Equilibrium distribution

postulate of maximum statistical entropy

- macrostate, fixed by a certain number of macroscopic variables, with which a large number of microstates are compatible
- need to construct an ensemble:

$$\rho = \sum_m P_m |\psi_m\rangle\langle\psi_m|$$

  - how do we fix the probabilities?
  - aim: choose the least biased P_m possible, using the available information only and nothing more
  - if no information: least biased set of P_m's is $P_m = 1/M$
- but we can have some information about the system (partial information)

(*) energy lies in an interval $E, E+\Delta E$, where ΔE is small on the macroscopic scale

$$\frac{\Delta E}{E} \ll 1$$

ΔE is large on the microscopic scale

$$\Rightarrow \quad g(E)\,\Delta E \gg 1 \;\Rightarrow\; \Delta E \gg 1/g(E)$$

microcanonical distribution:

$$H|\psi_r\rangle = E_r|\psi_r\rangle \Rightarrow E \le E_r \le E+\Delta E$$

(microcanonical ensemble)

$$P_m = 1/M \qquad M = g(E)$$

$$D = \sum_r |r\rangle \frac{1}{M} \langle r|$$

* other ensembles: averages are fixed, i.e.
  average energy: $\mathrm{Tr}\, HD = \bar{E}$, average particle number: $\mathrm{Tr}\, DN = \bar{N}$, etc.
  in general we can write: $A_i = \mathrm{Tr}\, \hat{D}\hat{A}_i$

to determine the probabilities, adopt postulate of maximum entropy

postulate of maximum statistical entropy

the right density operator, consistent with macroscopic constraints yet maximally unbiased is the one which maximizes the entropy under the constraints

→ in this case the density operator contains no information beyond what is given ensembles: canonical ensemble: $\underbrace{\bar{E} = \mathrm{Tr}\, D H}_{\text{fixed}}$

grand-canonical ensemble:

$$\bar{E} = \mathrm{Tr}\, D H \qquad \bar{N} = \mathrm{Tr}\, D N$$

in general:

$\cancel{\frac{1}{k} \tilde{S}_{st}[D] = }$

constraints: $\mathrm{Tr}\, \hat{D} \hat{A}_i = A_i \qquad \mathrm{Tr}\, D = 1$

$$\tilde{S}_{st}[D] = -\mathrm{Tr}\, D \ln D + \sum_i \lambda_i (\mathrm{Tr}\, \hat{D} \hat{A}_i - A_i) + \lambda_0 (\mathrm{Tr}\, D - 1)$$

$$d\tilde{S} = -\mathrm{Tr}[dD[\ln D - \lambda_i \hat{A}_i - \lambda_0]] = 0$$

$$D = e^{\sum \lambda_i \hat{A}_i + \lambda_0}$$

$$\mathrm{Tr}\, D = 1 \Rightarrow \mathrm{Tr}\, e^{\sum \lambda_i \hat{A}_i} = e^{-\lambda_0}$$

$$\boxed{D_B = \frac{e^{\sum_i \lambda_i \hat{A}_i}}{\mathrm{Tr}\, e^{\sum \lambda_i \hat{A}_i}}} \qquad \boxed{Z = \mathrm{Tr}\, e^{\sum \lambda_i \hat{A}_i}}$$

density matrix of the equilibrium state

called Boltzmann density matrix

$$S_B = -k \,\mathrm{Tr}\, D_B \ln D_B$$
$$= -k \,\mathrm{Tr}\, D_B \Big[\sum_i \lambda_i \hat{A}_i - \ln Z\Big]$$
$$= -k \sum_i \lambda_i A_i + k \ln Z$$

identity:

$$\mathrm{Tr}\, X \ln Y - \mathrm{Tr}\, X \ln X \le \mathrm{Tr}\, Y - \mathrm{Tr}\, X$$

$$\sum_m \sum_q X_m \ln Y_q |\langle q|m\rangle|^2 - \sum_{mq} X_m \ln X_m |\langle q|m\rangle|^2$$

since $\sum_q |\langle q|m\rangle|^2 = 1$

$$\sum_m \sum_q X_m \ln \frac{Y_q}{X_m} |\langle q|m\rangle|^2 \le \sum_q Y_q - \sum_m X_m$$

$\ln x \le x - 1$

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using this identity we can show that the Boltzmann density matrix is not only an extremum but a maximum

consider some other D (density matrix) also consistent with the constraints

$$-\mathrm{Tr}\, D \ln D \le -\mathrm{Tr}\, D \ln D_B$$

$$= -\mathrm{Tr}\, D \ln \frac{e^{\sum \lambda_i \hat{A}_i}}{Z}$$

$$= -\mathrm{Tr}\, D \sum_i \lambda_i \hat{A}_i + \mathrm{Tr}\, D \ln Z$$

$$\boxed{-\mathrm{Tr}\, D \ln D \le -\sum_i \lambda_i A_i + \ln Z} \boxed{= -\mathrm{Tr}\, D_B \ln D_B}$$

D_B is the unique solution to the equilibrium density matrix

Legendre transformation

Fluctuation - response

$$A_i = \mathrm{Tr}\, D_B \hat{A}_i = \frac{\mathrm{Tr}\, e^{\sum_j \lambda_j \hat{A}_j} A_i}{Z}$$

$$\boxed{\frac{\partial \ln Z}{\partial \lambda_j} = A_j}$$ thermodynamic average

Z is a function of the Lagrange multipliers $\lambda_1, \dots, \lambda_\nu \Rightarrow Z(\lambda_1, \dots, \lambda_\nu)$

we can also write

$$\frac{S_B}{k} = \ln Z - \sum_i \lambda_i \frac{\partial \ln Z}{\partial \lambda_i} = \ln Z - \sum_i \lambda_i A_i$$

$$\frac{1}{k} dS_B = d\ln Z - \sum_i d\lambda_i A_i - \sum_i \lambda_i dA_i$$

$$d\ln Z = \sum_i A_i d\lambda_i$$

$$dS_B = -k \sum_i \lambda_i dA_i$$

Legendre transform

it also holds that

$$\frac{\partial^2 \ln Z}{\partial \lambda_i \partial \lambda_j} = \langle \hat{A}_i \hat{A}_j \rangle - \bar{A}_i \bar{A}_j$$

$$\underbrace{\underbrace{\frac{\partial A_i}{\partial \lambda_j}}_{\text{response}} = \underbrace{\langle \hat{A}_i \hat{A}_j \rangle - \bar{A}_i \bar{A}_j}_{\text{fluctuation}}}_{\text{fluctuation-response theorem}}$$

can show that the matrix $\frac{\partial^2 \ln Z}{\partial \lambda_i \partial \lambda_j}$ is positive definite

<u>proof:</u> define $\hat{u} = \sum_k b_k (\hat{A}_k - \bar{A}_k)$

$$\langle \hat{u}^2 \rangle \geq 0$$

$$\Rightarrow \sum_{kl} b_k b_l \langle (\hat{A}_k - \bar{A}_k)(\hat{A}_l - \bar{A}_l) \rangle$$

$$= \sum_{kl} b_k b_l \frac{\partial^2 \ln Z}{\partial \lambda_k \partial \lambda_l} \geq 0$$

(here these are intercommuting operators A_i)

Canonical and Grand-Canonical

Ensembles

canonical: $\mathrm{Tr}\,\hat{H}\hat{D} = \bar{E}$

in this case $\hat{D} = \dfrac{e^{-\beta\hat{H}}}{\mathrm{Tr}\, e^{-\beta\hat{H}}}$ $\quad\beta$ – determine later

grand canonical $\quad\mathrm{Tr}\,\hat{H}\hat{D} = \bar{E}$

$$\mathrm{Tr}\,\hat{N}\hat{D} = \bar{N}$$

~~Tr~~ $\hat{D} = \dfrac{e^{-\beta(\hat{H}-\mu\hat{N})}}{\mathrm{Tr}\, e^{-\beta(\hat{H}-\mu\hat{N})}}$ $\quad\beta, \mu$ determine later