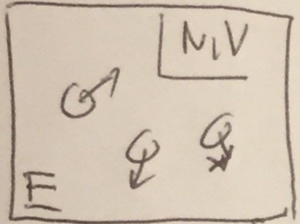
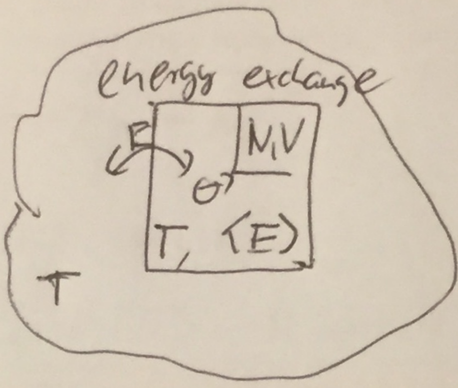
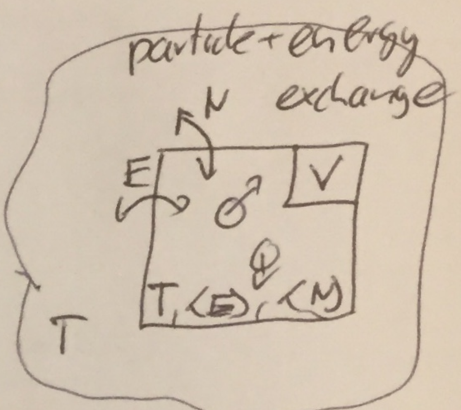
Recap Lecture 6/3/20



micro-canonical ensemble



canonical ensemble



grand-canonical

topic

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thermodynamical equilibrium:

entropy: $S = -\sum_i p_i \ln p_i$ $\quad \boxed{p_i = \frac{1}{Z} e^{-\beta E_i + \beta \mu N_i}}$

constraints: $\sum_i p_i = 1 \Rightarrow \boxed{Z = \sum_i e^{-\beta E_i + \beta \mu N_i}}$

$\langle E \rangle := \sum_i p_i E_i = \frac{E}{N} \rightarrow \beta$; $\quad \boxed{\beta = 1/T}$

$\langle N \rangle := \sum_i p_i N_i \overset{!}{=} N N_p$ (total number of particles)

$\boxed{\mu = ?}$

$\ln(ab) = \ln a + \ln b$ $\qquad \frac{1}{Z_g} e^{-\beta E_i + \beta\mu N_i}$

Constraints

$N\langle E\rangle = E$

$N\langle N\rangle = N N_p$

The following calculation should be familiar from a analogous one in subsection 4.1. Inserting (66) into the entropy equation (63) yields:

$$\boxed{\begin{aligned} S &= -N\sum_i p_i \ln p_i = -N\cdot\sum_i \frac{1}{Z_g} e^{-\beta E_i + \beta\mu N_i} \left[\ln Z_g - \beta E_i + \beta\mu N_i\right] \\ &= N\cdot \ln Z_g + \beta\cdot N\langle E\rangle - N\cdot\beta\mu\cdot\langle N\rangle = N\ln Z_g + \beta E - \beta\mu N N_p \end{aligned}}$$

$$S(E,N_p) = \beta(E,N_p)\,E - N\,[\beta\,\mu](E,N_p)\,N_p + N\ln Z_g\,.$$

We defined the temperature in (11), which we recall here:

$$\frac{1}{T(E,N_p)} = \frac{\partial S(E,N_p)}{\partial E}\bigg|_{N_p}.$$

After a short calculation:

$$\boxed{\begin{aligned} \frac{\partial S}{\partial E}\bigg|_{N_p} &= \beta'\cdot E + \beta - N\cdot N_p\,(\beta\mu)' \\ &\quad + N\,\underbrace{\frac{1}{Z_g}\left[\frac{\partial Z_g}{\partial\beta}\right.}_{-\langle E\rangle}\cdot\beta' + \underbrace{\left.\frac{\partial Z_g}{\partial(\beta\mu)}\right]}_{+\langle N\rangle}\cdot(\beta\mu)' \\ &= \beta' E + \beta - N N_p(\beta\mu)' - E\cdot\beta' + N N_p\cdot(\beta\mu)' = \beta \end{aligned}}$$

with Constr.:

$N\langle E\rangle = E$

$N\langle N\rangle = N N_p$

we find that for the Lagrange multiplier β the same expression as before (see (22)):

$$\frac{1}{T(E,N_p)} = \beta(E,N_p)\,. \tag{70}$$

We still have to find a meaning for the last remaining Lagrange multiplier μ. We calculate:

$$(\,)^\circ = \frac{\partial}{\partial N}(\,)$$

$$\frac{\partial S}{\partial N_p}\Big|_E = \mathring{\beta} E - N N_p (\beta\mu)^\circ - N\cdot(\beta\mu) + N\frac{1}{z_0}\frac{\partial z_0}{\partial \beta}\cdot\mathring{\beta} + N\frac{1}{z_0}\frac{\partial z_0}{\partial(\beta\mu)}\cdot(\beta\mu)^\circ$$

$$= \mathring{\beta} E - N N_p(\beta\mu)^\circ - N(\beta\mu) - \underbrace{N\langle E\rangle}_{NE}\cdot\mathring{\beta} + \underbrace{N\langle N\rangle}_{=NN_p}(\beta\mu)^\circ$$

$$= -N\cdot\beta\mu$$

Key Definition: The derived quantity

$$\mu = -T\frac{1}{N}\frac{\partial S}{\partial N_p}\Big|_E . \tag{71}$$

is called *chemical potential.* It is related to the change of the entropy of a statistical system by adding a particle to the system while keeping its energy constant.

This is a defintion that hinges on the "big" system, which is specified by the overall energy E and the total number of particles N_p. It also contains a reference to the number of boxes N. It would be convenient to have an expression for the chemical potential μ that only depends on "small" box properties. This can be indeed achieved.
Assume that we have calculated the entropy, which is consequently a function of E and N_p:

$$S = S(E, N_p). \tag{72}$$

If we solve this equation for E, i.e.,

$$E = E(S, N_p)\,,$$

we can use the latter to replace E as variable in all sort of equations. Hence, S and N_p are becoming our new *independent* variables. The constraint (68)