatrix}$$

$$(12.23)$$

with $c_1 = \sqrt{2(s+1)-2}$, $c_2 = \sqrt{4(s+1)-6}$, ..., $c_k = \sqrt{2k(s+1)-k(k+1)}$. Their commutation relation is $[A_1, A_2] = iA_3/s$ (and cyclic permutation of 123).

One might worry here whether the demand that the commutator $[A_i, A_j]$ be small compared to typical eigenvalues of A_i and A_j might be violated, as the statement $||A_j|| = 1$ guarantees only that the *largest* eigenvalue is 1. However, an inspection of the A_j (all of which have the same eigenvalues) shows that the eigenvalues are rather uniformly distributed over [-1, 1], so that the average absolute eigenvalue is $\frac{1}{2}$ (and typical eigenvalues are not near 0).

We will not make use of the details of this Proposition in the following. (Do not try to memorize the matrices.)

So for *arbitrary* operators A_1, \ldots, A_K we could not expect that they can be made to commute by a slight perturbation. Nevertheless, the operators A_1, \ldots, A_K we are interested in are of a special kind, and the following positive result suggests that in practice macro observables can indeed be made to commute. **Proposition 16** (Yoshiko Ogata 2013). ⁸⁹ Let L_1, \ldots, L_K be self-adjoint operators in \mathbb{C}^n . For every $N \in \mathbb{N}$ let $\mathscr{H}_N = (\mathbb{C}^n)^{\otimes N}$, let $L_{jk} : \mathscr{H}_N \to \mathscr{H}_N$ be L_j acting on the k-th factor of \mathscr{H}_N , and let

$$A_{jN} = \frac{1}{N} \sum_{k=1}^{N} L_{jk}$$
(12.24)

for all j = 1, ..., K. Then there exist operators M_{jN} on \mathscr{H}_N such that

$$\begin{bmatrix} M_{iN}, M_{jN} \end{bmatrix} = 0 \quad \forall i, j \quad and \tag{12.25}$$

$$\lim_{N \to \infty} \left\| M_{jN} - A_{jN} \right\| = 0 \quad \forall j \,. \tag{12.26}$$

Specifically, we have in mind the Heisenberg model (n = 2) with $L_1 = \sigma^x, L_2 = \sigma^y, L_3 = \sigma^z$, and perhaps further directions in 3-space.

From now on we take for granted that the macro observables M_1, \ldots, M_K satisfy von Neumann's properties 1–3. Further following von Neumann, we also have in mind that one of them, say M_1 , is the "macroscopic energy," which can be thought of as obtained from H by coarse-graining with resolution ΔE , i.e.,

$$M_1 = g(H) (12.27)$$

with g as in Figure 7 on page 58. It is natural to use here the same ΔE as in the micro-canonical interval $(E - \Delta E, E]$, so that \mathscr{H}_{mc} is one of the eigenspaces of M_1 . Since all M_i commute, every M_i maps \mathscr{H}_{mc} to itself, and we can (and will) regard the M_i as operators on \mathscr{H}_{mc} . As a consequence, each of the macro spaces \mathscr{H}_{ν} either lies in \mathscr{H}_{mc} or is orthogonal to \mathscr{H}_{mc} , so we also obtain an orthogonal decomposition

$$\mathscr{H}_{\rm mc} = \bigoplus_{\nu} \mathscr{H}_{\nu} \tag{12.28}$$

with a suitable subcollection of ν 's. The size of d_{ν} is in practice also of the rough order 10^N , though often very much smaller than $d_{\rm mc}$. (Note that, e.g., $10^{0.9999 \times 10^{20}}$ is smaller than $10^{10^{20}}$ by a factor of $10^{10^{16}}$).

Since the M_i commute with one another, every M_i commutes with the *coarse-grained* energy M_1 , but generally not with H, so it is generally not a conserved quantity. Correspondingly, the \mathscr{H}_{ν} are not invariant under the time evolution.

12.3 Entropy

Let us return to the formula for the quantum Boltzmann entropy

$$S(\nu) = S_{\rm qB}(\nu) = k \log d_{\nu}$$
 (12.29)

⁸⁹For the proof see Y. Ogata: Approximating macroscopic observables in quantum spin systems with commuting matrices. *Journal of Functional Analysis* **264**: 2005–2033 (2013) http://arxiv.org/abs/1111.5933

A version of it, with d_{ν} the "number of elementary states," was used already by Einstein in 1914.⁹⁰ It implies that entropy is *extensive*: If a system consists of two subsystems, s and s', with macro spaces $\mathscr{H} = \bigoplus_{\nu} \mathscr{H}_{\nu}$ and $\mathscr{H}' = \bigoplus_{\nu'} \mathscr{H}_{\nu'}$, and if the interaction between s and s' is negligible, then we can take

$$\mathscr{H} \otimes \mathscr{H}' = \bigoplus_{\nu,\nu'} \mathscr{H}_{\nu} \otimes \mathscr{H}_{\nu'}$$
(12.30)

as the macro spaces of the composite system. It then follows that the macro state (ν, ν') has entropy

$$S(\nu, \nu') = S(\nu) + S(\nu'), \qquad (12.31)$$

so entropy is extensive.

The question arises: If a system's wave function ψ is a non-trivial superposition of contributions from different macro spaces,

$$\psi = \sum_{\nu} c_{\nu} \psi_{\nu} \tag{12.32}$$

with $\psi_{\nu} \in \mathbb{S}(\mathscr{H}_{\nu})$, then what should its entropy be? In view of the fact that a quantum measurement of all macro observables would collapse ψ to one of the ψ_{ν} , resulting in the entropy value $S(\nu)$, it seems that no specific value can be regarded as "the" entropy value of ψ . Rather, just as we are accustomed to the idea that a system can be in a superposition of different energy values (or different momentum values, etc.), we should regard this system as being in a superposition of different entropy values, as if entropy was a quantum observable with the operator

$$\hat{S} = \sum_{\nu} S(\nu) P_{\nu} \,. \tag{12.33}$$

12.4 Von Neumann Entropy

The quantum analog of the Gibbs entropy (7.76) is the von Neumann entropy⁹¹

$$S_{\rm vN}(\rho) = -k \operatorname{tr}(\rho \log \rho), \qquad (12.34)$$

which associates a value with every density matrix ρ (just as the Gibbs entropy associates a value with every density function on phase space). As with the Gibbs entropy, it is understood here that $x \log x := 0$ for x = 0.

If we diagonalize ρ ,

$$\rho = \sum_{n} p_n |n\rangle \langle n| \tag{12.35}$$

⁹⁰See Eq. (4a) in A. Einstein: Beiträge zur Quantentheorie. Deutsche Physikalische Gesellschaft. Verhandlungen 16: 820–828 (1914). English translation in The Collected Papers of Albert Einstein, Vol. 6, pp. 20–26. Princeton University Press (1996).

 $^{^{91}\}mathrm{J.}$ von Neumann: Thermodynamik quantenmechanischer Gesamtheiten. Göttinger Nachrichten 273–291 (11. November 1927)

with some ONB $\{|n\rangle\}$ consisting of eigenvectors and p_n the eigenvalues, then

$$S_{\rm vN}(\rho) = -k \sum_{n} p_n \log p_n \,.$$
 (12.36)

Recall from Figure 11 on page 69 that $x \log x \le 0$ for $0 \le x \le 1$. Thus,

$$S_{\rm vN}(\rho) \ge 0. \tag{12.37}$$

The formula (12.36) can be regarded as the discrete Gibbs entropy of the probability distribution (p_n) , i.e., of the distribution over *n*'s that gives weight p_n to each *n*. Moreover, it shows that S_{vN} is proportional to the average value of $\log(1/p_n)$ and thus quantifies roughly the width of the distribution (p_n) , or log(over how many *n*'s the p_n are distributed). In particular, every pure state has

$$S_{\rm vN}(|\psi\rangle\langle\psi|) = 0 \tag{12.38}$$

because $p_1 = 1$ and all other p_n vanish. In contrast, mixed states have $S_{vN} > 0$ (because some p_n must lie strictly between 0 and 1). Highly mixed states (with many *n*'s that participate significantly) have large S_{vN} . That is why $S_{vN}(\rho)$ is sometimes used for quantifying "how mixed" ρ is. Correspondingly, for a reduced density matrix ρ_s^{ψ} , $S_{vN}(\rho_s^{\psi})$ quantifies "how entangled" *s* is with its complement *b* if $s \cup b$ is in the state ψ .

Another consequence of (12.36) is that $S_{\rm vN}$ does not depend on what the wave functions $|n\rangle$ look like: It does not matter whether they have large or small quantum Boltzmann entropy, or whether they are in thermal equilibrium or far from it.

If ρ is proportional to a projection, $\rho = d_R^{-1} P_R$ with P_R the projection to \mathscr{H}_R and $d_R = \dim \mathscr{H}_R$, then d_R of the p_n are d_R^{-1} , and the others vanish. Thus,

$$S_{\rm vN}(d_R^{-1}P_R) = k \log d_R.$$
 (12.39)

In particular, for $\mathscr{H}_R = \mathscr{H}_{\nu}$,

$$S_{\rm vN}(d_{\nu}^{-1}P_{\nu}) = k \log d_{\nu} = S_{\rm qB}(\nu)$$
(12.40)

(so that one can express actual entropy values as von Neumann entropies), and for $\mathscr{H}_R = \mathscr{H}_{mc}$,

$$S_{\rm vN}(\rho_{\rm mc}) = k \log d_{\rm mc} \approx S_{\rm qB}(\rm eq) \,, \qquad (12.41)$$

so that one can express thermal equilibrium entropy as a von Neumann entropy. Combining this fact with equivalence of ensembles,

$$\rho_{\rm can} \approx \rho_{\rm mc} \,,$$
(12.42)

we obtain that

$$S_{\rm vN}(\rho_{\rm can}) \approx S_{\rm vN}(\rho_{\rm mc}) \approx S_{\rm qB}({\rm eq}).$$
 (12.43)

As in the classical case, this is sometimes a practical way of computing S(eq). Another consequence of (12.39) is that S_{vN} is not bounded from above but can have arbitrarily large values. In a finite dimensional Hilbert space \mathscr{H} , however, there is an upper bound,

$$S_{\rm vN}(\rho) \le k \log \dim \mathscr{H}$$
. (12.44)

That is essentially because the distribution (p_n) cannot be spread out more than over dim \mathscr{H} places. The rigorous proof of (12.44) is nothing but the reasoning of Section 7.2.5, except that all terms containing β are dropped, so that the maximizer (p_n) has all p_n equal, which means $p_n = 1/\dim \mathscr{H}$.

Like the Gibbs entropy, the von Neumann entropy does not change during the unitary evolution,

$$S_{\rm vN}(e^{-iHt}\rho e^{iHt}) = S_{\rm vN}(\rho).$$
 (12.45)

This can be seen by noting that $e^{-iHt}\rho e^{iHt}$ has a different eigenbasis than ρ but the same eigenvalues, while by (12.36) the value of $S_{\rm vN}$ depends only on the eigenvalues and not on the basis.

The remarks I made in Section 7.3.3 about the status of the Gibbs entropy (compared to the Boltzmann entropy) apply here in an analogous way: Some books give the impression that the von Neumann entropy was the fundamental definition of entropy, and that entropy was just a property of a density matrix; that is rather misleading. As in the classical case, that approach can lead to various kinds of confusion.

By the way, von Neumann himself thought that $S_{\rm vN}$, while practical for some purposes, is "not applicable" in the context of a decomposition $\mathscr{H} = \bigoplus_{\nu} \mathscr{H}_{\nu}$. Instead, he made the rather awkward suggestion⁹² that the entropy of a system with wave function $\psi \in \mathbb{S}(\mathscr{H}_{\rm mc})$ is given by

$$\tilde{S}_{\rm vN}(\psi) = -k \sum_{\nu} \|P_{\nu}\psi\|^2 \log \frac{\|P_{\nu}\psi\|^2}{d_{\nu}}, \qquad (12.46)$$

For a macroscopic system, the contribution $k \sum_{\nu} \|P_{\nu}\psi\|^2 \log \|P_{\nu}\psi\|^2$ is usually small compared to the other term, so that

$$\tilde{S}_{\rm vN}(\psi) \approx k \sum_{\nu} \|P_{\nu}\psi\|^2 \log d_{\nu} \,. \tag{12.47}$$

This quantity is just the weighted average of the $S_{qB}(\nu)$, with the weight of ν given by the quantum-mechanical probability of ν associated with ψ . Thus, $\tilde{S}_{vN}(\psi)$ should better be regarded as the *mean entropy* of the system, than as its *entropy*. For comparison, for a classical system whose macro-state is unknown and has probability p_{ν} to be ν , we would not say that the quantity

$$\sum_{\nu} p_{\nu} k \log \operatorname{vol}(\Gamma_{\nu}), \qquad (12.48)$$

 $^{^{92}}$ J. von Neumann: Beweis des Ergodensatzes und des H-Theorems in der neuen Mechanik. Zeitschrift für Physik 57: 30–70 (1929)

is the entropy of the system, but we would say instead that the system's entropy S is random, that it equals $k \log \operatorname{vol}(\Gamma_{\nu})$ with probability p_{ν} , and that (12.48) is its expected value $\mathbb{E}S$. Moreover, there are situations in which $S(\psi)$ decreases, contrary to the second law of thermodynamics.⁹³

12.5 The Third Law of Thermodynamics

The third law asserts:

For every system, the equilibrium entropy at temperature 0 is 0. (12.49)

It is also known as Nernst's postulate, as a first version of it was hypothesized on empirical grounds by Walther Nernst (1864–1941) in 1906, before quantum mechanics. Since in classical mechanics there remains the freedom of choosing a unit of phase space volume, it must there be formulated as follows:

For every system, the equilibrium entropy at temperature 0 is the same. (12.50)

This means that changes in parameters of the equilibrium state such as pressure, volume, or external fields, or changes such as chemical reactions cannot change the system's equilibrium entropy at T = 0. However, the third law would be false in a world governed by classical mechanics.

It has been derived⁹⁴ from the third law that the so-called adiabatic-reversible method of cooling cannot reach temperature zero; it seems to be standard opinion⁹⁵ that the third law implies the same limitation for every other known method of cooling.

Here is a derivation of the third law.

- Realistic Hamiltonians are non-degenerate. While specific models, such as the ideal Bose gas, may be highly degenerate, arbitrarily small perturbations generically lift the degeneracy. (Say, taking the gravitation of Jupiter into account makes H non-degenerate.)
- Temperature 0 corresponds to the ground state. In the limit $T \to 0$ or $\beta \to \infty$, ρ_{can} becomes the normalized projection to the eigenspace of the smallest eigenvalue E_0 , or $|\phi_0\rangle\langle\phi_0|$ for non-degenerate H. Another way of looking at the issue is to say that the equilibrium entropy function S(E, V, N) gets transformed into S(T, V, N) by means of a relation E = E(T) or $E = E(\beta)$, which is naturally obtained in the form

$$E(\beta) = \operatorname{tr}\left(H\rho_{\operatorname{can}}(\beta)\right) \tag{12.51}$$

and thus yields $E(T = 0) = \lim_{\beta \to \infty} E(\beta) = E_0$.

⁹³See Section 7.1 of S. Goldstein, J. Lebowitz, R. Tumulka, and N. Zanghì: Long-Time Behavior of Macroscopic Quantum Systems. *European Physical Journal H* **35**: 173–200 (2010) http://arxiv.org/abs/1003.2129.

⁹⁴See, e.g., p. 522–523 in G. Joos: *Lehrbuch der theoretischen Physik*, tenth edition. Frankfurt am Main: Akademische Verlagsgesellschaft (1959).

⁹⁵See, e.g., p. 187 in R. J. Jelitto: *Thermodynamik und Statistik*, second edition. Wiesbaden: Aula (1989).

- The equilibrium entropy is the dimension of the energy shell. See (12.6). For non-degenerate H, this equals the number of energy levels in the micro-canonical energy interval.
- It is appropriate to not include excited states in the lowest micro-canonical energy shell. If we took the energy interval $(E - \Delta E, E]$ to contain, besides the ground state level E_0 , numerous excited levels E_1, E_2, \ldots , then the entropy would not be zero, and its value may well depend on parameters such as volume or external fields. Considering the number of energy levels in $(E - \Delta E, E]$ as a function of E(without approximations), see Figure 14, we see that the step function that it is actually reaches 0. That may be taken as a reason for saying that $S(E_0, V, N) = 0$ (or S(T = 0, V, N) = 0). Alternatively, if we extrapolate a smooth approximation of S(E, V, N) to E_0 , it should also reach 0. Alternatively, it could be argued that it is appropriate here to take ΔE so small that the lowest energy shell should contain only the ground state because of the special character of the ground state.⁹⁶



Figure 14: Graph of $k \log \#\{\alpha : E - \Delta E < E_{\alpha} \leq E\}$ as a function of E for a plausible example of non-degenerate H

Note that the ground state energy E_0 may well depend on parameters such as volume or external fields. For example, we have seen in (11.19) for the ideal Bose gas that $E_0 = Ne_0 \propto N/L^2$ with $L = V^{1/3}$ the length of the box. This fact does not affect the entropy of the ground state.

⁹⁶This reasoning can be questioned, and in fact some authors have criticized the third law for that and taken the view that it is violated, at least practically, for systems with the first few E_{α} very close to E_0 . For details see Wikipedia, https://en.wikipedia.org/wiki/Third_law_of_thermodynamics, or Appendix A of F. Schwabl: *Statistische Mechanik*, third edition. Berlin: Springer (2006).

Readers may notice that the formula (11.25) for the equilibrium entropy of the ideal Bose gas violates the third law, as it includes terms such as $\frac{3}{2}\log(E/N)$ which do not vanish at $E = E_0$ and others such as $\log(V/N)$ which still depend on parameters after fixing $E = E_0$. However, this formula was derived under the assumption of large E, and is not valid near the ground state.

12.6 Macroscopic and Microscopic Thermal Equilibrium (MATE and MITE)

12.6.1 Definition of MATE

Consider a macroscopic system with wave function $\psi \in \mathbb{S}(\mathscr{H}_{mc})$, and suppose that there is a dominant macro space \mathscr{H}_{eq} with

$$\frac{d_{\rm eq}}{d_{\rm mc}} = 1 - \varepsilon \,, \tag{12.52}$$

 $0 < \varepsilon \ll 1$. We say that the system is in *macroscopic thermal equilibrium* (MATE) iff

$$\langle \psi | P_{\text{eq}} | \psi \rangle \ge 1 - \delta.$$
 (12.53)

Here δ is a suitable constant with $\varepsilon \ll \delta \ll 1$. We also write MATE for the set of all $\psi \in \mathbb{S}(\mathscr{H}_{mc})$ satisfying (12.53).

We might have thought at first of defining that a system is in thermal equilibrium iff its wave function lies in \mathscr{H}_{eq} ; however, then a random wave function would have probability 0 of being in thermal equilibrium. That is different with the above definition that allows a certain tolerance δ : In a homework exercise it is shown that most ψ are in MATE, i.e.,

$$u_{\rm mc}({\rm MATE}) \ge 1 - \frac{\varepsilon}{\delta},$$
 (12.54)

which is close to 1 in the regime considered. Mathematically, this fact is a generalization of the "belt theorem" which asserts that in \mathbb{R}^d with large d, most of the surface area of the unit sphere is contained in a belt around the equator, i.e., in the δ -neighborhood of a given codimension-1 subspace; now we find that most of the surface area is also contained in the δ -neighborhood of a given subspace of dimension $d_{\rm eq}$, provided $d_{\rm eq}/d$ is close to 1.

Physically, the fact (12.54) means that most wave functions are in thermal equilibrium, in analogy to the fact that in classical mechanics, most phase points lie in Γ_{eq} . In practice, a realistic value may be

$$\varepsilon = 10^{-10^5},$$
 (12.55)

which leaves a lot of room for δ , say $\delta = 10^{-200}$. The relation (12.53) implies that a quantum measurement of any macro observable M_j will yield the equilibrium value of M_j with probability $\geq 1 - \delta$, and thus for $\delta = 10^{-200}$ that we can expect to never observe any other outcome than the equilibrium value.

MATE is the basic notion of thermal equilibrium. But a stronger statement is actually true of most wave functions, which is based on canonical typicality and which we will call *microscopic thermal equilibrium* (MITE).

12.6.2 Definition of MITE

While the concept of MATE is based on whether ψ is close to \mathscr{H}_{eq} , the concept of MITE is based on whether

$$\rho_s^{\psi} \approx \rho_s^{\rm can} \tag{12.56}$$

for subsystems s of the whole system. Here, ρ_s^{can} denotes the canonical density operator for s, $\rho_s^{\text{can}} := Z_s^{-1} \exp(-\beta H_s)$. Canonical typicality tells us that for any *one* fixed (not too large and not too strongly coupled) subsystem s, most ψ fulfill (12.56). The next observation is that most ψ actually fulfill (12.56) for *all* (not too large and not too strongly coupled) subsystems s *simultaneously*. And of those we say they are in MITE.

Let us approach the detailed definition of MITE step by step. The subsystems we want to consider correspond to spatial regions $s \subset \Lambda$, so we can talk about the diameter of s, diam(s), and its complement $s^c = \Lambda \setminus s$. We define the set MITE_{ℓ} of ψ s in "MITE on the length scale ℓ " for a given length ℓ by

$$\mathrm{MITE}_{\ell} = \bigcap_{s: \mathrm{diam}(s) \le \ell} \left\{ \psi \in \mathbb{S}(\mathscr{H}_{\mathrm{mc}}) : \rho_s^{\psi} \approx \rho_s^{\mathrm{mc}} \right\},$$
(12.57)

where

$$\rho_s^{\rm mc} = \operatorname{tr}_{s^c} \rho_{\rm mc} \,. \tag{12.58}$$

So MITE_{ℓ} is the set of wave functions for which *every* "small" subsystem has "canonical" density matrix. Note the following "subsubsystem property": If $\rho_s^{\psi} \approx \rho_s^{\rm mc}$ for some subsystem s then the same is true for every smaller subsystem s' contained in s, just by taking another partial trace (over $s' \setminus s$) on both sides of the approximate equation $\rho_s^{\psi} \approx \rho_s^{\rm mc}$. As a consequence, if a collection of regions $s_i \subseteq \Lambda$ is such that every $s \subseteq \Lambda$ with diam $(s) \leq \ell$ is contained in one of the s_i , then $\forall i : \rho_{s_i}^{\psi} \approx \rho_{s_i}^{\rm mc}$ suffices for $\psi \in \text{MITE}_{\ell}$. By canonical typicality, most ψ satisfy $\rho_{s_i}^{\psi} \approx \rho_{s_i}^{\rm mc}$ if the size (volume) of s_i is less than half of the size of the whole. Λ can be covered by a very moderate number (depending on the shape of Λ) of subsets s_i of nearly half the volume such that every set s of diameter ℓ is contained in one of them, even for not-very-small ℓ . For example, if Λ is a cube of side length a and the s_i are 8 cubes of side length b just under $2^{-1/3} a \approx 0.7937 a$ that each have one corner in common with Λ , then $\cup_i s_i = \Lambda$, $\operatorname{vol}(s_i) < \frac{1}{2} \operatorname{vol}(\Lambda)$, every ball of diameter $< 2b - a \approx 0.587 a$ is contained in one of the s_i , see Figure 15, and every set s of diameter $< b - a/2 \approx 0.293 a$ is contained in such a ball.⁹⁷ So ℓ can be up to 29% of a.

MITE is then defined to mean MITE_{ℓ_0} with ℓ_0 the largest ℓ small enough to ensure that $\rho_s^{\text{mc}} \approx \rho_{\text{can}}$ for every subsystem s with $\text{diam}(s) \leq \ell_0$. For this, we may need ℓ_0 substantially smaller than 29% of a; as a practical value, for example, we may take

$$\ell_0 = 10^{-3} \operatorname{diam}(\Lambda)$$
. (12.59)

⁹⁷One might have guessed that every set of diameter L fits into a ball of diameter L, but that is not true (the equilateral triangle of side L is a counter-example). But clearly, every set of diameter L fits into a ball of *radius* L.



Figure 15: Two-dimensional analog of the 3d situation of a cube Λ of side *a* covered by smaller cubes s_i (dashed) such that every ball (circle) of diameter a/2 is contained in one of the s_i . Some lines are drawn slightly shifted for better visibility.

In situations in which interaction cannot be neglected, deviations from ρ_{can} may be inevitable, but equivalence of ensembles still leads to

$$\rho_s^{\rm mc} \approx \rho_s^{\rm can} \,, \tag{12.60}$$

where $\rho_s^{\text{can}} = \text{tr}_{s^c} Z^{-1} e^{-\beta H}$ for H the Hamiltonian of the whole system Λ .

So MITE means "MITE on the appropriate length scale," and it is clear now that most $\psi \in \mathbb{S}(\mathscr{H}_{mc})$ are in MITE.

Next, I will argue that MITE implies MATE, i.e., every $\psi \in$ MITE also lies in MATE. For this it will be helpful to consider a more abstract perspective.

12.6.3 General Framework of MATE and MITE as Referring to Different Observables

MITE and MATE are special cases of the following scheme: Given a set \mathscr{A} of observables, we say that $\psi \in \mathbb{S}(\mathscr{H}_{mc})$ is in *thermal equilibrium relative to* \mathscr{A} if and only if for every $A \in \mathscr{A}$, the probability distribution over the eigenvalues a of $A = \sum_{a} a P_{a}$ defined by ψ ,

$$p(a) = \langle \psi | P_a | \psi \rangle, \qquad (12.61)$$

is approximately equal to that defined by $\rho_{\rm mc}$; that is,

$$\langle \psi | P_a | \psi \rangle \approx \operatorname{tr}(\rho_{\mathrm{mc}} P_a).$$
 (12.62)

For $\mathscr{A} = \mathscr{A}_{MATE} = \{M_1, \ldots, M_K\}$, one obtains MATE, and MITE is obtained for $\mathscr{A} = \mathscr{A}_{MITE} = \bigcup_s \mathscr{A}_s$ with the union taken over all spatial regions s of diameter $\leq \ell_0$ and \mathscr{A}_s the set of all self-adjoint operators on \mathscr{H}_s , more precisely

$$\mathscr{A}_{s} = \left\{ A_{0} \otimes I_{s^{c}} : A_{0} \text{ self-adjoint on } \mathscr{H}_{s} \right\}.$$
(12.63)

Indeed, the condition $\rho_s^{\psi} \approx \rho_s^{\rm mc}$ is equivalent to $\langle \psi | P | \psi \rangle \approx \operatorname{tr}(\rho_{\rm mc} P)$ for every projection of the form $P = P_0 \otimes I_{s^c}$ with P_0 a projection in \mathscr{H}_s .

In this sense, MATE means thermal equilibrium relative to the macro observables, whereas MITE is thermal equilibrium relative to all observables referring to any s of diameter $\leq \ell_0$. The latter observables include those of a more microscopic and local nature.

12.6.4 MITE Implies MATE for Macroscopic Systems

Indeed, since macro observables are sums or averages of local observables over spatial cells (say, of length L), it follows, as soon as $L \leq \ell_0$, that states ψ that display thermal behavior for micro observables (i.e., lead to the same probability distribution over the spectrum of the observable as $\rho_{\rm mc}$) also display thermal behavior for macro observables. And these ψ include those in MITE. The condition $L \leq \ell_0$ means that $\rho_s^{\psi} \approx \rho_s^{\rm mc}$ at least up to the length scale of the macro observables, which is commonly the case; e.g., for a cubic meter of gas at room conditions, we can realistically take $L \approx 10^{-4}$ m and $\ell_0 \approx 10^{-3}$ m.

Example. Here is a simple example of a state in MATE that is not in MITE. Consider a system of $N \gg 1$ non-interacting spins-1/2, $\mathscr{H} = (\mathbb{C}^2)^{\otimes N}$, with H = 0 so that $\mathscr{H}_{mc} = \mathscr{H}$ and $\rho_{mc} = 2^{-N}I$, in a pure product state $\psi = \otimes_i \psi_i$. Divide the N spins into m groups ("cells") Λ_j of $n \gg 1$ spins, so that nm = N, and take M_j to be a coarse-grained version of $\sum_{i \in \Lambda_j} \sigma_i^z$. Then the thermal equilibrium value of M_j is $\operatorname{tr}(\rho_{mc}M_j) = 0$, so $\mathscr{H}_{eq} = \bigcap_j \operatorname{kernel}(M_j)$ (where kernel means the eigenspace with eigenvalue 0), and a typical pure product state ψ lies in MATE. To see that ψ does not lie in MITE, note that for a single spin at site $i, s = \{i\}$,

$$\rho_s^{\rm mc} = \frac{1}{2} I_i \text{ whereas } \rho_s^{\psi} = |\psi_i\rangle \langle \psi_i|, \qquad (12.64)$$

so the two density matrices are not close to each other.

12.7 Approach to Thermal Equilibrium

We now give a derivation of the "zeroth law of thermodynamics" in the following form: Under conditions on the Hamiltonian that are typically satisfied, every $\psi \in \mathbb{S}(\mathscr{H}_{mc})$ sooner or later reaches thermal equilibrium and spends there most of the time in the long run. (The picture is that after a very long period in thermal equilibrium, the system will undergo a fluctuation away from thermal equilibrium, then after a while reach it again, then spend a very long time in equilibrium before the next fluctuation, etc.. By recurrence, it cannot remain in equilibrium forever if it started out in non-equilibrium.) The question can be considered separately for MATE and MITE.

12.7.1 Approach to MATE

A condition on H relevant to the approach to thermal equilibrium is the *eigenstate* thermalization hypothesis (ETH) introduced by Mark Srednicki in 1994:⁹⁸

Every eigenvector of H is in thermal equilibrium. (12.65)

A precise version of the ETH in terms of MATE is given by the condition (12.68) below. The following proposition asserts that under suitable conditions on H, all ψ approach MATE.

Proposition 17. Let \mathscr{H}_{mc} be any Hilbert space with finite dimension d_{mc} , let $H = \sum_{\alpha} E_{\alpha} |\phi_{\alpha}\rangle \langle \phi_{\alpha}|$ be self-adjoint, let $\mathscr{H}_{eq} \subset \mathscr{H}_{mc}$ be any subspace, and let

$$MATE_{\delta} = \left\{ \psi \in \mathbb{S}(\mathscr{H}_{mc}) : \langle \psi | P_{eq} | \psi \rangle > 1 - \delta \right\}.$$
 (12.66)

For every $\delta, \eta > 0$, if

$$H \text{ is non-degenerate}$$
 (12.67)

and

$$\forall \alpha : \quad \phi_{\alpha} \in \mathrm{MATE}_{\delta\eta} \,, \tag{12.68}$$

then every $\psi_0 \in \mathbb{S}(\mathscr{H}_{\mathrm{mc}})$ will spend $(1 - \eta)$ -most of the time in MATE_{δ}, i.e.,

$$\liminf_{T \to \infty} \frac{1}{T} \lambda \left\{ 0 < t < T : \psi_t \in \text{MATE}_{\delta} \right\} > 1 - \eta \,. \tag{12.69}$$

with λ the Lebesgue measure.

Proof. Let us denote time averages by

$$\overline{f(t)} = \lim_{T \to \infty} \frac{1}{T} \int_0^T dt f(t)$$
(12.70)

(keeping in mind that the limit might fail to exist) and ask what $\langle \psi_t | P_{eq} | \psi_t \rangle$ is. We write

$$\psi_0 = \sum_{\alpha=1}^{\dim \mathscr{H}} c_\alpha |\phi_\alpha\rangle, \qquad \text{so } \psi_t = \sum_{\alpha=1}^{\dim \mathscr{H}} e^{-iE_\alpha t} c_\alpha |\phi_\alpha\rangle.$$
(12.71)

Since

$$\overline{e^{iEt}} = \begin{cases} 1 & \text{if } E = 0\\ 0 & \text{if } E \in \mathbb{R} \setminus \{0\} \end{cases},$$
(12.72)

⁹⁸M. Srednicki: Chaos and quantum thermalization. *Physical Review E* 50: 888–901 (1994)

we obtain that

$$\overline{\langle \psi_t | P_{\rm eq} | \psi_t \rangle} = \sum_{\alpha, \beta} \underbrace{\overline{e^{i(E_\alpha - E_\beta)t}}}_{\delta_{\alpha\beta}} c^*_{\alpha} c_{\beta} \langle \phi_{\alpha} | P_{\rm eq} | \phi_{\beta} \rangle \tag{12.73}$$

$$=\sum_{\alpha} |c_{\alpha}|^{2} \underbrace{\langle \phi_{\alpha} | P_{\text{eq}} | \phi_{\alpha} \rangle}_{>1-\delta\eta}$$
(12.74)

$$> 1 - \delta \eta \tag{12.75}$$

and in particular that $\overline{\langle \psi_t | P_{\text{eq}} | \psi_t \rangle}$ exists.

The remaining step goes essentially as follows: If $\operatorname{error}(t) > \delta$ for more than η of the time then $\operatorname{error}(t) > \delta\eta$ (this is essentially the Markov inequality). Thus, $\langle \psi_t | P_{eq} | \psi_t \rangle > 1 - \delta$ for $(1 - \eta)$ -most of the time. A more careful formulation yields the lim inf. \Box

The first condition (non-degeneracy) is generically satisfied. Moreover, it was shown in a homework exercise that, for whichever H, most eigenvectors ϕ_{α} are in MATE. Here, however, the ETH (12.68) requires that all eigenvectors are in MATE, which is the case for some Hamiltonians and not for others. The following theorem asserts that it is the case for most Hamiltonians.

Theorem 24 (Typicality of ETH). Let ε , δ , $\eta > 0$, let E_{α} be pairwise distinct real values, let $\{\phi_{\alpha}\} \sim u_{ONB(\mathscr{H}_{mc})}$, and set $H = \sum_{\alpha} E_{\alpha} |\phi_{\alpha}\rangle \langle \phi_{\alpha}|$. If $d_{mc} > D(\varepsilon, \delta, \eta)$ and

$$\frac{\dim \mathscr{H}_{eq}}{\dim \mathscr{H}_{mc}} > 1 - \frac{\delta \eta}{2}, \qquad (12.76)$$

then the ETH in the form (12.68) is satisfied with probability $\geq 1 - \varepsilon$.

Outline of proof. ⁹⁹ We abbreviate $d_{\rm mc} = d$.

$$p := \mathbb{P}\Big(\forall \alpha : \langle \phi_{\alpha} | P_{\text{eq}} | \phi_{\alpha} \rangle > 1 - \delta \eta \Big)$$
(12.77)

$$= 1 - \mathbb{P}\left(\bigcup_{\alpha} \left\{ \langle \phi_{\alpha} | P_{\text{eq}} | \phi_{\alpha} \rangle \leq 1 - \delta \eta \right\} \right)$$
(12.78)

$$\geq 1 - d \max_{\alpha} \mathbb{P}\Big(\langle \phi_{\alpha} | P_{\text{eq}} | \phi_{\alpha} \rangle \leq 1 - \delta \eta \Big)$$
(12.79)

$$\geq 1 - d u_{\rm mc} \Big(\langle \Psi | P_{\rm eq} | \Psi \rangle \leq 1 - \delta \eta \Big)$$
(12.80)

(with $\Psi \sim u_{\rm mc}$) because $\mathbb{P}\left(\langle \phi_{\alpha} | P_{\rm eq} | \phi_{\alpha} \rangle \leq 1 - \delta \eta\right)$ is independent of α . We want to show that $p \geq 1 - \varepsilon$.

⁹⁹For the full proof, see S. Goldstein, J. L. Lebowitz, C. Mastrodonato, R. Tumulka, and N. Zanghi: Approach to Thermal Equilibrium of Macroscopic Quantum Systems. *Physical Review E* 81: 011109 (2010) http://arxiv.org/abs/0911.1724

Let $\mathbf{G} = (G_1, \ldots, G_d)$ be a Gaussian random vector in \mathscr{H}_{mc} with mean 0 and covariance *I*. Due to the rotational symmetry of the distribution of \mathbf{G} , Ψ can be constructed as $\mathbf{G}/||\mathbf{G}||$. Thus,

$$p \ge 1 - d \mathbb{P}\left(\sum_{\alpha=1}^{d_{\text{eq}}} \frac{|G_{\alpha}|^2}{\|\boldsymbol{G}\|^2} \le 1 - \delta\eta\right).$$
(12.81)

Now some thought shows that, assuming (12.76), the last \mathbb{P} is

$$\leq \mathbb{P}\Big(\Big|\|\boldsymbol{G}\|^2 - d\Big| \geq \frac{\delta\eta}{8}d\Big) + \mathbb{P}\Big(\Big|\sum_{\alpha=1}^{d_{eq}} |G_{\alpha}|^2 - d_{eq}\Big| > \frac{\delta\eta}{8}d_{eq}\Big)$$
(12.82)

$$\leq 2\exp\left(-\frac{d_{\rm eq}\delta\eta}{192}\right) + 2\exp\left(-\frac{d\delta\eta}{192}\right) \tag{12.83}$$

$$\leq 4 \exp\left(-\frac{d\delta\eta}{384}\right) \tag{12.84}$$

using $d_{\rm eq} > d/2$. Thus,

$$p \ge 1 - 4d \exp\left(-\frac{d\varepsilon^2}{384}\right) \xrightarrow{d \to \infty} 1.$$
 (12.85)

Of course, the fact that most H obey the ETH does not tell us whether specific models of H that we may be interested in do so, but at least that would be the first expectation. A recent numerical study of specific realistic models has found them to obey ETH.¹⁰⁰

12.7.2 Approach to MITE

The ideal gas provides an example of a system for which some states do not approach MITE. For example, if all particles have pretty much the same kinetic energy, it will stay that way in the absence of interaction, and also in subregions s_i all particles will have essentially the same kinetic energy, in stark contrast to the canonical density matrix.

We now ask, Under which conditions will all or most ψ approach MITE? There are several results in the literature, all of which assume the MITE version of the ETH, and that the Hamiltonian is non-degenerate and has non-degenerate energy gaps, i.e.,

$$E_{\alpha} - E_{\beta} \neq E_{\alpha'} - E_{\beta'} \text{ unless } \begin{cases} \text{either } \alpha = \alpha' \text{ and } \beta = \beta' \\ \text{or } \alpha = \beta \text{ and } \alpha' = \beta', \end{cases}$$
(12.86)

another condition that is generically fulfilled.

¹⁰⁰H. Kim, T. N. Ikeda, and D. A. Huse: Testing whether all eigenstates obey the Eigenstate Thermalization Hypothesis. *Physical Review E* **90**: 052105 (2014) http://arxiv.org/abs/1408.0535

We mention here two results, the first of which¹⁰¹ asserts that if all energy eigenstates in \mathscr{H}_{mc} are in MITE, then most $\psi \in S(\mathscr{H}_{mc})$ will spend most of the time in MITE in the long run. More precisely, those ψ will behave this way for which the effective number of significantly participating energy eigenstates is much larger than dim \mathscr{H}_s for any subsystem s of diameter $\leq \ell_0$.

The second result¹⁰² shows that *all* (rather than most) ψ will ultimately reach MITE and stay there most of the time, provided a certain extension of the ETH to off-diagonal elements holds: that for $A \in \mathscr{A}_{\text{MITE}}$ (as in Section 12.6.3),

$$\langle \alpha | A | \beta \rangle \approx 0 \text{ for } \alpha \neq \beta .$$
 (12.87)

Here is a precise formulation of this result.

Theorem 25. Let $\delta > 0$, $\eta > 0$, let $H = \sum_{\alpha} E_{\alpha} |\alpha\rangle \langle \alpha|$ be a non-degenerate Hamiltonian with non-degenerate energy gaps as in (12.86), and let $\mathscr{A} \neq \emptyset$ be a set of self-adjoint operators on \mathscr{H} . Set $\varepsilon = \sqrt{\eta} \delta/2$ and suppose that

$$(\mathscr{A}-ETH) \quad \forall \alpha \ \forall A \in \mathscr{A} : \left| \langle \alpha | A | \alpha \rangle - \operatorname{tr}(\rho_{\mathrm{mc}}A) \right| < \varepsilon$$
(12.88)

and

$$\forall \alpha \neq \beta \ \forall A \in \mathscr{A} : \left| \langle \alpha | A | \beta \rangle \right| < \varepsilon .$$
(12.89)

Then, for every $\psi_0 \in \mathbb{S}(\mathscr{H}_{mc})$ and every $A \in \mathscr{A}$,

$$\left|\langle\psi_t|A|\psi_t\rangle - \operatorname{tr}(\rho_{\mathrm{mc}}A)\right| < \delta \tag{12.90}$$

for $(1 - \eta)$ -most t. In particular, if every spectral projection of any $A \in \mathscr{A}$ is also contained in \mathscr{A} , then every ψ_0 spends most of the time in thermal equilibrium relative to \mathscr{A} . In particular, for $\mathscr{A} = \mathscr{A}_{\text{MITE}}$, every ψ_0 spends most of the time in MITE.

Proof. We first show that for all ψ_0 and A, the time average of $\langle \psi_t | A | \psi_t \rangle$ is thermal,

$$\left|\overline{\langle\psi_t|A|\psi_t\rangle} - \operatorname{tr}(\rho_{\mathrm{mc}}A)\right| < \varepsilon.$$
(12.91)

Indeed, since H is non-degenerate,

$$\overline{\langle \psi_t | A | \psi_t \rangle} = \sum_{\alpha, \beta} \langle \psi | \alpha \rangle \overline{e^{iE_{\alpha}t} \langle \alpha | A | \beta \rangle e^{-iE_{\beta}t}} \langle \beta | \psi \rangle$$
(12.92)

$$=\sum_{\alpha} \langle \psi | \alpha \rangle \langle \alpha | A | \alpha \rangle \langle \alpha | \psi \rangle , \qquad (12.93)$$

¹⁰¹P. Reimann: Foundation of Statistical Mechanics under Experimentally Realistic Conditions. *Physical Review Letters* **101**: 190403 (2008) http://arxiv.org/abs/0810.3092

N. Linden, S. Popescu, A. J. Short, and A. Winter: Quantum mechanical evolution towards thermal equilibrium. *Physical Review E* **79**: 061103 (2009) http://arxiv.org/abs/0812.2385

¹⁰²M. Rigol, V. Dunjko, and M. Olshanii: Thermalization and its mechanism for generic isolated quantum systems. *Nature* **452**: 854–858 (2008) http://arxiv.org/abs/0708.1324

 \mathbf{SO}

$$\left|\overline{\langle\psi_t|A|\psi_t\rangle} - \operatorname{tr}(\rho_{\mathrm{mc}}A)\right| = \left|\sum_{\alpha} \left|\langle\psi|\alpha\rangle\right|^2 \left(\langle\alpha|A|\alpha\rangle - \operatorname{tr}(\rho_{\mathrm{mc}}A)\right)\right|$$
(12.94)

$$\leq \sum_{\alpha} \left| \langle \psi | \alpha \rangle \right|^2 \left| \langle \alpha | A | \alpha \rangle - \operatorname{tr}(\rho_{\mathrm{mc}} A) \right|$$
(12.95)

$$\stackrel{(12.88)}{<} \sum_{\alpha} \left| \langle \psi | \alpha \rangle \right|^2 \varepsilon \tag{12.96}$$

$$=\varepsilon. (12.97)$$

Second, we show that the time variance of $\langle \psi_t | A | \psi_t \rangle$ is small,

$$\overline{\left(\langle\psi_t|A|\psi_t\rangle - \overline{\langle\psi_t|A|\psi_t\rangle}\right)^2} < \varepsilon^2.$$
(12.98)

Indeed, because of the non-degenerate energy gaps,

$$\overline{e^{i(E_{\alpha}-E_{\beta}+E_{\alpha'}-E_{\beta'})t}} = \delta_{\alpha\beta'}\delta_{\alpha'\beta} + \delta_{\alpha\beta}\delta_{\alpha'\beta'} - \delta_{\alpha\beta}\delta_{\beta\beta'}\delta_{\alpha'\beta'}.$$
(12.99)

Therefore,

$$\overline{\left(\langle\psi_t|A|\psi_t\rangle - \overline{\langle\psi_t|A|\psi_t\rangle}\right)^2} = \overline{\left(\sum_{\alpha,\beta}\langle\psi|\alpha\rangle e^{iE_{\alpha}t}\langle\alpha|A|\beta\rangle e^{-iE_{\beta}t}\langle\beta|\psi\rangle - \overline{\langle\psi_t|A|\psi_t\rangle}\right)^2}$$
(12.100)

$$= \left(\sum_{\alpha \neq \beta} \langle \psi | \alpha \rangle e^{iE_{\alpha}t} \langle \alpha | A | \beta \rangle e^{-iE_{\beta}t} \langle \beta | \psi \rangle + \sum_{\alpha} \langle \psi | \alpha \rangle \langle \alpha | A | \alpha \rangle \langle \alpha | \psi \rangle - \overline{\langle \psi_t | A | \psi_t \rangle} \right)^2 (12.101)$$

$$\stackrel{(12.93)}{=} \overline{\left(\sum_{\alpha \neq \beta} \langle \psi | \alpha \rangle e^{iE_{\alpha}t} \langle \alpha | A | \beta \rangle e^{-iE_{\beta}t} \langle \beta | \psi \rangle\right)^2}$$
(12.102)

$$=\overline{\sum_{\alpha\neq\beta,\alpha'\neq\beta'}\langle\psi|\alpha\rangle e^{iE_{\alpha}t}\langle\alpha|A|\beta\rangle e^{-iE_{\beta}t}\langle\beta|\psi\rangle\langle\psi|\alpha'\rangle e^{iE_{\alpha'}t}\langle\alpha'|A|\beta'\rangle e^{-iE_{\beta'}t}\langle\beta'|\psi\rangle}$$
(12.103)

$$\stackrel{(12.99)}{=} \sum_{\alpha \neq \beta} \langle \psi | \alpha \rangle \langle \alpha | A | \beta \rangle \langle \beta | \psi \rangle \langle \psi | \beta \rangle \langle \beta | A | \alpha \rangle \langle \alpha | \psi \rangle$$
(12.104)

$$=\sum_{\alpha\neq\beta} \left| \langle \psi | \alpha \rangle \right|^2 \left| \langle \alpha | A | \beta \rangle \right|^2 \left| \langle \beta | \psi \rangle \right|^2 \tag{12.105}$$

$$\stackrel{(12.89)}{\leq} \sum_{\alpha \neq \beta} \left| \langle \psi | \alpha \rangle \right|^2 \varepsilon^2 \left| \langle \beta | \psi \rangle \right|^2 \tag{12.106}$$

$$\leq \sum_{\alpha,\beta} \left| \langle \psi | \alpha \rangle \right|^2 \varepsilon^2 \left| \langle \beta | \psi \rangle \right|^2 \tag{12.107}$$

$$=\varepsilon^2.$$
 (12.108)

Third, the idea is that if the time average is the thermal value and the time variance is small, then the value must be close to the thermal value most of the time (it varies only a little). This conclusion is essentially provided by the Chebyshev inequality, although a subtlety comes from the limit $T \to \infty$ (or, put differently, from the fact that there is no uniform probability distribution on $[0, \infty)$). Leaving this subtlety aside for a moment, the Chebyshev inequality would yield that

$$\frac{1}{T}\lambda\left\{0 < \tau < T: \left|\langle\psi_{\tau}|A|\psi_{\tau}\rangle - \overline{\langle\psi_{t}|A|\psi_{t}\rangle}\right| < k\varepsilon\right\} \ge 1 - \frac{1}{k^{2}}$$
(12.109)

for any k > 0, say $k = 1/\sqrt{\eta}$. Since we want the inaccuracy $k\varepsilon$ to be δ (the right-hand side of (12.90)), we set $\varepsilon < \delta/k = \sqrt{\eta}\delta$. The difference (12.91), as well as the limit $T \to \infty$, enforce a further factor > 1 (say, 2) for obtaining the statement containing (12.90). The next statement is now immediate from the definition of "thermal equilibrium relative to \mathscr{A} ," see (12.62). The last statement follows from the fact that $\mathscr{A}_{\text{MITE}}$ contains all "local observables" $A_0 \otimes I_{s^c}$, in particular those for which A_0 is a projection.

12.8 Thermal Equilibrium of Ideal Quantum Gases

Let us see what the wave functions in \mathscr{H}_{eq} for the ideal mono-atomic Bose gas and the ideal mono-atomic Fermi gas look like. In order to study their properties, one may derive quantum corrections to the thermodynamic equation of state pV = NkT. Here, however, we will limit ourselves to an easier consideration concerning the thermal expectation values of the occupation number operators of the 1-particle energy.

We will exploit the equivalence of ensembles $\rho_{\rm mc} \approx \rho_{\rm can} \approx \rho_{\rm gc}$ with $\rho_{\rm gc}$ the grandcanonical density matrix

$$\rho_{\rm gc} = \frac{1}{Z_{\rm gc}} e^{-\beta(H-\mu N)}$$
(12.110)

with N the particle number operator, μ a parameter called the "chemical potential," and $Z_{\rm gc}$ the normalizing constant. The operator $\rho_{\rm gc}$ is defined on *Fock space* \mathscr{F} , the Hilbert space of a variable number of particles,

$$\mathscr{H} = \mathscr{F}_{\pm} = \bigoplus_{n=0}^{\infty} \mathscr{H}_{n}^{\pm}, \qquad (12.111)$$

where \mathscr{H}_n^{\pm} is the bosonic (fermionic) *n*-particle Hilbert space,

$$\mathscr{H}_n^{\pm} = P_{\pm} \mathscr{H}_1^{\otimes n} \tag{12.112}$$

with \mathscr{H}_1 the 1-particle Hilbert space, P_{\pm} the projection to the symmetric (anti-symmetric) subspace as in (11.15) and (11.16), and $P_{\pm}\mathscr{H}_1^{\otimes n}$ the range of this projection, i.e., the symmetric (anti-symmetric) subspace. An element of Fock space can be written as a sequence $\psi = (\psi^{(0)}, \psi^{(1)}, \dots, \psi^{(n)}, \dots)$ with $\psi^{(n)} \in \mathscr{H}_n = \mathscr{H}_n^{\pm}$. The particle number operator just multiplies by the particle number,

$$(N\psi)^{(n)} = n\psi^{(n)} \,. \tag{12.113}$$

The Hamiltonian H is, for non-interacting particles, related to the 1-particle Hamiltonian H_1 according to

$$(H\psi)^{(n)} = \sum_{j=1}^{n} I \otimes I \otimes \cdots \otimes \underbrace{H_1}_{j\text{-th place}} \otimes \cdots \otimes I \psi^{(n)}.$$
(12.114)

We are familiar with the fact that for $\mathscr{H}_1 = L^2(\Omega)$, $\psi^{(n)}$ can be written as a symmetric (anti-symmetric) function $\psi^{(n)}(\boldsymbol{q}_1, \ldots, \boldsymbol{q}_n)$ with $\boldsymbol{q}_j \in \Omega$. More generally, if we choose an ONB $\{|\ell\rangle\}$ of \mathscr{H}_1 , then we can express $\psi^{(n)}$ as a symmetric (anti-symmetric) function $\psi^{(n)}(\ell_1, \ldots, \ell_n)$,

$$\psi^{(n)} = \sum_{\ell_1,\dots,\ell_n} \psi^{(n)}(\ell_1,\dots,\ell_n) |\ell_1\rangle \otimes \dots \otimes |\ell_n\rangle.$$
(12.115)

For this fixed basis of \mathscr{H}_1 , the occupation number operator N_{ℓ} is defined to be, in this particular representation of ψ , the multiplication by the occupation number function

$$n_{\ell}(\ell_1, \dots, \ell_n) = \# \left\{ j \in \{1 \dots n\} : \ell_j = \ell \right\}.$$
(12.116)

Note that for fermions, the function n_{ℓ} assumes only the values 0 and 1, which therefore are also the eigenvalues of N_{ℓ} ; for bosons, the values of n_{ℓ} (and eigenvalues of N_{ℓ}) are 0, 1, 2, 3...

We will consider N_{ℓ} for $\{|\ell\rangle\}$ an eigenbasis of H_1 . These operators are not macro observables (some coarse-graining of $N_{\ell} + N_{\ell+1} + \ldots + N_{\ell+\Delta\ell}$ may be macro observables), but their quantum expectations provide helpful information nevertheless.

12.8.1 Thermal Expectation of Occupation Number Operators

Proposition 18. Let H be non-interacting and $H_1 = \sum_{\ell} e_{\ell} |\ell\rangle \langle \ell|$. Whenever ρ_{gc} exists,

$$\langle N_{\ell} \rangle := \operatorname{tr} \left(\rho_{\mathrm{gc}} N_{\ell} \right) = \frac{1}{e^{\beta(e_{\ell} - \mu)} \mp 1}$$
(12.117)

with the upper sign for bosons and the lower for fermions.

Proof. Consider bosons first. Let $\sum_{\ell_1...\ell_n}^{\infty}$ denote the sum over just one representative per

permutation class. Then, expressing the trace in the basis $P_+|\ell_1\rangle \otimes \cdots \otimes |\ell_n\rangle$,

$$Z_{\rm gc} = {\rm tr} \, e^{-\beta (H-\mu N)}$$
 (12.118)

$$=\sum_{n=0}^{\infty}\sum_{\ell_1...\ell_n}^{\sim} e^{-\beta(e_{\ell_1}+...+e_{\ell_n}-\mu n)}$$
(12.119)

$$=\sum_{n_1,n_2...=0}^{\infty} \prod_{\ell'} e^{-\beta(e_{\ell'}-\mu)n_{\ell'}}$$
(12.120)

$$=\prod_{\ell'}\sum_{n_{\ell'}=0}^{\infty}e^{-\beta(e_{\ell'}-\mu)n_{\ell'}}$$
(12.121)

$$= \prod_{\ell'} \left(1 - e^{-\beta(e_{\ell'} - \mu)} \right)^{-1}.$$
 (12.122)

The convergence of the geometric series $\sum q^n$ requires that $|q| = e^{-\beta(e_{\ell'}-\mu)} < 1$. By the same methods, using further that for |q| < 1 also

$$\sum_{n=0}^{\infty} n q^n = \frac{q}{(1-q)^2}, \qquad (12.123)$$

we obtain that

$$\langle N_{\ell} \rangle = \frac{1}{Z_{\rm gc}} \sum_{n=0}^{\infty} \sum_{\ell_1 \dots \ell_n}^{\sim} n_{\ell} \, e^{-\beta(e_{\ell_1} + \dots + e_{\ell_n} - \mu n)} \tag{12.124}$$

$$= \frac{1}{Z_{\rm gc}} \sum_{n_1, n_2 \dots = 0}^{\infty} n_\ell \, e^{-\beta(e_\ell - \mu)n_\ell} \prod_{\ell' \neq \ell} e^{-\beta(e_{\ell'} - \mu)n_{\ell'}}$$
(12.125)

$$= \frac{1}{Z_{\rm gc}} \sum_{n_\ell=0}^{\infty} n_\ell \, e^{-\beta(e_\ell - \mu)n_\ell} \prod_{\ell' \neq \ell} \sum_{n_{\ell'}} e^{-\beta(e_{\ell'} - \mu)n_{\ell'}}$$
(12.126)

$$= \frac{1}{Z_{\rm gc}} e^{-\beta(e_{\ell}-\mu)} (1 - e^{-\beta(e_{\ell}-\mu)})^{-2} \prod_{\ell' \neq \ell} (1 - e^{-\beta(e_{\ell'}-\mu)})^{-1}$$
(12.127)

$$=\frac{e^{-\beta(e_{\ell}-\mu)}(1-e^{-\beta(e_{\ell}-\mu)})^{-2}}{(1-e^{-\beta(e_{\ell}-\mu)})^{-1}}$$
(12.128)

$$=\frac{e^{-\beta(e_{\ell}-\mu)}}{1-e^{-\beta(e_{\ell}-\mu)}}$$
(12.129)

$$=\frac{1}{e^{\beta(e_{\ell}-\mu)}-1}\,.$$
(12.130)

For fermions, let $\sum_{\ell_1...\ell_n}^{\sim}$ denote the sum over pairwise distinct ℓ_j and just one repre-

sentative per permutation class. Then

$$Z_{\rm gc} = \sum_{n=0}^{\infty} \sum_{\ell_1 \dots \ell_n}^{\sim} e^{-\beta(e_{\ell_1} + \dots + e_{\ell_n} - \mu n)}$$
(12.131)

$$=\sum_{n_1,n_2...=0}^{1}\prod_{\ell'}e^{-\beta(e_{\ell'}-\mu)n_{\ell'}}$$
(12.132)

$$= \prod_{\ell'} \left(1 + e^{-\beta(e_{\ell'} - \mu)} \right), \qquad (12.133)$$

and thus

$$\langle N_{\ell} \rangle = \frac{1}{Z_{\rm gc}} \sum_{n_{\ell}=0}^{1} n_{\ell} e^{-\beta(e_{\ell}-\mu)n_{\ell}} \prod_{\ell' \neq \ell} \sum_{n_{\ell'}=0}^{1} e^{-\beta(e_{\ell'}-\mu)n_{\ell'}}$$
(12.134)

$$= \frac{e^{-\beta(e_{\ell}-\mu)}}{1+e^{-\beta(e_{\ell}-\mu)}}$$
(12.135)
$$= \frac{1}{e^{\beta(e_{\ell}-\mu)}+1}.$$
(12.136)

$$=\frac{1}{e^{\beta(e_{\ell}-\mu)}+1}\,.$$
(12.136)

For approximating $\rho_{\rm mc}$ (which has fixed E and N), the parameters β, μ have to be chosen to that $E = \operatorname{tr}(\rho_{\mathrm{gc}}H) = \sum_{\ell} e_{\ell} \langle N_{\ell} \rangle$ and $N = \operatorname{tr}(\rho_{\mathrm{gc}}N) = \sum_{\ell} \langle N_{\ell} \rangle$, where the N in the middle term is the number operator. We now turn to a discussion of the physical meaning of the formula (12.117).

12.8.2The Fermi Energy

Let us consider first fermions in the limit $T \to 0$ or $\beta \to \infty$:

$$\lim_{\beta \to \infty} \frac{1}{e^{\beta(e_{\ell} - \mu)} + 1} = \begin{cases} 1 & \text{for } e_{\ell} < \mu \\ \frac{1}{2} & \text{for } e_{\ell} = \mu \\ 0 & \text{for } e_{\ell} > \mu . \end{cases}$$
(12.137)

That is, if we prescribe the total particle number N, then all levels e_{ℓ} up to e_N are maximally occupied ("filled"), and all levels above e_N are "empty." The N-th energy level is called the *Fermi energy*. This situation corresponds to the ground state in \mathscr{H}_N . For T close to 0, the mean occupation numbers follow a curve that is a smooth approximation to the step function, see Figure 16.

12.8.3**Bose-Einstein Condensation**

For bosons, we obtain in the limit $T \to 0$ $(\beta \to \infty)$ for fixed $N = \sum_{\ell} \langle N_{\ell} \rangle$ that

$$\langle N_{\ell} \rangle = \begin{cases} N & \text{for } \ell = 0\\ 0 & \text{for } \ell > 0 \end{cases}$$
(12.138)



Figure 16: Graph of the function $1/(e^{\beta(E-\mu)}+1)$ for $\beta = \infty$ (T = 0, red) and β large (T small, blue)

That is, all particles are in the 1-particle ground state. Further analysis shows that for temperatures up to a certain *critical temperature* T_c ($0 < T < T_c$),

$$\lim \frac{\langle N_0 \rangle}{N} = 1 - \left(\frac{T}{T_c}\right)^{3/2} > 0$$
 (12.139)

in the thermodynamic limit $N \to \infty$, $V \to \infty$, $V/N \to v \in (0, \infty)$ (where T_c depends on v), so $\langle N_0 \rangle$ is macroscopically large; put differently, a nonzero fraction of all particles "occupy" the ground state. They are called the *Bose-Einstein condensate*. The excited states have nonzero average occupation numbers, but not macroscopically large ones. At T_c , $\lim \langle N_0 \rangle / N$ reaches 0, and it remains zero for all higher temperatures. The transition at T_c is called Bose-Einstein condensation.

12.8.4 The Planck Radiation Law

The Planck radiation law is a kind of analog to Maxwell's velocity distribution for the photon gas: The latter describes how many molecules have which velocity and thus which kinetic energy in a gas in thermal equilibrium, and the former describes how many photons have which energy in a photon gas in thermal equilibrium. A key difference between a gas of molecules and a photon gas in a container Λ is that photons can be absorbed and emitted by the walls of the container, so that the number of photons is not fixed. The emission of photons by the walls is the mechanism by which the walls reach thermal equilibrium with the photon gas in the container, and this is nothing but the familiar phenomenon that hot bodies glow. In fact, they also glow if the temperature is not particularly high, but this glow is not visible because almost all of the emitted radiation has frequency in the infrared part of the spectrum ("thermal radiation is infrared"). Since the photon gas in the container ultimately reaches thermal equilibrium with the walls, it follows that, if the walls are kept at constant temperature (say, by contact with a large heat bath), the density matrix of the photon gas in thermal equilibrium is

$$\rho = \rho_{\rm can} = \frac{1}{Z} e^{-\beta H},$$
(12.140)

understood as a density matrix on Fock space (based on the Hamiltonian on Fock space). Equivalently, $\rho = \rho_{\rm gc}$ with $\mu = 0$. This density matrix governs the total number of photons as well as how many photons have which energy; thus, while for a gas of molecules, N, E, and V are independent variables, only two of them are independent for the photon gas. Since the photons practically do not interact with each other, they form an ideal Bose gas. The photon gas in Λ in a thermal equilibrium state at temperature T is also known as the cavity radiation or thermal radiation, and its energy distribution coincides with that of the so-called black-body radiation at T (the radiation emitted by a "perfect black body," i.e., one that absorbs all incoming radiation, at T). The Hamiltonian of a single photon is, instead of $H = p^2/2m$, of the form $H = |\mathbf{p}|c$ with c the speed of light. A calculation analogous to that of the density of states of an ideal Bose gas in Section 11.2 then yields that the number of energy eigenvalues of a single photon in the interval [E, E + dE] is, to leading order in the limit $V \to \infty$, given by

$$\Omega(E) dE = \frac{8\pi V}{h^3 c^3} E^2 dE . \qquad (12.141)$$

As a consequence, the total occupation number of all 1-particle eigenstates in [E, E+dE] has thermal average

$$\sum_{\ell:e_{\ell}\in[E,E+dE]} \langle N_{\ell} \rangle = \frac{1}{e^{\beta E} - 1} \frac{8\pi V}{h^3 c^3} E^2 dE \,.$$
(12.142)

It is common to express the distribution as a function of frequency ν instead of energy E; the two are simply related by

$$E = h\nu. (12.143)$$

Then (12.142) becomes:

$$\langle N_{[\nu,\nu+d\nu]} \rangle = \frac{8\pi V}{c^3} \frac{\nu^2}{e^{h\nu/kT} - 1} d\nu .$$
 (12.144)

Moreover, it is common to specify, instead of the average number of photons in $[\nu, \nu + d\nu]$, the average of their total energy $\mathcal{E}_{[\nu,\nu+d\nu]} = h\nu N_{[\nu,\nu+d\nu]}$:

$$\langle \mathcal{E}_{[\nu,\nu+d\nu]} \rangle = \frac{8\pi Vh}{c^3} \frac{\nu^3}{e^{h\nu/kT} - 1} d\nu.$$
 (12.145)

This relation is the *Planck radiation law*, first obtained by Max Planck (1858–1947) in 1900 through a heuristic reasoning before the formulation of quantum mechanics; indeed, the Planck radiation law gave inspiration to the development of quantum mechanics.

12.9 Normal Typicality

As a last fact in this circle of results concerning the long-time behavior of typical systems, we describe "normal typicality." Consider again an orthogonal decomposition

$$\mathscr{H}_{\rm mc} = \bigoplus_{\nu} \mathscr{H}_{\nu} \,. \tag{12.146}$$

Observe that for most $\psi \in \mathbb{S}(\mathscr{H}_{\mathrm{mc}})$,

$$\|P_{\nu}\psi\|^2 \approx \frac{d_{\nu}}{d_{\rm mc}} \quad \forall \nu \,. \tag{12.147}$$

This follows from Lemma 3 on page 131 applied to $A = P_{\nu}$, which shows that for $\Psi \sim u_{\rm mc}$,

$$\mathbb{E} \|P_{\nu}\Psi\|^{2} = \frac{d_{\nu}}{d_{\mathrm{mc}}} \quad \text{and} \quad \operatorname{Var} \|P_{\nu}\Psi\|^{2} < \frac{1}{d_{\nu}} \left(\frac{d_{\nu}}{d_{\mathrm{mc}}}\right)^{2}.$$
(12.148)

We call ψ_0 normal iff for most times t,

$$\|P_{\nu}\psi_t\|^2 \approx \frac{d_{\nu}}{d_{\rm mc}} \quad \forall \nu \,. \tag{12.149}$$

As a corollary of Theorem 25 for $\mathscr{A} = \{P_{\nu}\}$, we obtain the following.

Proposition 19. Suppose H is non-degenerate and has non-degenerate gaps, and that for all ν

$$\forall \alpha : \quad \left| \langle \alpha | P_{\nu} | \alpha \rangle - \frac{d_{\nu}}{d_{\rm mc}} \right| < \varepsilon \tag{12.150}$$

and

$$\forall \alpha \neq \beta : \left| \langle \alpha | P_{\nu} | \beta \rangle \right| < \varepsilon .$$
(12.151)

Then every $\psi_0 \in \mathbb{S}(\mathscr{H}_{mc})$ is normal.

Theorem 26 (Normal typicality¹⁰³). Let $\{E_{\alpha}\}$ be pairwise distinct numbers with nondegenerate gaps. For sufficiently large d_{ν} 's, most ONBs $\{|\alpha\rangle\}$ are such that $H = \sum_{\alpha} E_{\alpha} |\alpha\rangle \langle \alpha |$ satisfies (12.150) and (12.151).

 $^{^{103}}$ J. von Neumann: Beweis des Ergodensatzes und des *H*-Theorems in der neuen Mechanik. Zeitschrift für Physik **57**: 30–70 (1929).

See also S. Goldstein, J. L. Lebowitz, C. Mastrodonato, R. Tumulka, and N. Zanghi: Normal Typicality and von Neumann's Quantum Ergodic Theorem. *Proceedings of the Royal Society A* **466**: 3203–3224 (2010) http://arxiv.org/abs/0907.0108

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