9/10

Last time:

$$dS = \frac{đQ}{T} = \frac{1}{T}\Big(d\bar{E} - \underbrace{\sum_{\alpha=1}^{n} \bar{X}_\alpha\, d\bar{x}_\alpha}_{đW}\Big) \quad ①$$

Also since $S = S(\bar{E}, x_\alpha)$

$$dS = \left(\frac{\partial S}{\partial \bar{E}}\right)_{x_\alpha} d\bar{E} + \sum_{\alpha=1}^{n} \left(\frac{\partial S}{\partial x_\alpha}\right)\Big|_{\bar{E}} d\bar{x}_\alpha \quad ②$$

we find (again) that

$$\frac{\partial S}{\partial \bar{E}}\Big|_{\bar{x}_\alpha} = \frac{1}{T} \quad \text{and} \quad \frac{\partial S}{\partial x_\alpha}\Big|_{\bar{E}} = \frac{\bar{X}_\alpha}{T}$$

Equation of state for an ideal gas via statistical mechanics.

We found before that

$$\Omega \propto V^N \chi(E)$$

$$\ln \Omega = N \ln V + \ln \chi(E) + C \qquad (1)$$

constant

$$S = k \ln \Omega \quad \text{and} \quad \left.\frac{\partial S}{\partial x_\alpha}\right|_E = \frac{\bar{X}_\alpha}{T}$$

If $x_\alpha = V$ and $\bar{X}_\alpha = \bar{p}$

$$k \frac{\partial \ln \Omega}{\partial V} = \frac{\bar{p}}{T} \quad \text{from (1)} \quad \frac{\bar{p}}{T} = k \frac{N}{V} \qquad (2)$$

Then from (2) we obtain that

$\bar{p} V = N k T$ equation of state for the ideal gas. Comparing with what we know from thermodynamics we see that $k \equiv k_B$ (Boltzmann's constant).

$\bar{p} = n k T$ if $n = \dfrac{N}{V}$ if $N = \nu N_a$ → Avogadro's #.

ν → # of moles

$$\bar{p} V = \nu \underbrace{N_a k}_{R} T = \nu R T$$

We also find that

$$\beta = \frac{\partial \ln \Omega}{\partial E} = \left.\frac{\partial \ln \chi(E)}{\partial E}\right|_{\bar{E}}$$

definition ideal gas

Then $\beta = \beta(\bar{E})$
or $\bar{E} = \bar{E}(\beta) = \bar{E}(T)$.

For an ideal gas $\bar{E}$ is only a function of T (not of V). $\bar{E}$ is independent of V.

Ensembles

Ch. 6 in Reif (read chapters 4 and 5 to refresh your knowledge of thermodynamics (macroscopic))

- Isolated system: (in equilibrium) Has energy E.

microcanonical ensemble (ensemble of isolated systems (identical to each other) in equilibrium).

Each member of the ensemble is in a state r with energy $E_r = E$ (this means $E \leq E_r \leq E + dE$) and with probability

$$P_r = \begin{cases} C & \text{if} \quad E \le E_r \le E + \delta E \\ 0 & \text{otherwise} \end{cases}$$

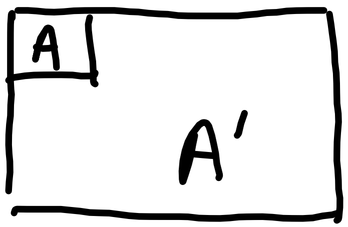
$$\sum_r P_r = 1$$ $\{r\}$ accessible states with energy $\sim E$.

→ restricted sum

Canonical ensemble: it consists of identical systems with $\langle E \rangle$ well defined or equivalently, all members of the ensemble are at the same temperature β.

We want to obtain P_r (probability distribution) for a system at a ~~fixed~~ temperature β. This can be studied via a system A in contact with a heat reservoir A' at temperature $\beta' = \beta$.

We want to know what is the probability P_r of A being in its microstate r.



$A + A' = A^{(0)}$ isolated

$A << A'$

In this case A has energy $E = E_r$ and A' has energy $E' = E^{(0)} - E_r$

$$P_r = C' \, \Omega'(E^{(0)} - E_r) \, \underbrace{\Omega(E_r)}_{1} \qquad (1)$$

# of states accessible to $A^{(0)}$ when A is in state r.

Now since P_r is a probability we know that

$$\sum_r P_r = 1 \qquad (3)$$

(unrestricted sum over ALL the states of A).

$f(x) \approx f(a) + f'(a)(x-a)$

Now $E' = x$, $E^{(0)} = a$, $x - a = -E_r$

Since $E_r \ll E^{(0)}$

$$\ln \Omega'(\overbrace{E^{(0)} - E_r}^{E'}) = \ln \Omega'(E^{(0)}) - \underbrace{\left.\frac{\partial \ln \Omega'}{\partial E'}\right|_{E^{(0)}}}_{\beta' = \beta} E_r + \cdots$$

Then

$$\ln \Omega'(E^{(0)} - E_r) = \ln \Omega'(E^{(0)}) - \beta E_r$$

or

$$\Omega'(E^{(0)} - E_r) = \Omega'(E^{(0)})\, e^{-\beta E_r} \qquad (2)$$

Replacing (2) in (1) we find that

$$P_r = C' \underbrace{\Omega'(E^{(0)})}_{\text{constant}} e^{-\beta E_r} = C e^{-\beta E_r}$$

To find C we use the normalization condition

(3) :

$$\sum_r P_r = \sum_r C\, e^{-\beta E_r} = 1$$

$$\therefore \quad C = \frac{1}{\sum_r e^{-\beta E_r}}$$

$$\therefore \quad \boxed{P_r = \frac{e^{-\beta E_r}}{\sum_r e^{-\beta E_r}}}$$

canonical distribution

$e^{-\beta E_r}$: Boltzmann's factor.

This probability distribution is a function of β.

sum over ALL state of A (unrestricted).

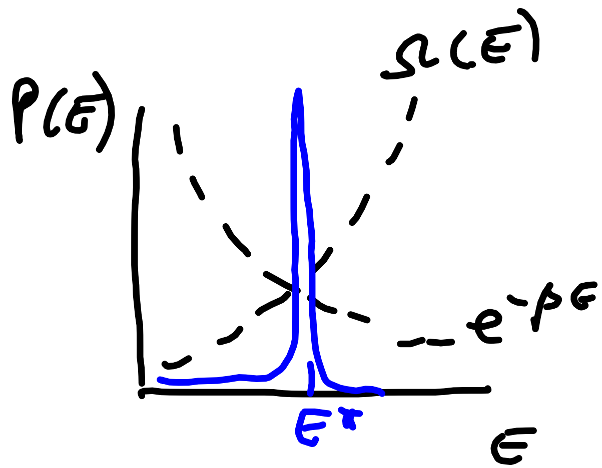
Correspondence between canonical and microcanonical distributions:

If we know that A has energy between E and E + δE – we can define

$$P(E) = \sum_r P_r \qquad (4)$$

E^*

restricted to states r with energy ~E



but $E_r \sim E$ in (4)

$$P(E) = \Omega(E) P_r = C\,\Omega(E) e^{-\beta E_r} = C\,\Omega(E) e^{-\beta E}$$

Averages in the canonical ensemble:

$$\bar{y} = \frac{\sum_r e^{-\beta E_r} y_r}{\sum_r e^{-\beta E_r}}$$

sum over all states (no constraints).

Advantage of using canonical instead of microcanonical is that there are no constraints on the states r to be considered.

Another way of thinking about the canonical ensemble:

We have "a" systems and we only know $\langle E \rangle$ for these systems.

In other words we know that

$$\frac{\sum_s a_s \bar{E}_s}{a} = \langle E \rangle$$

a_s: # of systems with energy $\bar{E}_s$.

Sum over all possible energies of the systems.

Then

$$\sum_s a_s \bar{E}_s = a \langle E \rangle = \text{constant}$$

if 1 system has energy E_r it means that

$(a-1)$ systems have energy $a\langle E\rangle - E_r = E'$

and $a\langle E\rangle >> E_r$

Then

$$P_r \propto e^{-\beta E_r}$$

and β can be found by requiring that

$$\langle E\rangle = \frac{\sum_r E_r e^{-\beta E_r}}{\sum_r e^{-\beta E_r}}$$ solve for β.

Partition Function

Let's define:

$$Z \equiv \sum_r e^{-\beta \epsilon_r}$$

(unrestricted sum)

Z (from Zustand summe which means sum over states in German). But some books call it Q.

We see:

$$-\frac{\partial \ln Z}{\partial \beta} = -\frac{1}{Z}\frac{\partial Z}{\partial \beta} = -\frac{\sum_r -\epsilon_r e^{-\beta \epsilon_r}}{\sum_r e^{-\beta \epsilon_r}} = \frac{\sum_r \epsilon_r e^{-\beta \epsilon_r}}{\sum_r e^{-\beta \epsilon_r}}$$

$$= \langle \epsilon \rangle$$

Then

$$\langle E \rangle = -\frac{\partial \ln Z}{\partial \beta}$$

Dispersion of E : $\overline{(\Delta E)^2} = \overline{(E - \bar{E})^2}$

$$\overline{E^2 - 2E\bar{E} + (\bar{E})^2} = \langle E^2 \rangle - 2\langle E \rangle^2 + \langle E \rangle^2 =$$

$$= \langle E^2 \rangle - \langle E \rangle^2$$

$$\langle E^2 \rangle = \frac{\sum_r E_r^2 e^{-\beta E_r}}{\sum_r e^{-\beta E_r}} = \frac{-\frac{\partial}{\partial \beta}\left(\sum_r E_r e^{-\beta E_r}\right)}{Z} =$$

$$= \frac{\left(-\frac{\partial}{\partial \beta}\right)^2 Z}{Z} = \frac{1}{Z}\frac{\partial^2 Z}{\partial \beta^2} \quad (5)$$

Notice that

$$\frac{\partial}{\partial\beta}\left(\frac{1}{Z}\frac{\partial Z}{\partial\beta}\right) = -\frac{1}{Z^2}\left(\frac{\partial Z}{\partial\beta}\right)^2 + \frac{1}{Z}\frac{\partial^2 Z}{\partial\beta^2} \qquad (6)$$

$$(5)\quad \langle E^2\rangle = \frac{1}{Z}\frac{\partial^2 Z}{\partial\beta^2} \overset{(6)}{=} \frac{\partial}{\partial\beta}\underbrace{\left(\frac{1}{Z}\frac{\partial Z}{\partial\beta}\right)}_{-\langle E\rangle} + \frac{1}{Z^2}\underbrace{\left(\frac{\partial Z}{\partial\beta}\right)^2}_{(-Z\langle E\rangle)^2} =$$

$$= -\frac{\partial\langle E\rangle}{\partial\beta} + \frac{Z^2}{Z^2}\langle E\rangle^2 .$$

$$\langle E^2\rangle - \langle E\rangle^2 = -\frac{\partial\langle E\rangle}{\partial\beta} + \cancel{\langle E\rangle^2} - \cancel{\langle E\rangle^2} = -\frac{\partial\langle E\rangle}{\partial\beta} \qquad (7)$$

From ⑦ :

$$\overline{(\Delta E)^2} = -\frac{\partial \bar{E}}{\partial \beta} = \frac{\partial^2 \ln Z}{\partial \beta^2} \geq 0$$

$$\therefore \frac{\partial \bar{E}}{\partial \beta} \leq 0 \quad \text{or} \quad \frac{\partial \bar{E}}{\partial T} \geq 0$$

Thus $\bar{E}$ always increases with T.