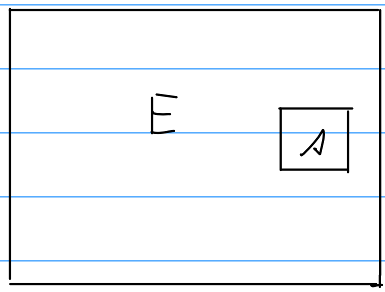
Constant temperature



E : environment

s : system

$\mathcal{E}_E + \mathcal{E}_s = \mathcal{E}$ = fixed.

States x_s, x_E Probability $P(x_s, x_E)$ = indep of x_s, x_E . = Const

$$P(x_s) = \sum_{x_E} P(x_s, x_E) = \text{Const}\cdot \Omega_E(\mathcal{E}_E)$$

$$\propto e^{S_E(\mathcal{E}_E)/k_B} = e^{S_E(\mathcal{E} - \mathcal{E}_s(x_s))/k_B} =$$

$$e^{S_E(\mathcal{E})/k_B}\, e^{-\mathcal{E}_s(x_s) \left.\frac{\partial S_E}{\partial \mathcal{E}}\right)_{NV} / k_B} =$$

$$\underset{\substack{\downarrow \\ 1/Z}}{\text{Const}}\; e^{-\mathcal{E}_s(x_s)/k_B T} = P(x_s)$$

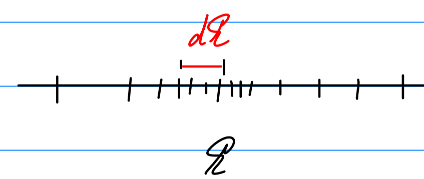
Boltzmann factor.

Const? $\sum_{x_s} P(x_s) = \langle 1 \rangle = 1$

So $\frac{1}{Z} \sum_{x_s} e^{-\mathcal{E}_s(x_s)/k_B T} = 1$

$\to Z = \sum_{x_s} e^{-\mathcal{E}_s(x_s)/k_B T}$ partition function.

$$\sum_x = \int \frac{d^{3N}p\, d^{3N}q}{N!\, h^{3N}} \quad \text{or Tr}$$

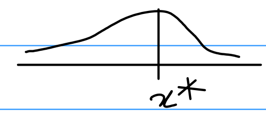


Let's write $\sum_x = C \cdot \int d\mathcal{E}\, \underbrace{\Omega(\mathcal{E})}$

DOS density of states. (C is a const).

Then: $\sum_{x} e^{-\mathcal{E}/k_BT} = \int d\mathcal{E}\, e^{-\mathcal{E}/k_BT}\, e^{+S(\mathcal{E})/k_B} = Z$

Math intermezzo:

$f:$ 

$$\int e^{+Nf(x)}\,dx \qquad N: \text{large} \qquad x = x^* + \delta x$$

$$= \int e^{+N\left(f(x^*) + \frac{1}{2}\delta x^2 \overset{<0}{f''(x^*)} + \dots\right)}\,dx =$$

$$e^{Nf(x^*)} \underbrace{\int_{-\infty}^{\infty} e^{-N\frac{\delta x^2}{2}a}\,dx}_{\sqrt{\frac{2\pi}{Na}}} \qquad a > 0$$

$$= e^{Nf(x^*) - \log\sqrt{2\pi/a} + \log N} \simeq e^{Nf(x^*)}.$$

'Saddle point approx'

$$f(\mathcal{E}) = -\mathcal{E}/k_BT + S(\mathcal{E})/k_B$$

$$\frac{\partial f}{\partial \mathcal{E}} = 0 \to -\frac{1}{k_BT} + \frac{1}{T}\frac{1}{k_B} = 0 \quad \text{fine!}$$

$$Z \simeq e^{-\mathcal{E}^*/k_BT + S(\mathcal{E}^*)/k_B} = e^{-(\mathcal{E}^* - TS)/k_BT}$$

$$= e^{-F/k_BT}$$

So $\underline{F = -k_BT \ln Z}$ Helmholz free energy.

$$Z = \sum_r e^{-\beta \mathcal{E}_r}$$

$$P_r = \frac{e^{-\beta \mathcal{E}_r}}{\sum_{r'} e^{-\beta \mathcal{E}_{r'}}} \; ; \qquad \sum_r e^{-\beta \mathcal{E}_r} = Z$$

partition function

$$F = -k_B T \ln Z \qquad \beta = 1/k_B T$$

1. Specific heat and fluctuations

$$\langle A_r \rangle = \sum_r P_r A_r \qquad Z = \sum_r e^{-\beta \mathcal{E}_r}$$

$$\mathcal{E} = \langle \mathcal{E}_r \rangle = \frac{\sum_r \mathcal{E}_r e^{-\beta \mathcal{E}_r}}{Z}$$

$$\left.\frac{\partial \ln Z}{\partial \beta}\right)_{N,V} = \frac{1}{Z}\frac{\partial Z}{\partial \beta} = \frac{-1}{Z}\sum_r \mathcal{E}_r e^{-\beta \mathcal{E}_r} = -\mathcal{E}$$

$$C_V = T\left.\frac{\partial S}{\partial T}\right)_{NV} = \left.\frac{\partial \mathcal{E}}{\partial T}\right)_{NV} = \frac{\partial \mathcal{E}}{\partial \beta} \cdot \frac{\partial \beta}{\partial T} = \frac{-1}{k_B T^2}\left.\frac{\partial \mathcal{E}}{\partial \beta}\right)_{N,V}$$

$$= -\frac{1}{k_B T^2}\left[\frac{1}{Z^2} \left(\frac{\partial Z}{\partial \beta}\right)^2 + \frac{1}{Z}\sum_r \mathcal{E}_r^2 e^{-\beta \mathcal{E}_r} \right].$$

$$= -\frac{1}{k_B T^2}\left(\langle \mathcal{E} \rangle^2 - \langle \mathcal{E}^2 \rangle \right) = \frac{1}{k_B T^2} \left(\delta \mathcal{E} \right)^2$$

$$\delta \mathcal{E} \sim \sqrt{C_V} \qquad \frac{\delta \mathcal{E}}{\mathcal{E}} \sim \frac{\sqrt{N}}{N} \sim \frac{1}{\sqrt{N}} \sim \frac{1}{10^{12}}$$

fluctuation-dissipation

(L.N. 3.3, P 3.16 & 3.17)

2. Entropy

$$F = -kT\ln Z = \mathcal{E} - TS$$

$$S = \frac{\mathcal{E}-F}{T} = \frac{\langle \mathcal{E}_r \rangle + kT\ln Z}{T}$$

$$\left(P_r = \frac{e^{-\beta \mathcal{E}_r}}{Z} \Rightarrow \mathcal{E}_r = -k_B T \ln(Z \cdot P_r) \right)$$

$$S = \frac{-\cancel{kT\ln Z} - k_B \cancel{T} \langle \ln P_r \rangle + \cancel{kT\ln Z}}{\cancel{T}}$$

$$= -k_B \sum_r P_r \ln P_r$$

Gibbs entropy.

Shannon entropy

Fix $\mathcal{E}$: microcanonical.

$S \to$ max.

Fix $\mathcal{E}$: each state r has energy $\mathcal{E}$.

$$\sum_r P_r = 1.$$

$$f = S - \lambda \sum_r P_r$$

λ Lagrange multiplier.

$$\frac{\partial f}{\partial P_r} = -k_B \ln P_r - k_B - \lambda = 0$$

P_r :

P_r = const (indep. of r).

→ Check that $S = k_B \ln \Omega$; $\Omega = \sum_r$

Canonical

Include <u>all</u> states r (i.e. we don't fix $\mathcal{E}$).

We fix $\langle \mathcal{E}_r \rangle = \sum_r \mathcal{E}_r p_r$

$$f = \overbrace{-k_B \sum_r p_r \ln p_r}^{S} - \lambda \overbrace{\sum_r p_r}^{\sum p_r = 1} - k_B \beta \sum_r \mathcal{E}_r p_r$$

$$\frac{\partial f}{\partial p_r} = -k_B - k_B \ln p_r - \lambda - k_B \beta \mathcal{E}_r = 0$$

$$\ln p_r = C - \beta \mathcal{E}_r$$

$$p_r \propto e^{-\beta \mathcal{E}_r} \quad \text{Boltzmann factor.}$$

(LN 3.5; P 3.12.2)

3. Partition function of noninteracting gas

$$Z = \sum_r e^{-\beta \mathcal{E}_r}; \quad \beta = 1/k_B T \qquad N \text{ part.}, \quad V = L \times L \times L$$

$$= \iint e^{-\sum_i \frac{p_i^2}{2m k_B T}} \frac{d^{3N}p \, d^{3N}q}{h^{3N} N!}$$

$$= \frac{V^N}{h^{3N} N!} \int e^{-\frac{p_{1x}^2}{2mk_BT}} dp_{1x} \int e^{-\frac{p_{1y}^2}{2mk_BT}} dp_{1y} \ldots$$

$$= \frac{V^N}{h^{3N} N!} \Bigg(\underbrace{\int_{-\infty}^{\infty} e^{-p^2/2mk_BT} dp}_{\sqrt{2\pi m k_B T}} \Bigg)^{3N} =$$

$$Z = \frac{V^N}{N! \, \Lambda^{3N}} \qquad \Lambda = \sqrt{\frac{h^2}{2\pi m k_B T}}$$

thermal wavelength.

$$F = -k_B T \ln Z = -k_B T N \ln\left(\frac{V}{\Lambda^3}\right) - N k_B T (\ln N - 1)$$

$$P = -\left.\frac{\partial F}{\partial V}\right)_{N,T} \Rightarrow PV = N k_B T$$

eq of state

$$\mathcal{E} = -\frac{\partial \ln Z}{\partial \beta}\Big)_{N,V} = +k_B T^2 \frac{\partial \ln Z}{\partial T} = k_B T^2 N \frac{\partial \ln(V/\Lambda^3)}{\partial T}$$

$$\Lambda = \frac{h}{\sqrt{2\pi m k_B T}} \longrightarrow \underline{\mathcal{E} = \frac{3}{2} N k_B T}$$

Equipartition theorem.

Brief summary.

$$Z = \sum_r e^{-\beta \mathcal{E}_r} \Rightarrow F = -k_B T \ln Z$$

$$F = \mathcal{E} - TS$$

$$\begin{aligned} dF &= d\mathcal{E} - T dS - S dT \\ &= \cancel{T dS} - P dV + \mu dN - \cancel{T dS} - S dT \\ &= -S dT - P dV + \mu dN \end{aligned}$$

$$\frac{\partial F}{\partial T}\Big)_{NV} = -S \; ; \; \frac{\partial F}{\partial V}\Big)_{TN} = -P \; ; \; \frac{\partial F}{\partial N}\Big)_{TV} = \mu .$$

$$S = -k_B \sum_r P_r \ln P_r$$