Equilibrium distributions

Canonical ensembles

We maximise the entropy under the conditions

$$\begin{aligned} \langle H \rangle &= \mathrm{Tr}\, \rho H = E = \text{constant} \\ \langle I \rangle &= \mathrm{Tr}\, \rho = 1. \end{aligned}$$

So, we require that

$$\delta(S - \lambda \langle H \rangle - \lambda' \langle I \rangle) = 0,$$

where λ are λ' are Lagrange multipliers. We get

$$\begin{aligned} &\delta \mathrm{Tr}\,(-k_B \rho \ln \rho - \lambda \rho H - \lambda' \rho) = \\ &\qquad \mathrm{Tr}\,(-k_B \ln \rho - k_B - \lambda H - \lambda' I)\delta\rho = 0. \end{aligned}$$

Since $\delta\rho$ is an arbitrary variation, we end up with the *canonical* or *Gibbs distribution*

$$\rho = \frac{1}{Z}\, e^{-\beta H},$$

where Z is the *canonical sum over states* (or *partition function*)

$$Z = \mathrm{Tr}\, e^{-\beta H} = \sum_n e^{-\beta E_n} = \int dE\, \omega(E) e^{-\beta E}.$$

Note In the canonical ensemble the number of particles is constant, i.e.

$$Z = Z(p, V, N, \ldots).$$

The probability for the state ψ is

$$p_\psi = \mathrm{Tr}\, \rho P_\psi = \frac{1}{Z}\, \langle \psi | e^{-\beta H} | \psi \rangle.$$

Partcularly, in the case of an eigenstate of the Hamiltonian,

$$H\, |n\rangle = E_n\, |n\rangle\,,$$

we have

$$p_n = \frac{1}{Z}\, e^{-\beta E_n}.$$

For one particle system we get *Boltzmann distribution*

$$p_\nu = \frac{1}{Z}\, e^{-\beta \epsilon_\nu};\;\; Z = \sum_\nu e^{-\beta \epsilon_\nu}.$$

Here ϵ_ν is the one particle energy.
Because in the canonical ensemble we have

$$\ln \rho = -\beta H - \ln Z,$$

the entropy will be

$$\begin{aligned} S &= -k_B \mathrm{Tr}\, \rho \ln \rho = -k_B \langle \ln \rho \rangle \\ &= k_B \beta E + k_B \ln Z. \end{aligned}$$

Here E is the expectation value of the energy

$$E = \langle H \rangle = \frac{1}{Z}\, \mathrm{Tr}\, H e^{-\beta H}.$$

The variation of the partition function is

$$\begin{aligned} \delta Z &= \mathrm{Tr}\, \delta \left(e^{-\beta H}\right) = -\delta\beta\, \mathrm{Tr}\, H e^{-\beta H} \\ &= -\delta\beta\, E Z. \end{aligned}$$

The variation of the enetropy is then

$$\begin{aligned} \delta S &= k_B \left(E\, \delta\beta + \beta\, \delta E + \frac{\delta Z}{Z} \right) \\ &= k_B \beta\, \delta E. \end{aligned}$$

According to thermodynamics the temperature will be

$$T = \left(\frac{\delta E}{\delta S} \right)_{V,N} = \frac{1}{k_B \beta},$$

or

$$\beta = \frac{1}{k_B T}.$$

Free energy
Since

$$\frac{\partial}{\partial \beta}\, Z = -\mathrm{Tr}\, e^{-\beta H} H = -Z\, \langle H \rangle$$

or

$$E = -\frac{\partial}{\partial \beta}\, \ln Z = k_B T^2 \frac{\partial \ln Z}{\partial T},$$

we can write

$$S = k_B \frac{\partial}{\partial T}\, (T \ln Z)\,.$$

The Helmholtzin free energy $F = E - TS$ can be expressed as

$$F = -k_B T \ln Z.$$

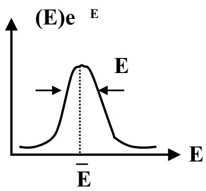
With the help of this the density operator takes the form

$$\rho = e^{\beta(F - H)}.$$

Fluctuations
Let us write the sum over states as

$$Z = \int dE\, \omega(E) e^{-\beta E} = \int dE\, e^{-\beta E + \ln \omega(E)}.$$

We suppose that the function $\omega(E)e^{-\beta E}$ has a sharp maximum at $E = \bar{E}$ and that $\omega(E) \approx$ microcanonical state density.



Now

$$\ln \omega(E) = \frac{1}{k_B}\, S(E)$$

and

$$\begin{aligned} &\ln \omega(E) - \beta E = \\ &\quad \ln \omega(\bar{E}) - \beta \bar{E} \\ &\quad + \overbrace{\left(\frac{1}{k_B}\, \frac{\partial S}{\partial E}\bigg|_{E=\bar{E}} - \beta \right)}^{=0,\ \text{maximum}} (E - \bar{E}) \\ &\quad + \frac{1}{2k_B}\, \frac{\partial^2 S}{\partial E^2}\bigg|_{E=\bar{E}} (E - \bar{E})^2 + \cdots. \end{aligned}$$

At the point of maximum $E = \bar{E}$ we have

$$\begin{aligned} k_B\beta &= \left.\frac{\partial S}{\partial E}\right|_{E=\bar{E}} = \frac{1}{T(\bar{E})} \\ &= \frac{1}{\text{average temperature}}. \end{aligned}$$

So T is the average temperature. In the Taylor series

$$\frac{\partial^2 S}{\partial E^2} = \frac{\partial}{\partial E}\left(\frac{1}{T}\right) = -\frac{1}{T^2}\frac{\partial T}{\partial E} = -\frac{1}{T^2 C_V},$$

so

$$Z \approx \omega(\bar{E})e^{-\beta\bar{E}} \int dE \ \underbrace{e^{-\frac{1}{2k_B T^2 C_V}(E-\bar{E})^2}}_{\text{normal distribution}} .$$

As the variance of the normal distribution in the integrand we can pick up

$$(\Delta E)^2 = k_B T^2 C_V$$

or

$$\Delta E = \sqrt{k_B T^2 C_V} = \mathcal{O}(\sqrt{N}),$$

because C_V, as well as E, is extensive ($\mathcal{O}(N)$). Thus the fluctuation of the energy is

$$\frac{\Delta E}{E} \propto \frac{1}{\sqrt{N}}.$$

Note Fluctuations can be obtained more straightforwardly from the free energy:

$$\left\langle (H - \langle H\rangle)^2 \right\rangle = -\frac{\partial^2(\beta F)}{\partial \beta^2}.$$

Grand canonical ensemble

Let's consider a system where both the energy and the number of particles are allowed to fluctuate. The Hilbert space of the system is then the direct sum

$$\mathcal{H} = \mathcal{H}^{(0)} \oplus \mathcal{H}^{(1)} \oplus \cdots \oplus \mathcal{H}^{(N)} \oplus \cdots$$

and the Hamiltonian operator the sum

$$H = H^{(0)} + H^{(1)} + \cdots + H^{(N)} + \cdots.$$

We define the (particle) number operator $\hat{N}$ so that

$$\hat{N}\left|\psi\right\rangle = N\left|\psi\right\rangle \ \forall \left|\psi\right\rangle \in \mathcal{H}^{(N)}.$$

We maximize the entropy S under constraints

$$\begin{aligned} \langle H\rangle &= \bar{E} = \text{given energy} \\ \left\langle \hat{N} \right\rangle &= \bar{N} = \text{given particle number} \\ \langle I\rangle &= 1. \end{aligned}$$

With the help of Lagrange multipliers we start with

$$\delta(S - \lambda\langle H\rangle - \lambda'\left\langle \hat{N}\right\rangle - \lambda''\langle I\rangle) = 0,$$

and end up with the *grand canonical distribution*

$$\rho = \frac{1}{Z_{\mathrm{G}}}\, e^{-\beta(H-\mu\hat{N})}.$$

Here

$$Z_{\mathrm{G}} = \mathrm{Tr}\, e^{-\beta(H-\mu\hat{N}))}$$

is the *grand canonical partition function.* In the base where the Hamiltonian is diagonal this is

$$Z_{\mathrm{G}} = \sum_N \sum_n e^{-\beta(E_n^{(N)} - \mu N)},$$

where

$$H\left|N;n\right\rangle = H^{(N)}\left|N;n\right\rangle = E_n^{(N)}\left|N;n\right\rangle,$$

when $\left|N;n\right\rangle \in \mathcal{H}^{(N)}$ is a state of N particles, i.e.

$$\hat{N}\left|N;n\right\rangle = N\left|N;n\right\rangle.$$

Number of particles and energy

Now

$$\begin{aligned} \frac{\partial \ln Z_{\mathrm{G}}}{\partial \mu} &= \frac{1}{Z_{\mathrm{G}}}\,\mathrm{Tr}\, e^{-\beta(H-\mu\hat{N})}\beta\hat{N} \\ &= \beta\left\langle \hat{N}\right\rangle = \beta\bar{N} \end{aligned}$$

and

$$\begin{aligned} \frac{\partial \ln Z_{\mathrm{G}}}{\partial \beta} &= -\frac{1}{Z_{\mathrm{G}}}\,\mathrm{Tr}\, e^{-\beta(H-\mu\hat{N})}(H-\mu\hat{N}) \\ &= -\langle H\rangle + \mu\left\langle \hat{N}\right\rangle = -\bar{E} + \mu\bar{N}, \end{aligned}$$

so

$$\begin{aligned} \bar{N} &= k_B T\,\frac{\partial \ln Z_{\mathrm{G}}}{\partial \mu} \\ \bar{E} &= k_B T^2 \frac{\partial \ln Z_{\mathrm{G}}}{\partial T} + k_B T\mu\,\frac{\partial \ln Z_{\mathrm{G}}}{\partial \mu}. \end{aligned}$$

Entropy

According to the definition we have

$$S = -k_B \mathrm{Tr}\,\rho\ln\rho = -k_B\left\langle \ln\rho\right\rangle.$$

Now

$$\ln\rho = -\beta H + \beta\mu\hat{N} - \ln Z_{\mathrm{G}},$$

so

$$S = \frac{\bar{E}}{T} - \mu\,\frac{\bar{N}}{T} + k_B \ln Z_{\mathrm{G}}.$$

Grand potential

In thermodynamics we defined

$$\Omega = E - TS - \mu N,$$

so in the grand canonical ensemble the *grand potential* is

$$\Omega = -k_B T \ln Z_{\mathrm{G}}.$$

With the help of this the density operator can be written as

$$\rho = e^{\beta(\Omega - H + \mu\hat{N})}.$$

Note The grand canonical state sum depends on the varaibles T, V and μ, i.e.

$$Z_{\rm G} = Z_{\rm G}(T, V, \mu).$$

Fluctuations
Now

$$\begin{aligned}\frac{\partial^2}{\partial\mu^2}\,{\rm Tr}\, e^{-\beta(H-\mu\hat{N})} &= {\rm Tr}\, e^{-\beta(H-\mu\hat{N})}\beta^2\hat{N}^2 \\ &= Z_{\rm G}\beta^2\left\langle \hat{N}^2\right\rangle,\end{aligned}$$

so

$$\begin{aligned}(\Delta N)^2 &= \left\langle (\hat{N}-\bar{N})^2\right\rangle = \left\langle \hat{N}^2\right\rangle - \bar{N}^2 \\ &= (k_BT)^2\frac{\partial^2 \ln Z_{\rm G}}{\partial\mu^2} = k_BT\frac{\partial\bar{N}}{\partial\mu} = \mathcal{O}(\bar{N}).\end{aligned}$$

Thus the particle number fluctuates like

$$\frac{\Delta N}{\bar{N}} = \mathcal{O}\left(\frac{1}{\sqrt{\bar{N}}}\right).$$

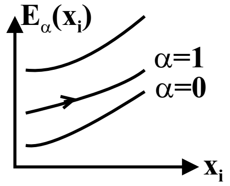
A corresponding expression is valid also for the fluctuations of the energy. For a mole of matter the fluctuations are $\propto 10^{-12}$ or the accuracy $\approx$ the accuracy of the microcanonical ensemble.

Connection with thermodynamics

Let us suppose that the Hamiltonian H depends on external parameters $\{x_i\}$:

$$H(x_i)\left|\alpha(x_i)\right\rangle = E_\alpha(x_i)\left|\alpha(x_i)\right\rangle.$$

Adiabatic variation
A system in the state $|\alpha(x_i)\rangle$ stays there provided that the parameters $x_i(t)$ are allowed to vary slowly enough.



Then the probabilities for the states remain constant and the change in the entropy

$$S = -k_B\sum_\alpha p_\alpha \ln p_\alpha$$

is zero. Now

$$\begin{aligned}\frac{\partial E_\alpha}{\partial x_i} &= \frac{\partial}{\partial x_i}\left\langle\alpha\right| H\left|\alpha\right\rangle = \left\langle\alpha\left|\frac{\partial H}{\partial x_i}\right|\alpha\right\rangle + E_\alpha\frac{\partial}{\partial x_i}\left\langle\alpha\right|\left.\alpha\right\rangle \\ &= \left\langle\alpha\left|\frac{\partial H}{\partial x_i}\right|\alpha\right\rangle,\end{aligned}$$

since $\langle\alpha|\,\alpha\rangle = 1$.
Let F_i be the generalized force

$$F_i = -\left\langle\alpha\left|\frac{\partial H}{\partial x_i}\right|\alpha\right\rangle = -\frac{\partial E_\alpha}{\partial x_i}$$

and δx_i the related displacement. Then

$$\delta\left\langle H\right\rangle = -\sum_i F_i\delta x_i.$$

Statistical study
Let us consider the density operator in an equilibrium state ($[H,\rho]=0$). In the base $\{|\alpha\rangle\}$, where the Hamiltonian is diagonal,

$$H\left|\alpha\right\rangle = E_\alpha\left|\alpha\right\rangle,$$

we have

$$\rho = \sum_\alpha p_\alpha P_\alpha,$$

where

$$P_\alpha = \left|\alpha\right\rangle\left\langle\alpha\right|.$$

We divide the variation of the density operator into two parts:

$$\begin{aligned}\delta\rho &= \overbrace{\sum_\alpha p_\alpha\delta P_\alpha}^{\text{adiabatic}} + \overbrace{\sum_\alpha \delta p_\alpha P_\alpha}^{\text{nonadiabatic}} \\ &= \delta\rho^{(1)} + \delta\rho^{(2)}.\end{aligned}$$

Then

$$\begin{aligned}\delta\left\langle H\right\rangle &= {\rm Tr}\,\delta\rho\, H + {\rm Tr}\,\rho\,\delta H \\ &= {\rm Tr}\,\delta\rho^{(1)}H + {\rm Tr}\,\delta\rho^{(2)}H + \sum_i\delta x_i{\rm Tr}\,\rho\,\frac{\partial H}{\partial x_i} \\ &= \sum_\alpha p_\alpha{\rm Tr}\,H\,\delta P_\alpha + {\rm Tr}\,\delta\rho^{(2)}H - \sum_i F_i\delta x_i.\end{aligned}$$

Now

$$\begin{aligned}{\rm Tr}\,H\,\delta P_\alpha &= \sum_\beta\left\langle\beta\right| H\left(\left|\alpha\right\rangle\left\langle\delta\alpha\right| + \left|\delta\alpha\right\rangle\left\langle\alpha\right|\right)\left|\beta\right\rangle \\ &= E_\alpha\delta\left\langle\alpha\right|\left.\alpha\right\rangle = 0,\end{aligned}$$

so

$$\delta\left\langle H\right\rangle = {\rm Tr}\,\delta\rho^{(2)}H - \sum_i F_i\delta x_i.$$

Since

$$\begin{aligned}\int dE\,\omega(E)f(E) &= \sum_\alpha\int dE\,\delta(E-E_\alpha)f(E) \\ &= \sum_\alpha f(E_\alpha),\end{aligned}$$

we can write the nonadiabatic term as

$$\begin{aligned}{\rm Tr}\,\delta\rho^{(2)}H &= \sum_\alpha\delta p_\alpha E_\alpha \\ &= \int dE\,\omega(E)E\,\delta p(E).\end{aligned}$$

According to the definition the statistical entropy is

$$S^{\rm stat} = -k_B \sum_\alpha p_\alpha \ln p_\alpha .$$

Its variation is

$$\begin{aligned} \delta S^{\rm stat} &= -k_B \sum_\alpha \delta p_\alpha \, \ln p_\alpha - k_B \overbrace{\sum_\alpha \delta p_\alpha}^{=0} \\ &= -k_B \sum_\alpha \delta p_\alpha \, \ln p_\alpha \\ &= -k_B \int dE \, \omega(E) \, \delta p(E) \, \ln p(E). \end{aligned}$$

In the microcanonical ensemble

$$p(E) \propto \frac{1}{Z_{E,\Delta E}} \propto \frac{1}{\omega(E)},$$

holds, so

$$-k_B \ln p(E) = k_B \ln \omega(E) = S^{\rm stat}(E),$$

where $S^{\rm stat}(E)$ is the microcanonical entropy. The variation of the entropy can be written as

$$\delta S^{\rm stat} = \int dE \, \omega(E) S^{\rm stat}(E) \, \delta p(E).$$

We expand $S^{\rm stat}(E)$ as a Taylor series in a neighborhood of the point $E = \bar{E}$:

$$\begin{aligned} S^{\rm stat}(E) &= S^{\rm stat}(\bar{E}) \\ &\quad + \left. \frac{\partial S^{\rm stat}(E)}{\partial E} \right|_{E=\bar{E}} (E - \bar{E}) + \cdots \\ &= S^{\rm stat}(\bar{E}) + \frac{E - \bar{E}}{T^{\rm stat}(E)} + \cdots . \end{aligned}$$

Since

$$\int dE \, \omega(E) \, \delta p(E) = \sum_\alpha \delta p_\alpha = 0,$$

we get

$$\begin{aligned} \delta S^{\rm stat} &= \frac{1}{T^{\rm stat}(\bar{E})} \int dE \, \omega(E) E \, \delta p(E) \\ &= \frac{1}{T^{\rm stat}(\bar{E})} \, {\rm Tr} \, \delta \rho^{(2)} H \end{aligned}$$

or

$$\delta \langle H \rangle = T^{\rm stat} \delta S^{\rm stat} - \sum_i F_i \delta x_i .$$

This is equivalent to the first law of the thermodynamics,

$$\delta U = T^{\rm therm} \delta S^{\rm therm} - \delta W,$$

provided we identify

$$\begin{aligned} \langle H \rangle &= \bar{E} = U = \text{internal energy} \\ T^{\rm stat} &= T^{\rm therm} \\ S^{\rm stat} &= S^{\rm therm} \\ \sum_i F_i \delta x_i &= \delta W = \text{work}. \end{aligned}$$

Einstein's theory of fluctuations

We divide a large system into macroscopical partial systems whose mutual interactions are weak.
$\Rightarrow \exists$ operators $\{\hat{X}_i\}$ corresponding to the extensive properties of the partial systems so that

$$\begin{aligned} [\hat{X}_i, \hat{X}_j] &\approx 0 \\ [\hat{X}_i, H] &\approx 0. \end{aligned}$$

$\Rightarrow \exists$ a mutual eigenstate $|E, X_1, \ldots, X_n\rangle$, which is one of the macrostates of the system, i.e. corresponding to the parameter set $(E, X_1, \ldots, X_n)$ there is a macroscopical number of microstates. Let $\Gamma(E, X_1, \ldots, X_n)$ be the number of the microstates corresponding to the state $|E, X_1, \ldots, X_n\rangle$ (the volume of the phase space).
The total number of the states is

$$\Gamma(E) = \sum_{\{X_i\}} \Gamma(E, X_1, \ldots, X_n)$$

and the relative probability $(E, X_1, \ldots, X_n)$ of the microstates

$$f(E, X_1, \ldots, X_n) = \frac{\Gamma(E, X_1, \ldots, X_n)}{\Gamma(E)} .$$

The entropy of the state $|E, X_1, \ldots, X_n\rangle$ is

$$S(E, X_1, \ldots, X_n) = k_B \ln \Gamma(E, X_1, \ldots, X_n)$$

or

$$f(E, X_1, \ldots, X_n) = \frac{1}{\Gamma(E)} \, e^{\frac{1}{k_B} S(E, X_1, \ldots, X_n)} .$$

In the thermodynamic equilibrium the entropy S has its maximum

$$S^0 = S(E, X_1^{(0)}, \ldots, X_n^{(0)}).$$

Let us denote by

$$x_i = X_i - X_i^{(0)}$$

deviations from the equilibrium positions.
The Taylor series of the entropy will be

$$S = S^0 - \frac{1}{2} k_B \sum_{i,j} g_{ij} x_i x_j + \cdots ,$$

where

$$g_{ij} = \frac{1}{k_B} \left. \left(\frac{\partial^2 S}{\partial X_i \partial X_j} \right) \right|_{\{X_i^{(0)}\}} .$$

We use notation

$$x = \begin{pmatrix} x_1 \\ \vdots \\ x_n \end{pmatrix} \text{ and } g = (g_{ij}).$$

Then

$$f(x) = C e^{-\frac{1}{2} x^T g x},$$

where

$$C = (2\pi)^{-n/2} \sqrt{\det g}.$$

Correlation functions can be written as

$$\begin{aligned}\langle x_p \cdots x_r \rangle &\equiv \int dx\, f(x) x_p \cdots x_r \\ &= \left[\frac{\partial}{\partial h_p} \cdots \frac{\partial}{\partial h_r} F(h) \right]_{h=0},\end{aligned}$$

where

$$dx = dx_1 \cdots dx_n$$

and

$$F(h) = e^{\frac{1}{2} h^T g^{-1} h}.$$

pVT-system
When studying the stability conditions of matter we found out that

$$\Delta S = -\frac{1}{2T} \sum_i (\Delta T_i \Delta S_i - \Delta p_i \Delta V_i + \Delta \mu_i \Delta N_i).$$

Supposing that there is only one volume element in the system we get

$$f = C e^{-\frac{1}{2k_B T} (\Delta T\, \Delta S - \Delta p\, \Delta V + \Delta \mu\, \Delta N)}.$$

We suppose that the system is not allowed to exchange particles, i.e. $\Delta N = 0$. Employing the definitions of the heat capacity and compressibility we can write

$$f(\Delta T, \Delta V) \propto e^{-\frac{1}{2} \left[\frac{C_V}{k_B T^2} (\Delta T)^2 + \frac{1}{V k_B T \kappa_T} (\Delta V) \right]}.$$

We can now read out the matrix g:

$$g = \begin{array}{c} \\ T \\ V \end{array} \begin{array}{c} \begin{array}{cc} \quad T & \qquad V \end{array} \\ \begin{pmatrix} \frac{C_V}{k_B T^2} & 0 \\ 0 & \frac{1}{V k_B T \kappa_T} \end{pmatrix} \end{array}.$$

The variances are then

$$\begin{aligned}\left\langle (\Delta T)^2 \right\rangle &= \frac{k_B T^2}{C_V} \\ \left\langle (\Delta V)^2 \right\rangle &= V k_B T \kappa_T.\end{aligned}$$

Reversibel minimum work
Let $x = X - X^{(0)}$ be the fluctuation of the variable X. For one variable we have

$$f(x) \propto e^{-\frac{1}{2} g x^2}.$$

Now $S = S(U, X, \ldots)$ holds and

$$dU = T\, dS - F\, dX - đW_{\text{other}}.$$

We get the partial derivative

$$\frac{\partial S}{\partial X} = \frac{F}{T}.$$

On the other hand we had

$$\begin{aligned}S &= S^0 - \frac{1}{2} k_B \sum_{i,j} g_{ij} x_i x_j \\ &= S^0 - \frac{1}{2} k_B g x^2,\end{aligned}$$

so

$$\frac{\partial S}{\partial X} = -k_B g x$$

and

$$F = -k_B T g x.$$

When there is no action on X from outside, the deviation x fluctuates spontaneously. Let us give rise to the same deviation x by applying *reversible* external work:

$$dU = -F\, dx = k_B T g x\, dx.$$

Integrating this we get

$$(\Delta U)_{\text{rev}} \equiv \Delta R = \frac{1}{2} k_B T g x^2,$$

where ΔR is the minimum reversible work required for the fluctuation ΔX. We can write

$$f(\Delta X) \propto e^{-\frac{\Delta R}{k_B T}}.$$