Prof. Dr. Roderich Tumulka
Eberhard Karls University Tübingen

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Mathematical Statistical Physics: Assignment 7

Problem 32: *Gibbs entropy* (hand in, 30 points)
Compute the same function $S(E, V, N)$ as in Problem 31 in a different way using equivalence of ensembles, the Gibbs formula

$$S(\mathrm{eq}) = -k \int_\Gamma dx\, \rho(x)\, \log \rho(x)\,,$$

and the canonical density $\rho(x) = Z^{-1} e^{-\beta H(x)}$. As in Problem 31, give only the leading order terms.
Instructions. In order to find the correct N dependence, use an N-dependent Λ_N with volume $V_N = Nv$ (and $v = \mathrm{const.}$) and either $\Gamma = {}^N\Gamma_1$ or the volume measure $dx/N!$ on $\Gamma = \Gamma_1^N$ (both of which lead to a further factor $N!^{-1}$ in Z).

Problem 33: (don't hand in)
Show that the Gibbs entropy of a probability density ρ does not change under the Hamiltonian time evolution.

Problem 34: *Entropy of mixing* (hand in, 35 points)
We consider two ideal (mono-atomic) gases A, B of different substances in separate containers $\Lambda_A \cap \Lambda_B = \emptyset$, each in thermal equilibrium by itself with parameters $N_i, E_i, V_i = \mathrm{vol}(\Lambda_i)$ for $i = A, B$. We assume that they have the same particle number density $n = N_i/V_i$ and the same temperature or, equivalently, the same energy per particle $\overline{e} = E_i/N_i$. Now we remove the wall between the containers, thereby allowing the gases to spread in the entire volume $\Lambda = \Lambda_A \cup \Lambda_B$ and reach a new thermal equilibrium.

(a) Show that the total entropy increases by

$$\Delta S = S_{\mathrm{after}} - S_{\mathrm{before}} = -kN \Big[\alpha \log \alpha + (1-\alpha) \log(1-\alpha) \Big] + o(N)$$

with $\alpha = N_A/N = V_A/V$ and $V = V_A + V_B$. This expression is called the *entropy of mixing*. (Use the result of Problem 32 or Problem 31 of Assignment 6.)

(b) Neglecting the $o(N)$ term, show that $\Delta S > 0$ for all $0 < \alpha < 1$.

(c) Now let A, B be identical gases. Then the macro state should not change by removing the wall, so the entropy should not increase. Let us verify that. For simplicity, let us ignore velocities and consider only the configuration space $\mathcal{Q} = {}^N\Lambda$; we replace the energy surface by the *accessible set* $M \subset \mathcal{Q}$. Specify the sets M_{before} and M_{after} and determine $\log \mathrm{vol}\, M_{\mathrm{before}}$ and $\log \mathrm{vol}\, M_{\mathrm{after}}$ to leading order in N while assuming $V_i = N_i v$ with constant $v = 1/n$ and constant α.

Problem 35: Entropy increase in finite sets (hand in, 35 points)
(a) Assume that the finite set M (playing the role of an energy shell Γ_{mc}) has $10^{100}-1$ elements and is partitioned in Γ_ν, $\nu = 1, \dots, 100$, with $\#\Gamma_\nu = 0.9 \times 10^\nu$. The "trajectory" $(x(0), x(1), x(2), \dots)$ starts at a random element $x(0) = x$ of Γ_{50}. If the discrete time evolution T is a random bijection $M \to M$, what is the most probable history $t \mapsto S(x(t))$ in the first 1000 time steps? What if T is ergodic? (Here, we do not aim at rigor of proof; plausible arguments suffice.)

(b) The behavior of part (a) does not occur in reality because some Γ_ν do not even border on other $\Gamma_{\nu'}$. To improve our simple model, let us now demand of $T : M \to M$ that $x \in \Gamma_\nu$ can only jump to an element of $\Gamma_{\nu-1} \cup \Gamma_\nu \cup \Gamma_{\nu+1}$ (of $\Gamma_1 \cup \Gamma_2$ for $x \in \Gamma_1$, and of $\Gamma_{99} \cup \Gamma_{100}$ for $x \in \Gamma_{100}$). Then what is the most probable history $t \mapsto S(x(t))$ in the first 1000 time steps?

(c) An *entropy valley* is a time interval $[t_1, t_2]$ (with $t_1, t_2 \in \mathbb{Z}$) such that $S(t_1 - 1) > S(t)$ for all $t \in [t_1, t_2]$ and $S(t_1 - 1) \le S(t_2 + 1)$; its *duration* is $t_2 + 1 - t_1$ and its *depth* $\max\bigl\{S(t_1 - 1) - S(t) : t \in [t_1, t_2]\bigr\}$. What can you say about the frequency, depth, and duration of entropy valley in the models of part (a) and part (b)? What if T must be ergodic?

Problem 36: *Refined model* (computer problem, optional extra credit 50 points)
A main reason why some macro sets in phase space do not border on others lies in *local conservation laws*: energy, momentum, or particle number in a region $\Delta \subset \Lambda$ can only change by transport across $\partial\Delta$. If, in thermal equilibrium, energy and particle number are uniformly distributed throughout the volume Λ, then many non-equilibrium states cannot pass directly into equilibrium because the transport requires time and intermediate macro states. We thus consider the following, more realistic variant of the finite model.

Of 100 identical particles, each one can assume one of 10^{10} different micro states; so, $M = {}^N\Gamma_1$ with $N = 100$ and $\#\Gamma_1 = 10^{10}$. We ignore energy; let Γ_1 be divided in 10 cells A_i of equal size, and let T be purely random subject to the constraint that only one particle moves in every time step, and that it can only move from A_i to $A_{i-1} \cup A_i \cup A_{i+1}$. Let the macro variables be $N_i = \#\{j = 1, \dots, N : x_j \in A_i\}$ (without any coarse graining such as rounding). We start at a random x with $N_1 = N$, $N_2 = \dots = N_{10} = 0$.

(a) Determine approximately the probabilities of a transition from one macro set to another. What changes if T is required to be ergodic?

(b) Create a numerical simulation of the history $t \mapsto S(x(t))$ in the first 1000 time steps. Use a programming language or math software of your choice.

Remark. Our definition of "macro set" requires rounding. As a consequence of not rounding the N_i, the largest macro set is not dominant and entropy fluctuates more than usually, although the upwards trend is still visible.

Hand in: Wednesday, June 19, 2019, in the exercise class.