$S(x) = k \log \mathrm{vol}\, \Gamma_\nu$ with $x \in \Gamma_\nu$.

Boltzmann's macro variables

Γ_1 $\qquad\qquad$ $\Gamma \ni x$

partition: $A_1 \ldots A_\nu \subseteq \Gamma_1$

$\Delta_i = \mathrm{vol}_6(A_i)$,

occupation no.

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

$$f_i = \left[\frac{N_i}{N \Delta_i \Delta f}\right] \Delta f \qquad \Delta f$$

macro variables

$$f = (f_i)_{i=1}^{r} = \nu$$

$$\mathrm{vol}_{6N} \Gamma_\nu = \frac{1}{N!} \quad \overset{?}{\ldots\ldots\ldots}$$

multinomial coeff = #(fcts $\{1 \ldots N\} \to \{1 \ldots r\}$ s.t. i occurs N_i times) $= \dfrac{N!}{N_1!\, N_2! \cdots N_r!}$

$$\mathrm{vol}_{6N}\{x : \text{given } N_i\} = \frac{1}{N!} \binom{N}{N_1 \ldots N_r} \prod_{i=1}^{r} \Delta_i^{N_i}$$

$$N\left(f_i - \frac{\Delta f}{2}\right)\Delta_i \le N_i < N\left(f_i + \frac{\Delta f}{2}\right)\Delta_i$$

interval of length $N \Delta f \Delta_i$

regard vol $\{x : \text{given } N_i\}$ as const. in this interval, $N_i \leftarrow f_i N \Delta_i$,

so $$\mathrm{vol}\,\Gamma_\nu \approx \frac{1}{N!}\left(\prod_{i=1}^{r} N\Delta f \Delta_i\right)\left(\prod_{i=1}^{r} \frac{\Delta_i^{N_i}}{N_i!}\right)$$

$\Gamma(n+1) \approx$

use Stirling's formula $n! \approx n^n e^{-n} \sqrt{n}\sqrt{2\pi}\,(1+o(1))$ as $n \to \infty$

so $\log \mathrm{vol}\,\Gamma_\nu =$

$$\log n! \approx n \log n - n + o(n)$$
$$+ \cancel{\tfrac{1}{2}\log n + \log\sqrt{2\pi}}$$

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

$$\approx k \log \prod_{i=1}^{r} \left(N \Delta f \Delta_i \frac{\Delta_i^{N f_i \Delta_i}}{(N f_i \Delta_i)!} \right)$$

with $x! = \Gamma(x+1)$

$$\overset{\text{stirling}}{\approx} k \sum_{i=1}^{r} \Big(\log N + \log \Delta f + \log \Delta_i + N f_i \Delta_i \log \Delta_i - N f_i \Delta_i \lg (N f_i \Delta_i) + \cancel{\log} N f_i \Delta_i + o(N) \Big)$$

$$= \underbrace{kr\log N}_{o(N)} + \underbrace{kr\log \Delta f}_{o(N)} + \underbrace{k\sum_{i=1}^{r} \log \Delta_i}_{o(N)} + \cancel{k\sum_i N f_i \Delta_i \log \Delta_i}$$

$$- k\sum N f_i \Delta_i \log (N f_i) - \cancel{k \sum N f_i \Delta_i \log \Delta_i}$$

$$+ \underbrace{k \sum N f_i \Delta_i}_{\approx N} + o(N)$$

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

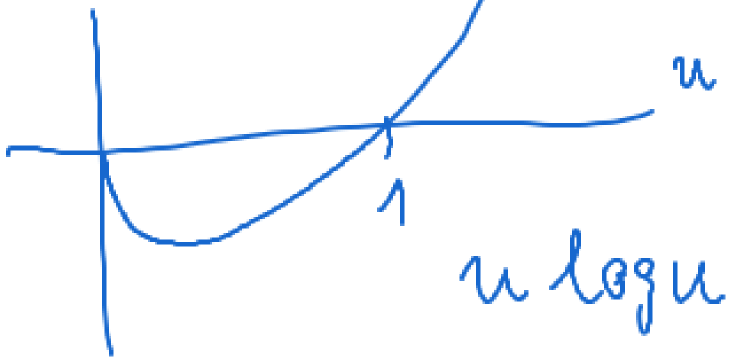
or $s(f) = \dfrac{S(f)}{N} = \cancel{-k\log N} + k - k\sum_i \Delta_i f_i \log f_i$

continuum limit $r \to \infty$

$$s(f) = \cancel{-k \log N + k} - k \int_{\Gamma_1} dx_1 \, f(x_1) \log f(x_1)$$

Remarks

1)



$$\lim_{u \downarrow 0} u \log u = 0$$

$u \log u : (0,\infty) \longrightarrow \mathbb{R}$

$u \log u : [0,\infty) \longrightarrow \mathbb{R}$

$0 \log 0 := 0$

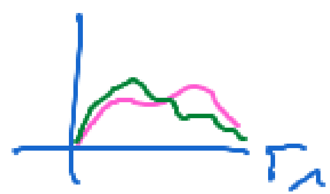
2) Boltzmann wrote

$$S(f) = -k \int_{\Gamma_1} dx_1 \, \underbrace{N f(x_1)}_{f} \log \big(\underbrace{N f(x_1)}_{f} \big)$$

misleading

3) dramatic size differences

$$\frac{\mathrm{vol}\ \Gamma_{\nu = f}}{\mathrm{vol}\ \Gamma_{\nu' = f'}} \approx e^{N(s(f) - s(f'))/k}$$



Dominant macro states

Assume interaction energy is negligible

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

$$\Rightarrow \quad E \approx N \int_{\Gamma_1} dx_1 \, H_1(x_1) f_1(x_1)$$

$\approx H_1(x_1)$ $\forall x_1 \in A_i$.

(as an approx. of $\quad E \approx N \sum_{i=1}^{r} H_i \, \Delta i \, f_i$

Maximize $S(f) = -\cancel{kN} \sum_{i=1}^{r} \Delta_i f_i \log f_i$

under the constraints

1) $\sum_i \Delta_i f_i = 1$

2) $\sum_i H_i \Delta_i f_i = \frac{E}{N} =: e$

$$-\sum_i \Delta_i f_i \log f_i + \alpha \left(1 - \sum_i \Delta_i f_i\right) + \beta \left(e - \sum_i H_i \Delta_i f_i\right)$$

$= \max!$

$$0 = \frac{\partial}{\partial f_k} \sum_i \Delta_i f_i \left[-\log f_i - \alpha - \beta H_i \right]$$

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

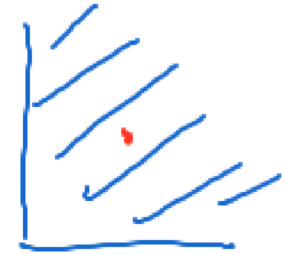
$$= \Delta_k \left(-\log f_k - \alpha - 1 - \beta H_k \right)$$

$$\Longleftrightarrow \quad \log f_k = -\alpha - 1 - \beta H_k$$

$$\Longleftrightarrow \quad f_k = e^{-\alpha - 1 - \beta H_k} = \frac{1}{Z} e^{-\beta H_k}$$

Maxw.-Boltzm. Distr.

2nd derivative test



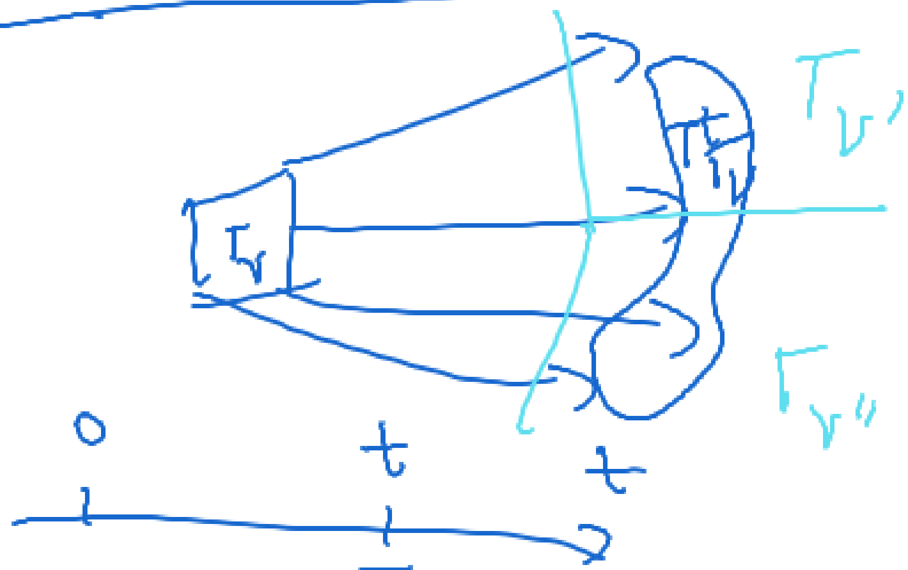
$[0,\infty)^r$

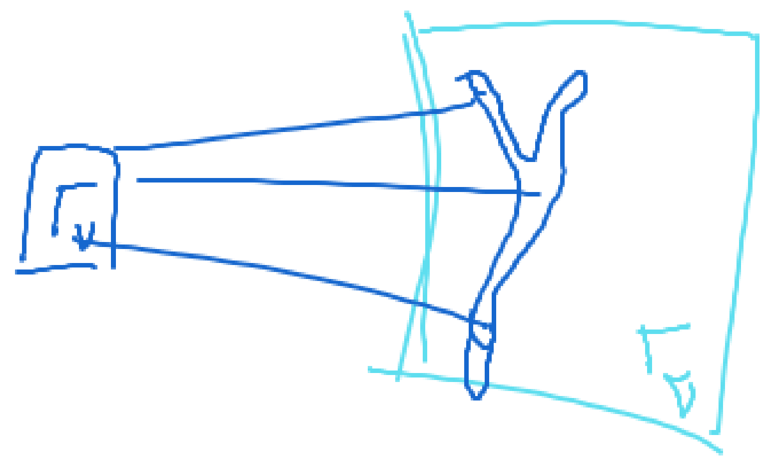
Hess $S(f)$ =

$$\partial_{f_j}\partial_{f_k} S(f) = -\delta_{jk}\,\Delta_k \frac{1}{f_k}$$

in fact, it is a global max.

The Case of Autonomous Macro Evolution





$$\bar\nu = F_t(\nu)$$

$T(x,t)$

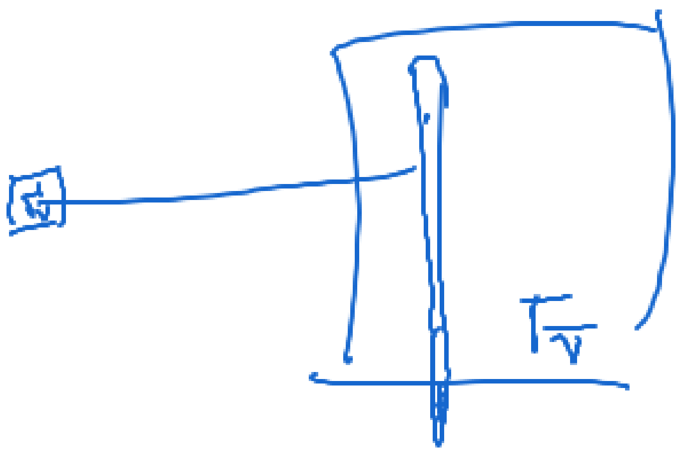
macro evolution, almost deterministic

- Euler eq.s
- Navier-Stokes eq.s

- heat eq. $\frac{\partial T}{\partial t} = \pm \Delta T$
- Boltzmann eq. $\frac{\partial f}{\partial t} = \cdots$

Conseq: If macro evolution, then

$$S(X_t) \geq S(X_0)$$ (except for a minority of phase points).



$$S(\bar{v}) \gtrsim S(v)$$

Ergodicity

Statement: " $m_j^{eq} \approx \langle M_j \rangle$ "

A suggested Explanation: "Any macro measurements will take a time long on a micro time scale, so $\approx \infty$, so result $\neq M_j(X_t)$ but result $=$ time average of $M_j(X_t)$

$\overset{\text{ergodicity}}{=}$ ens. average of $M_j = \langle M_j \rangle$."

incorrect.