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Last time:

$$\Gamma = \frac{a!}{a_1! a_2!}$$

of ways in which
 "a" particles could be
 distributed among r
 states.

We found that the
 distribution that maximizes Γ by
 calculating $\delta(\ln \Gamma) = 0$ and we obtained

$$\bar{E} = \frac{\sum_r \bar{E}_r e^{-\beta \bar{E}_r}}{\sum_r e^{-\beta \bar{E}_r}}$$

canonical distribution

Now the generic (as opposed to the definition that maximizes Γ) probability was

$$P_r = \frac{a_r}{a} \quad \Rightarrow \quad a_r = a P_r \quad \textcircled{1}$$

$$\ln \Gamma = a \ln a - \sum_r a_r \ln a_r =$$

$$\stackrel{\textcircled{1}}{=} a \ln a - \sum_r a P_r \ln(a P_r) =$$

$$= a \ln a - a \sum_r P_r (\ln a + \ln P_r) =$$

$$= a \cancel{\ln a} - a \cancel{\ln a} \underbrace{\sum_r P_r} - a \sum_r P_r \ln P_r =$$

$$= -a \sum_r P_r \ln P_r = -a H' \quad \textcircled{*}$$

So the canonical distribution maximizes
 $-\sum_r P_r \ln P_r$ for the fix value of the
 average energy $\bar{E} = \sum_r P_r E_r$.

Since $S = -k \sum_r P_r \ln P_r \Rightarrow \frac{S}{k} = -\sum_r P_r \ln P_r$

Then from (8) we see that

$$\ln \Gamma = \frac{aS}{k}$$

$\sum_r P_r \ln P_r$ measures information which is the
 opposite of disorder.

Ch. 7:

Partition Function Z (canonical ensemble).

- If we know β or \bar{E} for a system we can calculate

$$Z = \sum_r e^{-\beta E_r} \quad \text{partition function}$$

then:

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

$$\bar{p} = \frac{1}{\beta} \frac{\partial \ln Z}{\partial \beta}$$

$$S = k (\ln Z + \beta \bar{E})$$

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

The hard part is to find E_r (you may need to diagonalize a Hamiltonian matrix).

- Weakly interacting systems:

$$\text{If } A = A' + A'' \quad \text{with } E_{rs} = E_r' + E_s''$$

Then

$$\begin{aligned} Z &= \sum_{r,s} e^{-\beta E_{rs}} = \sum_{r,s} e^{-\beta (E_r' + E_s'')} = \\ &= \sum_{r,s} e^{-\beta E_r'} e^{-\beta E_s''} = \underbrace{\sum_r e^{-\beta E_r'}}_{Z'} \underbrace{\sum_s e^{-\beta E_s''}}_{Z''} = \\ &= Z' Z'' \end{aligned}$$

If we have N weakly interacting systems

$$\text{so that } A = \sum_{i=1}^N A_i \text{ and}$$

$$E_{j_1, j_2, \dots, j_N} = \sum_{i=1}^N \bar{E}_{i, j_i}$$

Then

$$Z = \sum_{j_1, j_2, \dots, j_N} e^{-\beta E_{j_1, \dots, j_N}} = \sum_{j_1, \dots, j_N} e^{-\beta (\bar{E}_{1, j_1} + \bar{E}_{2, j_2} + \dots + \bar{E}_{N, j_N})}$$

$$= \underbrace{\sum_{j_1} e^{-\beta \bar{E}_{1, j_1}}}_{Z_1} \underbrace{\sum_{j_2} e^{-\beta \bar{E}_{2, j_2}}}_{Z_2} \dots \underbrace{\sum_{j_N} e^{-\beta \bar{E}_{N, j_N}}}_{Z_N}$$

Then

$$Z = \prod_{i=1}^N \left(\sum_{j_i} e^{-\beta \bar{E}_{i,j_i}} \right) = \prod_{i=1}^N z_i$$

Then

$$\ln Z = \sum_{i=1}^N \ln z_i$$

If you find that a system is formed by N weakly interacting, identical small parts with partition function z , then $Z = z^N$. ("single particle" approach)

The energy can be defined up to some arbitrary constant which is thermodynamically irrelevant.

$$\begin{aligned} \text{If } \bar{E}_r^* &= \bar{E}_r + \epsilon_0 \\ z^* &= \sum_r e^{-\beta \bar{E}_r^*} = \underbrace{\sum_r e^{-\beta \bar{E}_r}}_z e^{-\beta \epsilon_0} = \\ &= z e^{-\beta \epsilon_0} \end{aligned}$$

Now

$$\bar{E}^* = -\frac{\partial \ln z^*}{\partial \beta} = \epsilon_0 + \bar{E} \quad \text{as expected}$$

But

$$\ln z^* = -\beta \epsilon_0 + \underbrace{\ln z}_{\text{independent of } \epsilon_0}$$

then

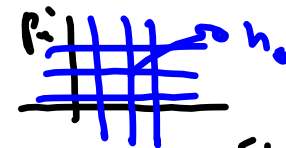
$$S^* = k (\ln z^* + \beta \bar{\epsilon}^*) = k (-\cancel{\beta \epsilon_0} + \ln z + \beta \bar{\epsilon} + \cancel{\beta \epsilon_0}) = k (\ln z + \beta \bar{\epsilon}) \equiv S$$

Same for $\bar{p} = \frac{1}{\beta} \frac{\partial \ln z}{\partial V}$, etc.

Example: equation of state of the ideal
gas using the canonical formalism.
(monatomic) classical

See next page

To construct Z we need E_r :



N : # of molecules.

$$E = \sum_{i=1}^N \frac{|\bar{p}_i|^2}{2m} + \underbrace{U(\bar{r}_1, \bar{r}_2, \dots, \bar{r}_N)}_{\text{for ideal gas}}$$

$$Z = \int e^{-\beta \left[\frac{1}{2m} (p_1^2 + p_2^2 + \dots + p_N^2) + U(\bar{r}_1, \dots, \bar{r}_N) \right]} \frac{d^3 r_1 \dots d^3 r_N d^3 p_1 \dots d^3 p_N}{h_0^{3N}}$$

If $U=0$ $\int \{d^3 r_i\} = V^N$

to get the number of cells in $\{d^3 r_i\} \{d^3 p_i\}$

$$Z = \frac{V^N}{h_0^{3N}} \int_{-\infty}^{\infty} e^{-\beta \frac{p_1^2}{2m}} d^3 p_1 \int_{-\infty}^{\infty} e^{-\beta \frac{p_2^2}{2m}} d^3 p_2 \dots \int_{-\infty}^{\infty} e^{-\beta \frac{p_N^2}{2m}} d^3 p_N$$

$$Z = \frac{V^N}{h_0^{3N}} \left(\int_{-\infty}^{\infty} e^{-\frac{\beta p^2}{2m}} d^3p \right)^N = \left[\underbrace{\frac{V}{h_0^3} \int_{-\infty}^{\infty} e^{-\frac{\beta p^2}{2m}} d^3p}_{z} \right]^N$$

z : partition function for one single molecule.

For the ideal gas because of the weak (null) interaction between molecules we can use the single particle approach.

Then $Z = z^N$.

$$\int_{-\infty}^{\infty} e^{-\frac{\beta p^2}{2m}} d^3p = \left(\int_{-\infty}^{\infty} e^{-\frac{\beta p^2}{2m}} dp \right)^3 = \left(\sqrt{\frac{2\pi m}{\beta}} \right)^3$$

(A.4.2)

Then

$$z = \frac{V}{h_0^3} \left(\frac{2\pi m}{\beta} \right)^{3/2} = V \left(\frac{2\pi m}{h_0^2 \beta} \right)^{3/2} \quad \text{for one atom.}$$

Then $Z = z^N$ and

$$\ln Z = N \ln z = N \left[\ln V + \frac{3}{2} \ln \frac{2\pi m}{h_0^2} - \frac{3}{2} \ln \beta \right]$$

$$\bar{p} = \frac{1}{\beta} \frac{\partial \ln Z}{\partial V} = \frac{1}{\beta} \frac{N}{V} = kT \frac{N}{V} \Rightarrow \boxed{\bar{p} V = N k T} \quad \text{equation of state.}$$

We also find that

$$\bar{E} = -\frac{\partial \ln Z}{\partial \beta} = \frac{N 3}{2 \beta} = \frac{3}{2} N k T = N \epsilon$$

then $\epsilon = \frac{3}{2} k T$: kinetic energy of one single atom.

$$C_V = \left. \frac{\partial \bar{E}}{\partial T} \right|_V = \frac{3}{2} k N = \frac{3}{2} k \frac{\nu N_A}{N} = \frac{3}{2} \nu \frac{k N_A}{R} = \frac{3}{2} \nu R$$

$$\boxed{\frac{C_V}{\nu} = \frac{3}{2} R} \quad \text{per mole.}$$

Also

$$\frac{\Delta^* E}{\bar{E}} = \frac{[\overline{CDE^2}]^{1/2}}{\bar{E}} = \frac{\left(-\frac{\partial \bar{E}}{\partial \rho}\right)^{1/2}}{\bar{E}} = \frac{\left(\frac{3}{2} Nk^2 T^2\right)^{1/2}}{\frac{3}{2} NkT} =$$

$$= \sqrt{\frac{2}{3N}}$$

very sharp peak in E if
 $N \sim N_a$

However, not everything works fine. Let's get the entropy:

$$\begin{aligned}
 S &= k (\ln Z + \beta \bar{E}) = k N \left[\ln V + \frac{3}{2} \ln \frac{2\pi m}{h_0^2} + \frac{3}{2} \ln kT \right] \\
 &\quad + \frac{k}{kT} \frac{3NkT}{2} \\
 &= k N \left[\ln V + \frac{3}{2} \ln T + \frac{3}{2} \ln \frac{2\pi m k}{h_0^2} + \frac{3}{2} \right] = \underbrace{\frac{3}{2} \ln k + \frac{3}{2} \ln T}_{\text{blue}} \\
 &= Nk \left[\ln V + \frac{3}{2} \ln T + \sigma \right]
 \end{aligned}$$

$$\sigma = \frac{3}{2} \ln \left(\frac{2\pi m k}{h_0^2} \right) + \frac{3}{2}$$

Notice that

$$\lim_{T \rightarrow 0} S \neq 0!$$

Not in agreement with the third law.

Gibbs paradox (discovered before quantum mechanics).

The expression for S also has the problem that it does not behave as an extensive property.

If we increase V by a factor α then $V' = \alpha V$

If we also increase N " " " " " $N' = \alpha N$

We would expect that $S' = \alpha S$.

Notice that if $\bar{E} = N \frac{3}{2} kT$

$$\bar{E}' = \alpha N \frac{3}{2} kT = \alpha \bar{E}$$

but

$$S' = \alpha N k \left[\ln \alpha V + \frac{3}{2} \ln T + \sigma \right] \quad (1)$$

$$= \alpha N k \left[\ln \alpha + \ln V + \frac{3}{2} \ln T + \sigma \right] =$$

$$= \underbrace{\alpha N k \left[\ln V + \frac{3}{2} \ln T + \sigma \right]}_{\alpha S} + \underbrace{\alpha N k \ln \alpha}_{\text{what is this? PROBLEM.}}$$

what is this?
PROBLEM.

From ① we see that $S \propto N$

but

S'	S''
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$$S = S' + S''$$

If $S' = S''$ with $V' = V''$ and $N' = N''$

$$S' = S'' = N' k \left[\ln V' + \frac{3}{2} \ln T + \sigma \right]$$

$$2S' = \underbrace{2N'}_2 k \left[\ln \frac{V}{2} + \frac{3}{2} \ln T + \sigma \right] \neq S'$$

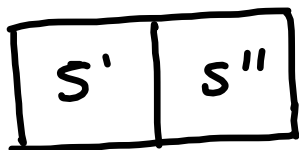
Since $S = N k \left[\ln V + \frac{3}{2} \ln T + \sigma \right]$

$$V' = \frac{V}{2}$$

$$N' = \frac{N}{2}$$

$$\text{or } S - 2S' = 2N'k \ln 2 = Nk \ln 2 \neq 0!$$

Gibbs paradox x



$$S' = S''$$

(position put for a gas in equilibrium)

so we know that $S = S_1 + S_2$

Since exchanging two atoms of the same gas does not increase the amount of disorder \mathcal{Z} needs to be corrected. We need to divide it by $N!$ the number of ways in which we can rearrange N particles.

Then

$$\mathbb{Z}^2 = \mathbb{Z} \times \mathbb{Z} = \mathbb{Z}^2$$