Variational Principle in Stat Mech

— the Entropy —

Let us consider the expression

$$\mathrm{tr}\, \rho \ln \rho$$

and proof that it is proportional to (−) the entropy at equilibrium

classical $\quad \mathrm{tr} = \int \frac{d p^{3N} d q^{3N}}{h^{3N} N!} (\ldots)$

quantum $\quad \mathrm{tr} = \sum_{\alpha} \langle \alpha | (\ldots) | \alpha \rangle$

In the Canonical ensemble

$$\mathrm{tr}\, \frac{e^{-\beta \hat{H}}}{Z} (-\beta \hat{H} - \ln Z) = -\beta \langle H \rangle \underbrace{- \ln Z}_{+\beta F} = \beta (F - U)$$

$$F = U - TS$$

$$\mathrm{tr}\, \rho \ln \rho = - S / k_B$$

$$\boxed{S = -k_B \,\mathrm{tr}\, \hat{\rho} \ln \hat{\rho}}$$

this is also true in the Grand Canonical & Micro Canonical ensembles

Grand-Canonical

$$\mathrm{tr}\,\hat{\rho}\ln\hat{\rho} = \beta(\underset{\substack{\uparrow \\ F-\mu N \\ | \\ U-TS}}{\Omega} - U + \mu\langle N\rangle) = -S/k_B$$

Micro-Canonical

$$\mathrm{tr}\,\hat{\rho}\ln\hat{\rho} = \mathrm{tr}\left[\Delta(E-\hat{H})\ln\left(\frac{\Delta(E-\hat{H})}{\mathrm{tr}\,\Delta(E-\hat{H})}\right)\right]\frac{1}{\mathrm{tr}\,\Delta(E-\hat{H})}$$

where $\Delta(E-\hat{H}) = \begin{cases} 1 \text{ if } E-\Delta < H < E \\ 0 \text{ otherwise} \end{cases}$ (classical case)

$$= \begin{cases} 1 \text{ if } E-\Delta < E_n < E \\ 0 \quad \text{otherwise} \end{cases} \quad \text{(quantum case)}$$

when $\Delta(E-H) \neq 0$ then $\Delta(E-H) = 1$ therefore

$$\mathrm{tr}\,\hat{\rho}\ln\hat{\rho} = \mathrm{tr}\,\Delta(E-\hat{H})\underset{\text{number}}{\ln\left(\frac{1}{\mathrm{tr}\,\Delta(E-H)}\right)}\frac{1}{\mathrm{tr}\,\Delta(E-H)}$$

$$= \ln\left(\frac{1}{\mathrm{tr}\,\Delta(E-\hat{H})}\right)\frac{\cancel{\mathrm{tr}\,\Delta(E-\hat{H})}}{\cancel{\mathrm{tr}\,\Delta(E-\hat{H})}} = -\ln Z_{\text{micro}}$$

$$= -S/k_B$$

Variational Principle
(Maximum entropy method)

Equilibrium density matrix or distribution ρ is obtained trough a variational principle by minimising

a functional + constraints

Constraints

- normalisation
- other constraints depending on the control variables and/or kind of system (e.g. closed open isolated...)

Isolated System

the constraint is the normalisation alone - the functional is

$$\begin{cases} \Psi[\rho] = \mathrm{tr}\,\rho \ln \rho \\ \mathrm{tr}\,\rho = 1 \end{cases}$$

Calculation were done for a classical system

Minimise

$$\Psi[\rho] + \alpha \operatorname{tr} \rho$$

↑
Lagrange multiplier

$$\delta\Psi[\rho] + \alpha\delta \operatorname{tr}\rho = 0$$

$$\delta\Psi[\rho] = \Psi[\rho+\delta\rho] - \Psi[\rho]$$

$$\Psi[\rho+\delta\rho] = \operatorname{tr}(\rho+\delta\rho)\ln(\rho+\delta\rho) =$$

$$= \underbrace{\boxed{\operatorname{tr}\rho\ln(\rho+\delta\rho)}}_{(a)} + \underbrace{\boxed{\operatorname{tr}\delta\rho\ln(\rho+\delta\rho)}}_{(b)}$$

to the first order in $\delta\rho$

b) $\operatorname{tr}\delta\rho\ln\rho$

a) $\operatorname{tr}\rho\left(\ln\rho + \ln\left(1+\frac{\delta\rho}{\rho}\right)\right) =$

$$= \operatorname{tr}\rho\ln\rho + \operatorname{tr}\delta\rho$$

this results can be proved also for quantum system where ρ is an operator $\hat{\rho}$

therefore

$$\delta\Psi[\rho] + \alpha\delta\operatorname{tr}\rho = \operatorname{tr}\delta\rho + \operatorname{tr}\delta\rho\ln\rho + \alpha\operatorname{tr}\delta\rho = 0$$

$$\operatorname{tr}\delta\rho[1+\alpha+\ln\rho] = 0 \qquad \forall\,\delta\rho$$

⇙

in the extrema $\bar{\rho}$: $\ln\bar{\rho} = -(1+\alpha)$ Constant moreover

$$\mathrm{tr}\,\bar\rho\,[1+\alpha+\ln\bar\rho]=0$$

and

$$\mathrm{tr}\,\bar\rho=1$$

which eliminates the Lagrange multiplier

$$1+\alpha+\mathrm{tr}\,\bar\rho\ln\bar\rho=0$$

$$\mathrm{tr}\,\bar\rho\ln\bar\rho=\psi[\bar\rho]=-(1+\alpha)$$

taking into account the extrema condition

$$\ln\bar\rho=\psi[\bar\rho]\Rightarrow\bar\rho=e^{\psi[\bar\rho]}=\text{const}$$

for an isolated system $\bar\rho=0$ if $E\neq\hat H$

therefore

$$\boxed{\bar\rho=\Delta(E-\hat H)\,e^{\psi[\bar\rho]}}$$ isolated system

having trace $=1$,

$$1=\underbrace{[\mathrm{tr}\,\Delta(E-\hat H)]}_{Z_{micro}}e^{\psi[\bar\rho]}$$

$$\rightarrow\quad Z_{micro}=e^{-\psi[\bar\rho]}=e^{S/k_B}$$

Closed system

Here the energy is not conserved but it is defined its average value which we consider as a constraint

minimise

$$\Phi[\rho] = \mathrm{tr}\,\rho \ln \rho$$

Constraint

$$\mathrm{tr}\,\rho = 1$$

$$\mathrm{tr}\,\rho H = U$$

$$\delta\left(\Phi[\rho] + \alpha\,\mathrm{tr}\,\rho + \beta\,\mathrm{tr}\,\rho H\right) = 0$$

this gives

$$\mathrm{tr}\,\delta\rho + \mathrm{tr}\,\delta\rho \ln\rho + \alpha\,\mathrm{tr}\,\delta\rho + \beta\,\mathrm{tr}\,\delta\rho H = 0$$

$$\mathrm{tr}\,\delta\rho\left[1 + \alpha + \ln\rho + \beta H\right] = 0 \quad \forall\,\delta\rho$$

at the extrema $\rho = \bar{\rho}$

$$1 + \alpha + \ln\bar{\rho} + \beta H = 0$$

which means

$$\bar{\rho} = e^{-(1+\alpha)}\, e^{-\beta H}$$

as before

$$\mathrm{tr}\,\bar\rho\,[\,1+\alpha+\ln\bar\rho+\beta H\,]=0$$

is customary to redefine the functional

as

$$\Psi[\rho]\longrightarrow(\Psi[\rho]+\beta\,\mathrm{tr}\,\rho H)\rightarrow\beta\Psi[\rho]$$

i.e. consider two kind of constants the normalization (α) and all other included in the definition of Ψ therefore

$$\beta\Psi[\rho]=\mathrm{tr}\,\rho\ln\rho+\beta\,\mathrm{tr}\,\rho H$$

and

$$\beta\Psi[\bar\rho]=-(1+\alpha)$$

$$\bar\rho=e^{\beta\Psi[\bar\rho]}\,e^{-\beta H}$$

one can check immediately that

$$\Psi[\bar\rho]=F$$

Open System

Here N is fluctuating but its average is defined therefore we minimise

$$\mathrm{tr}\,\rho\ln\rho$$

with the constraints

$$\mathrm{tr}\,\rho = 1$$

$$\mathrm{tr}\,\rho H = U$$

$$\mathrm{tr}\,\rho N = \langle N\rangle$$

$$\delta\left(\boxed{\mathrm{tr}\,\rho\ln\rho} + \alpha\,\mathrm{tr}\,\rho + \boxed{\beta\,\mathrm{tr}\,\rho H - \beta\mu\,\mathrm{tr}\,\rho N}\right) = 0$$

$$\beta\Psi[\rho]$$

as before we get

$$\bar\rho = e^{\beta\Psi[\bar\rho]}\,e^{-\beta(H-\mu N)}$$

$$\beta\Psi[\bar\rho] = \mathrm{tr}\,\bar\rho\ln\bar\rho + \beta\,\mathrm{tr}\,\bar\rho H - \beta\mu\,\mathrm{tr}\,\bar\rho N$$

$$-\frac{S}{k_B} \quad + \quad \beta U \quad + \quad \beta\mu N = \beta\Omega$$

The extremum is indeed a minimum

for classical systems

$$\mathrm{tr}\,\rho \ln \rho = \mathrm{tr}\,\bar{\rho} \ln \bar{\rho} + \mathrm{tr}\,\delta\rho\,(\ln \bar{\rho} + 1)$$

$$+ \mathrm{tr}\,\delta\rho^2 \frac{1}{\bar{\rho}} + \mathcal{O}(\delta\rho^3)$$

positive quantity