Review of previous lecture (April 21)

macroscopic observables in the microscopic ensemble

$$T^{-1} = \frac{\partial S(E,V,N)}{\partial E}\Big|_{V,N}$$

$$p = T\,\frac{\partial S(E,V,N)}{\partial V}\Big|_{E,N}$$

$$\mu = T\,\frac{\partial S(E,V,N)}{\partial N}\Big|_{E,V}$$

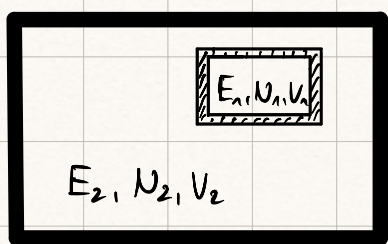
first law of thermodynamics:

$$\underline{dE} = T\cdot \underline{dS} - p\cdot \underline{dV} + \mu\cdot \underline{dN}$$

state variables

canonical ensemble:

$$E = E_1 + E_2\,, \quad E_2 \gg E_1$$
$$N = N_1 + N_2\,, \quad N_2 \gg N_1$$
$$V = V_1 + V_2\,, \quad V_2 \gg V_1$$



Hamiltonian: $H = H_1 + H_2 + W$

↳ energy exchange between subsystems

Consider expectation value of an operator A_1 that only acts on states of system 1:

$$\langle A_1 \rangle = \mathrm{Tr}(\rho A_1)$$
$$= \mathrm{Tr}\left(\rho_{mc}^{(1+2)} A_1\right)$$
$$= \mathrm{Tr}_1 \mathrm{Tr}_2 \left(\rho_{mc}^{(1+2)} A_1\right)$$
$$\equiv \mathrm{Tr}_1 \left(\rho^{(1)} A_1\right)$$

integrated out states of system 2

derive explicit form of $\rho^{(1)}$:

$$\rho^{(1)} = \mathrm{Tr}_2\, \rho_{mc}^{(1+2)}$$
$$= \mathrm{Tr}_2 \left(Z_{mc}^{(1+2)}(E)\right)^{-1} \underbrace{\sum_n |n\rangle\langle n|}_{\sum_{n_1,n_2} |n_1 n_2\rangle\langle n_1 n_2|} \underbrace{\delta_{H_1+H_2,E}}_{\delta_{H_2,E-H_1}}$$

$$= \sum_{n_1} \frac{Z_{mc}^{(2)}(E-H_1)}{Z_{mc}^{(1+2)}(E)} |n_1\rangle\langle n_1|$$

here we can use the fact that $\frac{E_1}{E} \ll 1$ and expand:

$$Z_{mc}^{(2)}(E-H_1) = Z_{mc}^{(2)}(E) - \frac{\partial Z_{mc}^{(2)}}{\partial E} H_1 + \dots$$

note that $Z_{mc}^{(2)}(E)$ is a rapidly varying function (typically $Z_{mc}(E) \sim E^N$)

$\Rightarrow$ it is much more useful and efficient to expand the logarithm $\log\left(Z_{mc}^{(2)}(E-H_1)\right)$ instead

$$\log Z_{mc}^{(2)}(E-H_1) \approx \log Z_{mc}^{(2)}(E) - \frac{\partial \log Z_{mc}^{(2)}(E)}{\partial E} H_1$$
$$= \log Z_{mc}^{(2)}(E) - \frac{H_1}{k_B T}$$

$$\Rightarrow \quad Z^{(2)}_{mc}(E - H_1) \approx Z^{(2)}_{mc}(E)\, e^{-\frac{H}{k_B T}}$$

$$\rho^{(1)} = \underbrace{\frac{Z^{(2)}_{mc}(E)}{Z^{(1+2)}_{mc}(E)}}_{\text{normalization constant}} \sum_n \underbrace{e^{-\frac{H_1}{k_B T}} |n\rangle\langle n|}_{e^{-\frac{E_1}{k_B T}} |n\rangle\langle n|}$$

$$= c \cdot \mathrm{Tr}_1\, e^{-\frac{H_1}{k_B T}}$$

partition function and density matrix of canonical ensemble

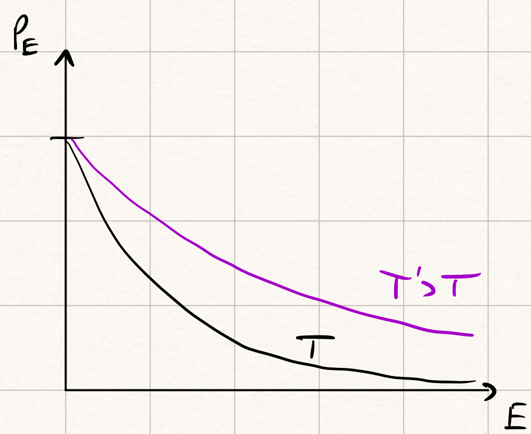
$$\boxed{\begin{aligned} Z_c(T) &= \mathrm{Tr}\, \exp\left(-\frac{H_1}{k_B T}\right) \\ \rho_c &= Z_c^{-1} \exp\left(-\frac{H_1}{k_B \cdot T}\right) \\ \mathrm{Tr}\, \rho_c &= 1 \end{aligned}}$$

probability that system 1 has particular energy E_n

$$\rho^{(1)} = Z_c^{-1} \sum_n e^{-\frac{E_n}{k_B T}} |n\rangle\langle n|$$

$$= \sum_n p_{E_n} |n\rangle\langle n|$$

$$\hookrightarrow \quad p_{E_n} = \frac{e^{-\frac{E_n}{k_B T}}}{Z_c}$$



entropy in canonical ensemble

$$S_c = -k_B \cdot \mathrm{Tr}\,(\rho_c \log \rho_c)$$
$$= -k_B \; \mathrm{Tr}\left[\rho_c \cdot \left(\log Z_c^{-1} - \frac{H}{k_B T}\right)\right]$$
$$= +k_B \log Z_c \; \mathrm{Tr}\,\rho_c + k_B \cdot \mathrm{Tr}\left(\rho_c \frac{H}{k_B T}\right)$$
$$= +k_B \cdot \log Z_c + \frac{1}{T} \underbrace{\mathrm{Tr}\,(\rho_c H)}_{=\langle H\rangle = E}$$

$$= +k_B \log Z_c + \frac{E}{T}$$

$\hookrightarrow$ note that E is not fixed externally in the canonical ensemble, but given by an ensemble average of the Hamiltonian

note that entropy is not of the form $S = c \cdot \log Z_c$ anymore due to the additional term $\frac{E}{T}$

$\Rightarrow$ define a new state function of the canonical ensemble:

$$F = -k_B \cdot T \cdot \log Z_c(T) \quad \text{free energy}$$

this implies: $S_c = -\frac{F}{T} + \frac{E}{T} \Rightarrow F = E - TS_c$

the density matrix in the canonical ensemble depends on:

$$\rho_c = \rho_c(T, V)$$

in Hamiltonian, e.g. via hard-wall interactions at boundaries

explicitly via $e^{-\beta}$

$$\Rightarrow \quad F = F(T,V) \quad \text{compared to} \quad E = E(S,V)$$

$$dF = dE - T\cdot dS - S\cdot dT$$

$$= -p\, dV - S\cdot dT \qquad (dN = 0)$$

↳ Legendre transformation

(exercise)

thermodynamic observables in the canonical ensemble

$$E = \langle H \rangle = \mathrm{Tr}(\varrho_c H)$$

$$= Z_c^{-1}\, \mathrm{Tr}\left(H e^{-\beta H}\right)$$

$$= -Z_c^{-1} \frac{\partial}{\partial \beta} \mathrm{Tr}\left(e^{-\beta H}\right)$$

$$= -Z_c^{-1} \frac{\partial}{\partial \beta} Z_c = -\frac{\partial}{\partial \beta} \log Z_c$$

$$p = -\left\langle \frac{\partial H}{\partial V} \right\rangle = -\mathrm{Tr}\left(\varrho_c \frac{\partial H}{\partial V}\right)$$

$$= -Z_c^{-1}\, \mathrm{Tr}\left(\frac{\partial H}{\partial V} e^{-\beta H}\right)$$

$$= +Z_c^{-1} \beta^{-1} \frac{\partial}{\partial V} Z_c$$

$$= +k_B T \frac{\partial}{\partial V} \log Z_c$$

$$S_c = k_B \frac{\partial}{\partial T}\left(T\cdot \log Z_c\right) \qquad \text{(using the relations above)}$$

$$dF = d\left(-k_B T \log \mathrm{Tr}\, e^{-\beta H}\right)$$

$$= -k_B\, dT \underbrace{\log \mathrm{Tr}\, e^{-\beta H}}_{\log Z_c} - k_B\cdot T\, Z_c^{-1}\, \mathrm{Tr}\left[\left(\underbrace{\frac{dT}{k_B\cdot T^2} H}_{\downarrow\ \frac{E}{k_B T^2}\cdot dT} \underbrace{- \frac{1}{k_B\cdot T} \frac{\partial H}{\partial V}\cdot dV}_{-\frac{1}{k_B T}\left\langle \frac{\partial H}{\partial V}\right\rangle \cdot dV}\right) e^{-\beta H}\right]$$

$$= -\frac{dT}{T}\left(k_B T \log Z_c + E\right) + \left\langle \frac{\partial H}{\partial V}\right\rangle dV$$

$$= -S_c\cdot dT - p\cdot dV \quad (+\mu\cdot dN)$$

Various ensembles and its properties

ensemble	microcanonical	canonical	grandcanonical
System type	isolated	energy exchange with heatbath	energy + particle exchange
density matrix	$Z_{mc}^{-1}[\Theta(E-H)-\Theta(H-(E-\Delta E))]$	$Z_c^{-1}\exp(-\frac{H}{k_B T})$	$Z_{gc}^{-1}\exp(-\frac{H-\mu\cdot N}{k_B\cdot T})$
state variables	E, V, N	T, V, N	T, V, μ
state function	$S = +k_B \log Z_{mc}$	$F = -k_B T \log Z_c$	$\Phi = -k_B T \log Z_{gc}$

all thermodynamic quantities can be extracted from the <u>partition function</u> resp. the <u>state function</u> and its derivatives.

Key task in statistical physics is the computation of the partition function Z, typically Z_c (canonical ensemble) in this course.

Ergodicity

consider a classical system

a system is <u>ergodic</u> if

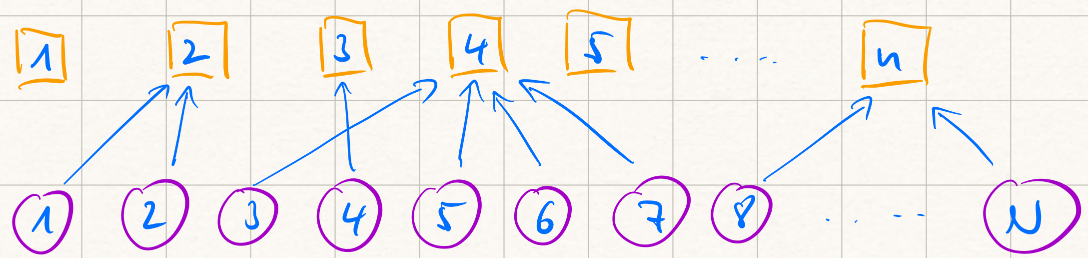
$$\lim_{T\to\infty} \frac{1}{T}\int_0^T dt\; A(\{x_i(t), p_i(t)\}) = \int \frac{dx^{3N}\, dp^{3N}}{h^{3N}\, N!}\, \underbrace{\rho_{eq}(\{x_i, p_i\})}_{\substack{\text{equilibrium probability} \\ \text{distribution}}}\, A(\{x_i, p_i\})$$

that means: time average = ensemble average

over sufficiently long periods of time the microstates of the system approaches every point in phase space

<u>illustration</u>: human behaviour and ergodicity

consider n restaurants ("phase space") and N people who visit the restaurants on a regular basis



<u>time average</u>: pick one person and measure how often the different restaurants have been visited

<u>ensemble average</u>: snapshot of <u>all</u> people at a given time

Is this system ergodic?

generally not! Why? → find counter examples

How about systems in statistical physics?

also not, breaking of ergodicity closely related to phase transitions and spontaneous symmetry breaking

More soon!