Direction of time and foundations of statistical physics

The H-theorem and the notion of equilibrium

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Setup

We consider a system consisting of a large number of identical subsystems ("particles").

N	number of particles
m	number of states for each particle
m^N	number of microstates
$N_i \;\; (i = 1, ..., m)$	occupation number
$\{N_i\}_{i=1,...,m}$	distribution
$Y(\{N_i\})$	realization number
$S = k \ln Y(\{N_i\})$	entropy

Assumptions

1) Possible processes

- Two-particle interaction ("collision"):[1] $ij \to kl$
- (Free motion: $i \to k$, where i and k only differ in the position of the particle. We will not include this.)[2]

2) Stoßzahlansatz

Number of collisions of type $ij \to kl$ during unit time:

$$n_{ij\to kl} \approx W_{ij}^{kl} N_i N_j \quad \left(W_{ij}^{kl} \geq 0\right)$$

[1] The order of state indices doesn't matter: for example, $12 \to 34$ and $21 \to 43$ denote the same process.

[2] One approach is to say that the one-particle states i, j, k, l only incorporate the momentum degrees of freedom; and the position degrees of freedom are taken care of separately. This is justified to the extent that we will be interested in the entropy of the system and the entropy associated with the momentum and position degrees of freedom just add up. More precisely, in case where the one-particle states are labeled by pairs of coarse-grained position and momentum indices, $i = (\alpha, \beta)$, then $Y(\{N_i\}) = Y(\{N_\alpha\})\, Y\left(\{N_\beta\}\right)$ and so $S = k\ln Y(\{N_\alpha\}) + k\ln Y\left(\{N_\beta\}\right) = S_{position} + S_{momentum}$.

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3) Time reversal invariance + rotation symmetry + local interactions

$$W_{ij}^{kl} = W_{kl}^{ij}$$

Illustration of Assumption 3

Suppose that states are $(\mathbf{x}, \mathbf{p})$-s (position + momentum) coarse-grained into small phase space cells.

Assume for simplicity that we are in 2D and consider the following transformations of states:

- Time reversal:
$$T(\mathbf{x}, \mathbf{p}) = (\mathbf{x}, -\mathbf{p})$$
- Spatial rotation by 180° about the origin of a given coordinate system:
$$R(\mathbf{x}, \mathbf{p}) = (-\mathbf{x}, -\mathbf{p})$$

Their combination yields
$$RT(\mathbf{x}, \mathbf{p}) = (-\mathbf{x}, \mathbf{p})$$

Illustration of Assumption 3

Assume that particles only collide if they are in the same spatial cell, and consider an R whose axis goes through the spatial cell where a given collision $ij \to kl$ takes place, such that $\mathbf{x}$ and $-\mathbf{x}$ fall into the same spatial cell, for the position $\mathbf{x}$ of each particle that figures in the collision, both before and after the collision. Then we have

$$"RT\,(ij \to kl)" = RTk, RTl \to RTi, RTj = kl \to ij \tag{1}$$

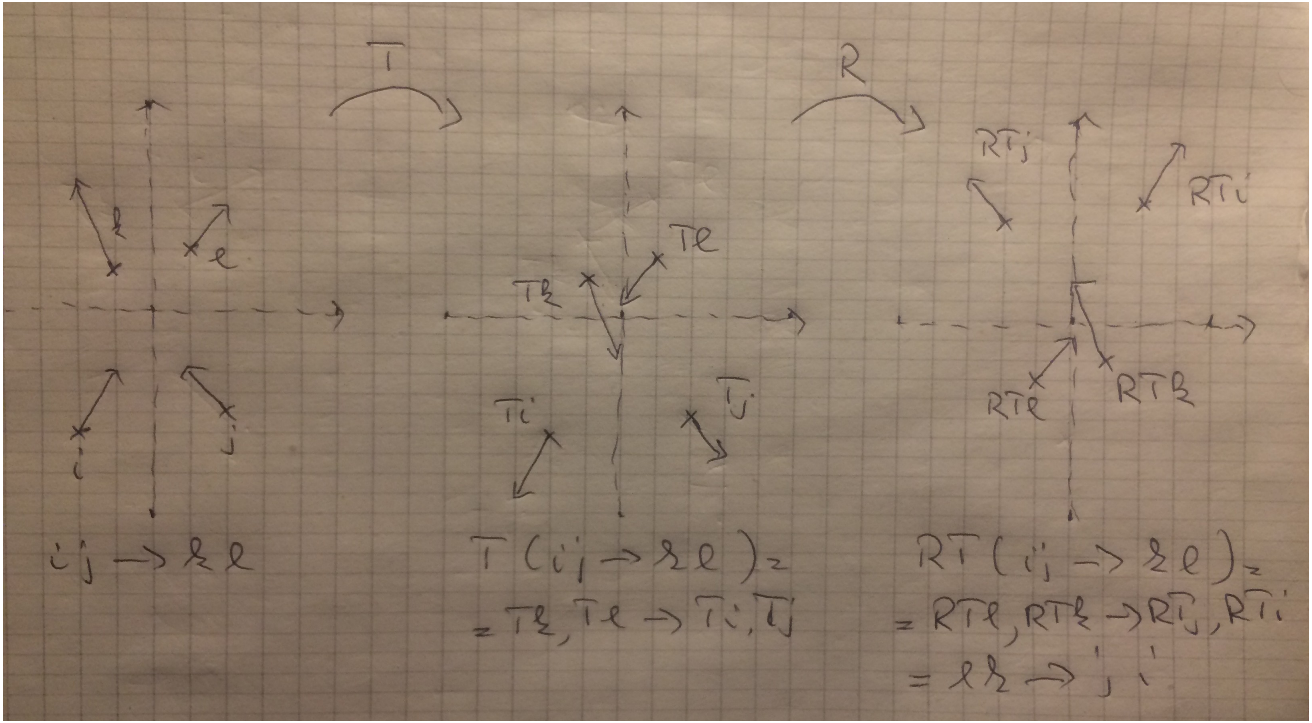
On the other hand, assume the interaction obeys the following symmetries:

- Time reversal invariance:
$$W_{Tk,Tl}^{Ti,Tj} = W_{ij}^{kl} \tag{2}$$
- Rotation invariance:
$$W_{Ri,Rj}^{Rk,Rl} = W_{ij}^{kl} \tag{3}$$

All in all, we have

$$W_{kl}^{ij} \overset{(1)}{=} W_{RTk,RTl}^{RTi,RTj} \overset{(2)\&(3)}{=} W_{ij}^{kl}$$

Illustration of Assumption 3



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Assumptions

4) Energy conservation

- For any collision $ij \to kl$:
$$E_i + E_j = E_k + E_l$$
- Since energy doesn't change in processes, the total energy is conserved:
$$E = \sum_i N_i E_i$$

Change of occupation numbers during unit time

$$\begin{aligned}
\Delta N_i &= \sum_{pq,r\neq i} n_{pq\to ir} + 2\sum_{pq} n_{pq\to ii} - \sum_{pq,r\neq i} n_{ir\to pq} - 2\sum_{pq} n_{ii\to pq} \\
&= \sum_{pq,r\neq i} \left(n_{pq\to ir} - n_{ir\to pq}\right) + 2\sum_{pq} \left(n_{pq\to ii} - n_{ii\to pq}\right) \\
&\overset{2.}{\approx} \sum_{pq,r\neq i} \left(W_{pq}^{ir} N_p N_q - W_{ir}^{pq} N_i N_r\right) + 2\sum_{pq} \left(W_{pq}^{ii} N_p N_q - W_{ii}^{pq} N_i N_i\right) \\
&\overset{3.}{=} \sum_{pq,r\neq i} W_{pq}^{ir} \left(N_p N_q - N_i N_r\right) + 2\sum_{pq} W_{pq}^{ii} \left(N_p N_q - N_i N_i\right)
\end{aligned}$$

Qualitative analysis:

- If N_i is large(r than typical occupation numbers), then $\Delta N_i < 0$
- If N_i is small(er than typical occupation numbers), then $\Delta N_i > 0$

Hence, “occupation numbers tend to equalize.”

A more precise analysis: change of entropy during unit time

$$S = k\ln Y\left(\{N_i\}\right) = k\ln\frac{N!}{N_1!\ldots N_m!} = k\ln N! - \sum_i k\ln N_i! \overset{\text{Stirling}}{\approx} kN\ln N - k\underbrace{\sum_i N_i \ln N_i}_{\text{Boltzmann's } H \text{ function}}$$

$$\begin{aligned}\Delta S &\approx \frac{dS}{dt} \approx -k\sum_i\left(\frac{dN_i}{dt}\ln N_i + N_i\frac{d\ln N_i}{dN_i}\frac{dN_i}{dt}\right) = -k\sum_i\frac{dN_i}{dt}\left(\ln N_i + 1\right)\\ &= -k\sum_i\frac{dN_i}{dt}\ln N_i - k\sum_i\frac{dN_i}{dt} = -k\sum_i\frac{dN_i}{dt}\ln N_i - k\frac{dN}{dt} = -k\sum_i\frac{dN_i}{dt}\ln N_i\\ &\approx -k\sum_i\Delta N_i\ln N_i\end{aligned}$$

A more precise analysis: change of entropy during unit time

$$
\begin{aligned}
\Delta S &\approx -k \sum_r \Delta N_r \ln N_r \\
&= -k \sum_{\substack{ijkl \\ i\le j, k\le l}} n_{ij\to kl} \left(\ln N_k + \ln N_l - \ln N_i - \ln N_j\right) = -k \sum_{\substack{ijkl \\ i\le j, k\le l}} n_{ij\to kl} \ln \frac{N_k N_l}{N_i N_j} \\
&= -k \sum_{\substack{ijkl \\ i\le j, k\le l, ij\le kl}} \left(n_{ij\to kl} \ln \frac{N_k N_l}{N_i N_j} + n_{kl\to ij} \ln \frac{N_i N_j}{N_k N_l} \right) \\
&\overset{2.}{\approx} -k \sum_{\substack{ijkl \\ i\le j, k\le l, ij\le kl}} \left(W_{ij}^{kl} N_i N_j \ln \frac{N_k N_l}{N_i N_j} + W_{kl}^{ij} N_k N_l \ln \frac{N_i N_j}{N_k N_l} \right) \\
&\overset{3.}{=} -k \sum_{\substack{ijkl \\ i\le j, k\le l, ij\le kl}} W_{ij}^{kl} \left(N_i N_j - N_k N_l \right) \ln \frac{N_k N_l}{N_i N_j}
\end{aligned}
$$

$ij \le kl$ means $i \le k$, and $j \le l$ if $i = k$, that is pairs of states are ordered lexicographically. For example, $12 \le 34$ and $24 \le 33$.

A more precise analysis: change of entropy during unit time

$$\Delta S \approx -k \sum_{\substack{ijkl \\ i\leq i, k\leq l, ij\leq kl}} W_{ij}^{kl} \left(N_i N_j - N_k N_l\right) \ln \frac{N_k N_l}{N_i N_j}$$

Each term in this sum is of the form

$$c\,(x-y)\ln\frac{y}{x}$$

with $c \leq 0$, $x, y > 0$, thus:

- If $x \geq y$, then $x - y \geq 0$ and $\ln\frac{y}{x} \leq 0$ and so $c\,(x-y)\ln\frac{y}{x} \geq 0$
- If $x \leq y$, then $x - y \leq 0$ and $\ln\frac{y}{x} \geq 0$ and so $c\,(x-y)\ln\frac{y}{x} \geq 0$

Hence, each term in this sum ≥ 0 and so

$$\Delta S \geq 0$$

Equilibrium distribution

$$\frac{dN_i}{dt} = 0 \ (i = 1, ..., m) \quad \Rightarrow \quad \frac{dS}{dt} = 0$$

Since each term of

$$\frac{dS}{dt} \approx -k \sum_{\substack{ijkl \\ i \leq i, k \leq l, ij \leq kl}} W_{ij}^{kl} \left(N_i N_j - N_k N_l \right) \ln \frac{N_k N_l}{N_i N_j}$$

is non-negative individually, equilibrium entails

$$N_i N_j = N_k N_l$$

if $W_{ij}^{kl} \neq 0$.[3]

[3]This means that in equilibrium, for all *ijkl* we have: $n_{ij \to kl} = n_{kl \to ij}$

Distribution of maximum entropy (the most "homogeneous" distribution)

$$S \approx kN\ln N - k\sum_i N_i \ln N_i \;\to\; \max \text{ in } \{N_i\}$$

under the constraints

$$\sum_i N_i = N$$

$$\sum_i N_i E_i = E$$

Interlude: method of Lagrange multipliers for constrained optimization

$$f\left(x_1, ..., x_n\right) \to \max$$

under the constraints

$$g_1\left(x_1, ..., x_n\right) = c_1$$
$$\vdots$$
$$g_M\left(x_1, ..., x_n\right) = c_M$$

Interlude: method of Lagrange multipliers for constrained optimization

Introduce the following so-called Lagrange function:

$$L\left(x_1,...,x_n,\lambda_1,...,\lambda_M\right) := f\left(x_1,...,x_n\right) - \sum_k \lambda_k \left(g_k\left(x_1,...,x_n\right) - c_k\right)$$

with added variables $\lambda_1,...,\lambda_M$, so-called Lagrange multipliers.

Necessary condition for maximizing f under the given constraints:

$$\frac{\partial L\left(x_1,...,x_n,\lambda_1,...,\lambda_M\right)}{\partial x_i} = \frac{\partial f\left(x_1,...,x_n\right)}{\partial x_i} - \sum_k \lambda_k \frac{\partial g_k\left(x_1,...,x_n\right)}{\partial x_i} = 0 \quad (i = 1,...,n)$$

$$g_k\left(x_1,...,x_n\right) = c_k \quad (k = 1,...,M)$$

yielding $n + M$ equations for the $n + M$ unknowns $x_1,...,x_n,\lambda_1,...,\lambda_M$.

Interlude: meaning of the Lagrange multipliers

Let $x_1^*(\mathbf{c}), ..., x_n^*(\mathbf{c}), \lambda_1^*(\mathbf{c}), ..., \lambda_M^*(\mathbf{c})$ be the solution of the above equations, regarded as a function of the parameters $\mathbf{c} := (c_1, ..., c_M)$, and introduce

$$f^*(\mathbf{c}) := f(x_1^*(\mathbf{c}), ..., x_n^*(\mathbf{c}))$$

the maximal value of f as a function of the parameters $c_1, ..., c_M$. Then

$$\lambda_i^*(\mathbf{c}) = \frac{\partial f^*(\mathbf{c})}{\partial c_i}$$

Proof.

$$\begin{aligned}
\frac{\partial f^*(\mathbf{c})}{\partial c_i} &= \sum_j \frac{\partial f}{\partial x_j}(x_1^*(\mathbf{c}), ..., x_n^*(\mathbf{c})) \frac{\partial x_j^*}{\partial c_i}(\mathbf{c}) \overset{\frac{\partial L}{\partial x_j}=0}{=} \sum_j \left(\sum_k \lambda_k(\mathbf{c}) \frac{\partial g_k}{\partial x_j}(x_1^*(\mathbf{c}), ..., x_n^*(\mathbf{c})) \right) \frac{\partial x_j^*}{\partial c_i}(\mathbf{c}) \\
&= \sum_k \lambda_k(\mathbf{c}) \left(\sum_j \frac{\partial g_k}{\partial x_j}(x_1^*(\mathbf{c}), ..., x_n^*(\mathbf{c})) \frac{\partial x_j^*}{\partial c_i}(\mathbf{c}) \right) \\
&= \sum_k \lambda_k(\mathbf{c}) \frac{\partial g_k(x_1^*(\mathbf{c}), ..., x_n^*(\mathbf{c}))}{\partial c_i} \overset{g_k = c_k}{=} \lambda_i(\mathbf{c})
\end{aligned}$$

Distribution of maximum entropy (the most "homogeneous" distribution)

$$S \approx kN\ln N - k\sum_i N_i \ln N_i \;\rightarrow\; \text{max in } \{N_i\}$$

under the constraints

$$\sum_i N_i = N$$
$$\sum_i N_i E_i = E$$

If the N_i-s are large enough, we can consider them as continuous variables, and apply the method of Lagrange multipliers.

Distribution of maximum entropy (the most "homogeneous" distribution)

Lagrange function:

$$L\left(N_1, ..., N_m, \alpha, \beta\right) = kN\ln N - k\sum_i N_i \ln N_i - \alpha\left(\sum_i N_i - N\right) - \beta\left(\sum_i N_i E_i - E\right)$$

Necessary condition for maximum entropy under the given constraints:

$$\frac{\partial L\left(N_1, ..., N_m, \alpha, \beta\right)}{\partial N_i} = -k\left(\ln N_i + 1\right) - \alpha - \beta E_i = 0 \quad (i = 1, ..., m)$$

$$\sum_i N_i = N$$

$$\sum_i N_i E_i = E$$

yielding $m + 2$ equations for the $m + 2$ unknowns $N_1, ..., N_m, \alpha, \beta$.

Distribution of maximum entropy (the most "homogeneous" distribution)

The solution is the Maxwell–Boltzmann distribution:

$$N_i^* = \frac{N e^{-\frac{\beta^* E_i}{k}}}{Z}$$

with $Z(N,E) = \sum_j e^{-\frac{\beta^* E_j}{k}}$, and $\beta^*(N,E) = \frac{\partial S^*(N,E)}{\partial E}$ due the meaning of Lagrange multipliers.

This is an equilibrium distribution since it satisfies

$$N_i N_j = N_k N_l$$

if $W_{ij}^{kl} \neq 0$, given that

$$E_i + E_j = E_k + E_l$$

due to energy conservation.

Equilibrium distribution

Conversely, any equilibrium distribution of the form

$$N_i = f(E_i)$$

must be the Maxwell–Boltzmann distribution.

Proof. We have

$$f(E_i) f(E_j) = f(E_k) f(E_l)$$
$$E_i + E_j = E_k + E_l$$

$E_j = 0$ yields

$$f(E_i) = f(E_k + E_l) = \frac{f(E_k) f(E_l)}{f(0)}$$

which is the form

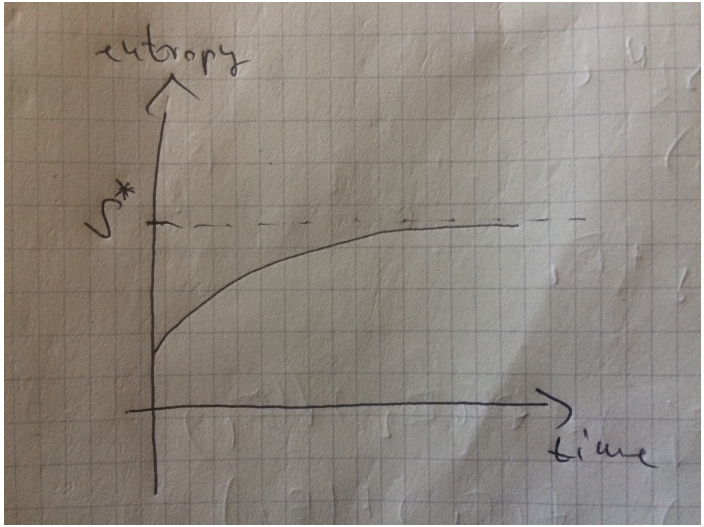
$$f(x+y) = af(x) f(y)$$

Assuming that x and y can take any real value, differentiate this with respect to y and take $y = 0$:

$$f'(x) = af(x) f'(0) = bf(x)$$

The only solution of this differential equation is an exponential function $f(x) = Ae^{bx}$, with $N_i = f(E_i)$ subjected to the same constraints $\sum_i N_i = N$ and $\sum_i N_i E_i = E$ as the Maxwell–Boltzmann distribution.

Picture of time evolution



Maximum entropy:

$$S^*(N,E) = k\ln Y(\{N_i^*\}) \approx kN\ln N - k\sum_i N_i^*\ln N_i^* = kN\ln Z(N,E) + \beta^*(N,E)\,E$$

Subtle questions for consideration

- Is the Maxwell–Boltzmann distribution really the only equilibrium distribution?
- Does the system evolve into/approach the Maxwell–Boltzmann distribution? ($\frac{dS}{dt} \geq 0$ does not itself ensure this.)