Review of previous lecture (April 13)

microcanonical ensemble:

collection of all microstates that have a energy in the range $[E-\Delta E, E]$

postulate:

all microstates have the same probability:

$$\rho_{mc} = \begin{cases} Z_{mc}^{-1} & \text{for } E-\Delta E \leq H \leq E \\ 0 & \text{else} \end{cases}$$

with the microcanonical partition function

$$Z_{mc}(E) = \mathrm{Tr}\left[\Theta(E-H) - \Theta(H-(E-\Delta E))\right]$$

↳ phase space integral (classical systems)
resp. discrete sum over states (QM systems)

and the density matrix

$$\varrho_{mc}(E) = \sum_n{}' Z_{mc}^{-1}(E) |n\rangle\langle n|$$

restricted sum over all states with energies in the range $[E-\Delta E, E]$

$$\mathrm{Tr}\, \varrho_{mc}(E) = 1$$

entropy:

$$S(E) = -k_B \, \mathrm{Tr}\,(\varrho \log \varrho)$$

$$\Rightarrow S_{mc}(E) = -k_B \log Z_{mc}(E)$$

temperature:

$$T^{-1} = \frac{\partial S}{\partial E}$$

Interlude: negative temperatures

for a <u>free gas</u> one can show that

$$S(E) \sim \log\left(E^{\frac{3}{2}N}\right)$$

$\Rightarrow T \sim \frac{3}{2} E N k_B$ linearly increasing with E

now consider a paramagnetic system of N spins

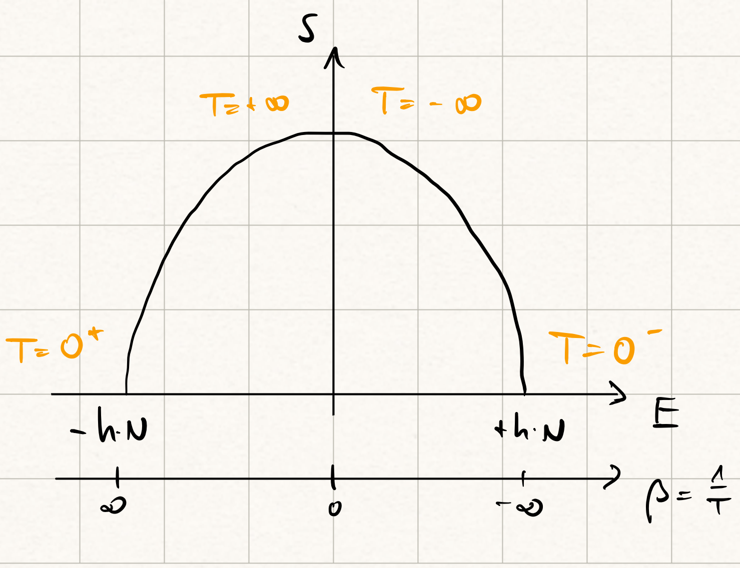
$$H = -h \sum_{i=1}^{N} \sigma_i$$

$$Z_{mc} = \exp\left[-\frac{N}{2}\left[(1+e)\log\frac{1+e}{2} + (1-e)\log\frac{1-e}{2}\right]\right]$$

mit $e = \frac{E}{Nh}$

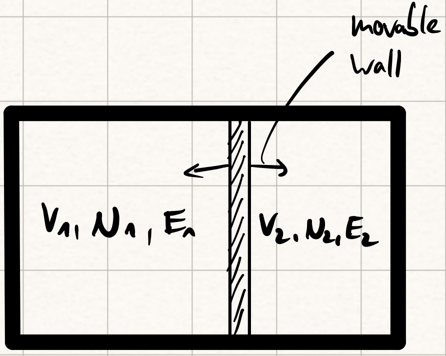
there is a <u>maximal</u> and <u>minimal</u> energy for this system

$E_{min} = -h \cdot N$ $E_{max} = +h \cdot N$



Pressure

consider now an isolated system consisting of two subsystems 1 and 2 that are divided by a movable wall, i.e. V_1 and V_2 are variable with $V_1 + V_2 = V$



following the same arguments like above for the energy we obtain the following relation for the most probable volume $\bar{V}_1$:

$$\underbrace{\frac{\partial}{\partial V_1} S_1(E_1, V_1)\Big|_{V_1 = \bar{V}_1}}_{\frac{p_1}{T}} = \underbrace{\frac{\partial}{\partial V_2} S_2(E_2, V_2)\Big|_{V_2 = V - \bar{V}_1}}_{\frac{p_2}{T}}$$

Definition of pressure:

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

chemical potential:

if we also allow for particle exchange between subsystems 1 and 2 we obtain:

$$\underbrace{\frac{\partial S_1(E_1, V_1, N_1)}{\partial N_1}\Big|_{N_1 = \bar{N}_1}}_{\frac{\mu_1}{T}} = \underbrace{\frac{\partial S_2(E_2, V_2, N_2)}{\partial N_2}\Big|_{N_2 = N - \bar{N}_1}}_{\frac{\mu_2}{T}}$$

Definition of chemical potential:

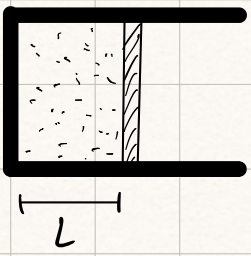
$$\mu = T \frac{\partial}{\partial N} S(E,V,N)\Big|_{E,V}$$

First law of thermodynamics

Question: How are changes of S, E, V and N related?

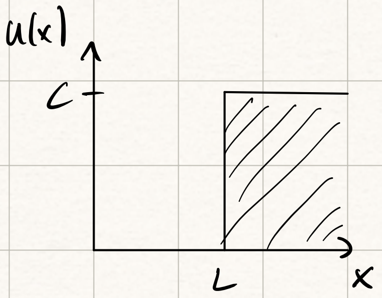
consider Hamiltonian that depends on an external parameter a, e.g. the volume or the length dimension of the system

$$H(a) = H_0 + H_1(a)$$



consider case a = V with simple external trapping potential

$$H(V) = \sum_{i=1}^{N} u(x_i, L) = \sum_{i=1}^{N} \Theta(x_i - L)$$



Study change of partition function Z_{mc} when a is varied:

$$dZ_{mc} = d\,\mathrm{Tr}\left[\Theta(E-H(a)) - \Theta(H(a)-(E-\Delta E))\right]$$

$$= \mathrm{Tr}\left[\delta(E-H(a)) + \underbrace{\delta(\cancel{E-\Delta E}-H(a))}_{\text{can be neglected due to rapid increase of phase space with E}}\right]\cdot\left[dE - \frac{\partial H}{\partial a}\cdot da\right]$$

$$= \underbrace{\left[\mathrm{Tr}\,\delta(E-H(a))\right]}_{\text{integral over energy surface in phase space}}\cdot\left[dE - \underbrace{\left\langle\frac{\partial H}{\partial a}\right\rangle}_{\text{average over energy surface}} da\right]$$

Hence for the change in entropy we obtain:

$$dS = k_B \, d\log Z_{mc}$$

$$= k_B \frac{\partial Z_{mc}}{Z_{mc}} = \underbrace{k_B \frac{\mathrm{Tr}\,\delta(E - H(a))}{Z_{mc}}}_{= \frac{\partial S}{\partial E} = T^{-1}} \left[dE - \left\langle \frac{\partial H}{\partial a} \right\rangle da \right]$$

$$\Rightarrow \quad dS = \frac{1}{T} dE - \left\langle \frac{\partial H}{\partial a} \right\rangle \cdot da$$

Consider $\left\langle \frac{\partial H}{\partial a} \right\rangle$ for $a = V$.

Here to total force of the wall on the particles is given by

$$F = \sum_{i=1}^{N} F_i = - \sum_{i=1}^{N} \frac{\partial U(x_i, L)}{\partial x_i} = + \sum_{i=1}^{N} \frac{\partial U(x_i, L)}{\partial L} = \frac{\partial H}{\partial L}$$

The pressure on the wall is the given by

$$p = - \frac{\langle F \rangle}{\textcircled{A}} = - \left\langle \frac{\partial H}{\partial V} \right\rangle$$

↳ surface area of wall

$$\Rightarrow \quad dS = T^{-1} (dE + p \cdot dV)$$

allowing also the number of particles to vary $(a = N)$ gives

$$\boxed{dS = T^{-1} (dE + p \cdot dV - \mu \cdot dN)}$$

first law of thermodynamics

equivalently: $\underset{\text{heat}}{\underset{\downarrow}{dE = T \cdot dS}} - \underset{\text{mechanical work}}{\underset{\downarrow}{p\,dV}} + \underset{\text{adding/removing matter}}{\underset{\downarrow}{\mu\,dN}}$ (energy balance of different contributions)

⇒ the state variables of the microcanonical ensemble are

S, E, V and N

with the state functions

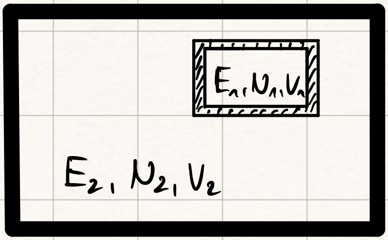
$S = S(E, V, N)$ or equivalently $E = E(S, V, N)$

Canonical ensemble

- in practice it is very hard to fix or determine the entropy of a system, i.e. the entropy as a state variable is not very convenient
- theoretical calculations of microcanonical partition functions complicated by sharp cutoffs and restrictions of phase space

Consider an isolated system consisting of a small subsystem 1 and a large subsystem 2 ("heatbath").

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



Hamiltonian: $H = H_1 + H_2 + W$

↳ again negligible contributions to bulk properties of subsystems, but allows for energy exchange between subsystems 1 and 2

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

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

integrated out states of system 2

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

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

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

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

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

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