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Last time:

We found that

$$\tilde{Z} = \frac{Z}{N!} = \frac{\xi^N}{N!}$$ for a classical ideal gas.

We had to divide Z by $N!$ which is all the ways in which N atoms can be rearranged to solve the Gibbs paradox, i.e., that S obtained from Z was not extensive.

With

$$Z \equiv \tilde{Z} = \frac{\xi^N}{N!}$$

$$\xi = V\left(\frac{2\pi m}{h_0^2 \beta}\right)^{3/2}$$

$$\ln \xi = \ln V + \frac{3}{2}\ln T + C$$

$$\ln Z = N \ln \xi - \ln N! \overset{\text{stirling}}{\simeq} N \ln \xi - N \ln N + N$$

Now

$$S = k(\ln Z + \underbrace{\beta \bar{E}}_{\frac{3}{2}\frac{kTN}{kT} = \frac{3}{2}N}) = kN\left[\ln V + \frac{3}{2}\ln T + \sigma - \ln N + 1\right] = kN\left[\ln\frac{V}{N} + \frac{3}{2}\ln T + \sigma_0\right] \quad (2)$$

$$\sigma = \frac{3}{2}\ln\left(\frac{2\pi m k}{h_0^2}\right) + \frac{3}{2} \qquad \sigma_0 = \sigma + 1$$

We see that now in 1 if I change

$V \to \alpha V$ and $N \to \alpha N$ now $S \to \alpha S$

and it is extensive as expected.

- Notice that S still has the problem that it does not go to zero as $T \to 0$.

This is because the "ideal gas" approximation is not valid as $T \to 0$.

When is the ideal gas approximation valid?

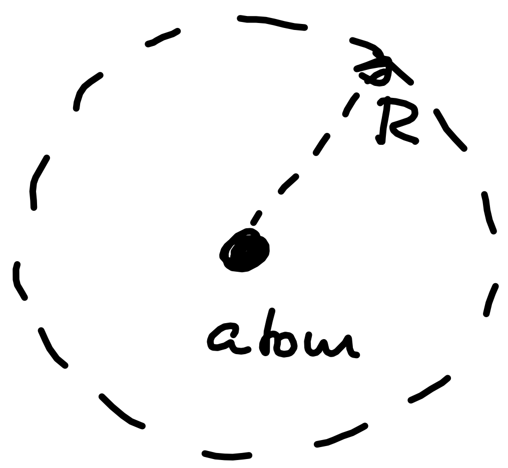
- Classical mechanics has to apply then

p_i, r_i : it should be ok to consider them as independent variables.

$\Delta q \, \Delta p \gtrsim \hbar$

$\bar{p}$: mean momentum

$\bar{R}$: mean separation

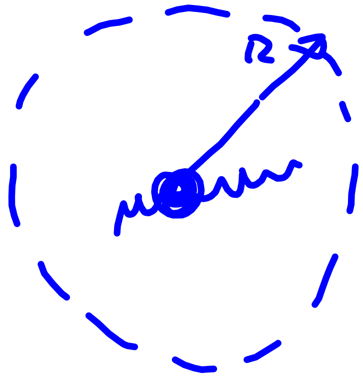


We want that

$$\bar{p}\,\bar{R} >> \hbar$$

$$\Rightarrow \bar{R} >> \frac{\hbar}{p} = \frac{h}{2\pi p} = \frac{\lambda}{2\pi}$$

$\lambda = \frac{h}{p}$ De Broglie wave length.



We need $\boxed{\bar{R} >> \lambda}$

• If $V = \bar{R}^3 N \Rightarrow \bar{R} = \left(\frac{V}{N}\right)^{1/3}$

• $\frac{N}{V}$ has to be low (low density).

• $\frac{\bar{p}^2}{2m} \approx \bar{\varepsilon} = \frac{3}{2}kT \;\therefore\; \bar{p} \approx \sqrt{3mkT}$

and $\lambda = \frac{h}{p} = \frac{h}{\sqrt{3mkT}}$

(• T has to be high)
• m has to be large

The ideal gas approximation applies at

- high T
- low density
- low mass for the particles.

Grand canonical partition function for an ideal gas.

Macrostate: (T, μ, V) This means that we will have to obtain $\langle E \rangle$ and $\langle N \rangle$.

Microstates: $\{\bar{p}_1, \bar{q}_1, \bar{p}_2, \bar{q}_2 \dots\}$ 6 N variables (but now $\underline{\underline{N}}$ is NOT fixed).

$$\mathcal{Z}(T, \mu, V) = \mathcal{Z}(\beta, \mu, V) = \sum_{N=0}^{\infty} e^{\beta \mu N} .$$

$$\frac{1}{N!} \int \left(\prod_{i=1}^{N} \frac{d^3 \bar{q}_i \, d^3 \bar{p}_i}{h_0^3} \right) e^{-\beta \sum_i \frac{p_i^2}{2m}} =$$

to fix Gibbs paradox

$$\boxed{\mathcal{Z}(\beta,\mu,V)} = \sum_{N=0}^{\infty} e^{\beta\mu N} \frac{\zeta^N}{N!} =$$

as we'll see $\mu < 0$ so $e^{\beta\mu N}$ decreases with N and ζ^N increases so sharp maximum at $N = \bar{N}$.

$$= \sum_{N=0}^{\infty} \frac{e^{\beta\mu N}}{N!} V^N \left(\frac{2\pi m}{h_0^2 \beta}\right)^{3N/2} =$$

$$= \sum_{N=0}^{\infty} \frac{e^{\beta\mu N}}{N!} \left(\frac{V}{\lambda^3}\right)^N = \qquad \lambda = \frac{h_0}{\sqrt{2\pi m kT}}$$

$$= \sum_{N=0}^{\infty} \frac{\left(e^{\beta\mu} \frac{V}{\lambda^3}\right)^N}{N!} = \boxed{e^{e^{\beta\mu}\frac{V}{\lambda^3}}} \quad (1)$$

$$e^x = \sum_{n=0}^{\infty} \frac{x^n}{n!}$$

Remember that

$$\tilde{\Omega}(T,\mu,V) = -kT \ln \tilde{Z} = -kT\, e^{\beta\mu} \frac{V}{\lambda^3} \quad (2)$$

But $\tilde{\Omega} = F - \mu N$ and

$$d\tilde{\Omega} = dF - \mu\, dN - N\, d\mu = -S\,dT - P\,dV - N\,d\mu =$$

$$= \underbrace{\left.\frac{\partial \tilde{\Omega}}{\partial T}\right|_{V,\mu}}_{-S} dT + \underbrace{\left.\frac{\partial \tilde{\Omega}}{\partial V}\right|_{T,\mu}}_{-P} dV + \underbrace{\left.\frac{\partial \tilde{\Omega}}{\partial \mu}\right|_{T,V}}_{-N} d\mu \quad (4)$$

Then $P = -\left.\frac{\partial \tilde{\Omega}}{\partial V}\right|_{T,\mu}$ (3)

Plugging ② in ③:

$$\bar{P} = -\frac{\partial \tilde{\Omega}}{\partial V}\Big|_{\mu,T} = \frac{kT e^{\beta\mu}}{\lambda^3} \quad ⑤$$

and from ④

$$\bar{N} = -\frac{\partial \tilde{\Omega}}{\partial \mu}\Big|_{T,V} = +\frac{kT}{kT} e^{\beta\mu}\frac{V}{\lambda^3} = e^{\beta\mu}\frac{V}{\lambda^3} \quad ⑥$$

Then from ⑥

$$\frac{e^{\beta\mu}}{\lambda^3} = \frac{\bar{N}}{V} \quad ⑦$$

plugging ⑦ in ⑤:

$$\bar{P} = \frac{kT\bar{N}}{V} \text{ or } \boxed{\bar{P}V = \bar{N}kT}$$

equation of state.

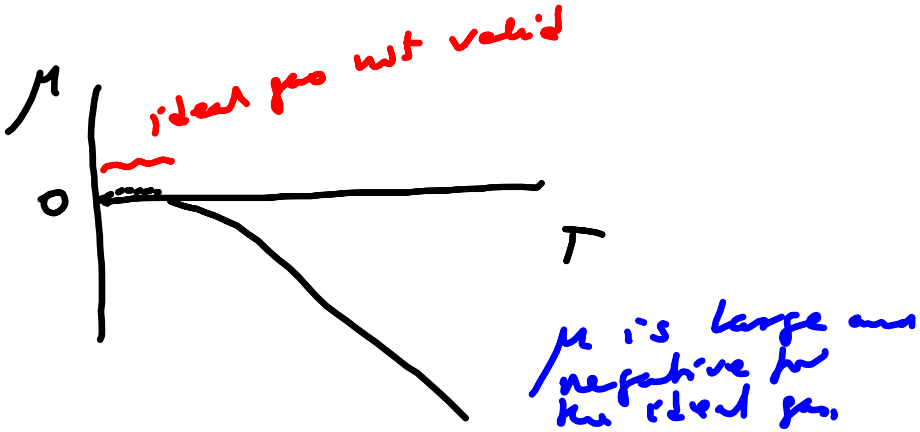
From ⑦ we get that:

$$\frac{e^{\beta\mu}}{\lambda^3} = \frac{\bar{N}}{V}$$

$$\beta\mu - 3\ln\lambda = \ln\frac{\bar{N}}{V}$$

$$\therefore \mu = \frac{1}{\beta}\ln\frac{\bar{N}\lambda^3}{V} = kT\ln\left(\frac{N\lambda^3}{V}\right) = kT\ln\left(\frac{\bar{P}\lambda^3}{kT}\right)$$

$$\mu \propto -T\ln T$$



Equipartition Theorem

If

$$E = E(q_1,\dots,q_f,p_1,\dots p_f) = \underbrace{\varepsilon_i(p_i)}_{b p_i^2} + E'(q_1,\dots q_f)$$

then at $T = \frac{1}{k\beta}$ in equilibrium

$$\bar{\varepsilon}_i = \frac{\int_{-\infty}^{\infty} e^{-\beta E}\, \varepsilon_i \, dq_1 \dots dp_f}{\int_{-\infty}^{\infty} e^{-\beta E}\, dq_1 \dots dp_f} = \frac{b\int_{-\infty}^{\infty} p_i^2 e^{-\beta b p_i^2} dp_i \cancel{\int e^{-\beta E'} dp_i' dq_i}}{\int_{-\infty}^{\infty} e^{-\beta b p_i^2} dp_i \cancel{\int e^{-\beta E'} dp_i' dq_i}}$$

$$= -\frac{\partial}{\partial \beta} \ln\left(\int_{-\infty}^{\infty} e^{-\beta \varepsilon_i} dp_i\right)$$

Canonical

$\bar{\varepsilon}_i$ for quadratic terms in $\bar{E}$.

But $\varepsilon_i = b p_i^2$ then

$y = \sqrt{\beta}\, p_i$

$dy = \sqrt{\beta}\, dp_i$

$$\int_{-\infty}^{\infty} e^{-\beta b p_i^2} dp_i =$$

$$\beta^{-1/2} \int_{-\infty}^{\infty} e^{-by^2} dy$$

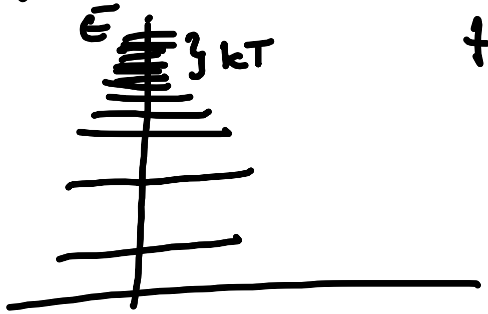
then

$$\ln \left[\int_{-\infty}^{\infty} e^{-\beta \varepsilon_i} dp_i \right] = -\frac{1}{2} \ln \beta + \underbrace{\ln \int_{-\infty}^{\infty} e^{-by^2} dy}_{\text{indep. of } \beta}$$

$$\bar{\varepsilon}_i = -\frac{\partial}{\partial \beta}\left(-\frac{1}{2} \ln \beta\right) = \frac{1}{2}\,\frac{1}{\beta} = \boxed{\frac{kT}{2}}$$

- The mean value of each independent quadratic term in the energy is $\frac{1}{2}kT$.
- It is only valid at the classical level.

gas



true when T is such that many energy levels fit in the energy interval kT.

Examples:

1) Molecule in a gas:

$$K = \frac{1}{2m}\left(p_x^2 + p_y^2 + p_z^2\right) \qquad \overline{K} = 3\,\frac{1}{2}kT = \frac{3}{2}kT$$

Then for a whole gas with N ~~atoms~~:

$$\overline{E} = N\overline{K} = \frac{3}{2}NkT$$ as we found before.

3) Brownian motion: $\overline{v_x} = 0$ but $\overline{v_x^2} \neq 0$ fluctuations.

since $\overline{\frac{1}{2}m v_x^2} = \frac{\overline{p_x^2}}{2m} = \frac{1}{2}kT \neq 0 \qquad \overline{v_x^2} = \frac{kT}{m}$

- increases with T
- decreases with m.

3) Classical Harmonic Oscillator: (1D)

$$E = \frac{p^2}{2m} + \frac{1}{2}k_0 x^2$$

$$\bar{E} = \frac{1}{2}kT + \frac{1}{2}kT = kT$$

Notice that for a real oscillator $\bar{E} \neq 0$ if $T \to 0$ then this theorem breaks down at low T. We need to use quantum mechanics:

$$E_n = \left(n + \frac{1}{2}\right)\hbar\omega \qquad n = 0, 1, 2, \ldots \qquad \omega = \sqrt{\frac{k_0}{m}}$$

Now we can use the canonical formalism to evaluate $\bar{E}$:

$$\bar{E} = \frac{\sum_{n=0}^{\infty} E_n e^{-\beta E_n}}{\sum_{n=0}^{\infty} e^{-\beta E_n}} = -\frac{1}{Z}\frac{\partial Z}{\partial \beta} = -\frac{\partial}{\partial \beta}\ln Z$$

$$Z = \sum_{n=0}^{\infty} e^{-\beta E_n} = \sum_{n=0}^{\infty} e^{-\beta \hbar\omega(n+\frac{1}{2})} =$$

$$e^{-\beta\frac{\hbar\omega}{2}} \underbrace{\sum_{n=0}^{\infty} e^{-\beta\hbar\omega n}}_{\frac{1}{1-e^{-\beta\hbar\omega}}} = \frac{e^{-\beta\frac{\hbar\omega}{2}}}{1-e^{-\beta\hbar\omega}}$$

Then

$$\bar{E} = -\frac{\partial \ln Z}{\partial \beta} = \frac{\hbar\omega}{2} + \frac{\hbar\omega\, e^{-\beta\hbar\omega}}{1-e^{-\beta\hbar\omega}} =$$

$$= \frac{\hbar\omega}{2} + \frac{\hbar\omega}{e^{\beta\hbar\omega}-1} = \boxed{\hbar\omega\left(\frac{1}{2} + \frac{1}{e^{\beta\hbar\omega}-1}\right)}$$

If $\frac{\hbar\omega}{kT} << 1$ high T

$$\bar{E} \approx \hbar\omega\left(\frac{1}{2} + \frac{1}{1+\beta\hbar\omega-1}\right) = \hbar\omega\left(\frac{1}{2} + \frac{kT}{\hbar\omega}\right) \approx$$

$$\approx \frac{\cancel{\hbar\omega}\, kT}{\cancel{\hbar\omega}} = kT$$

If $\frac{\hbar\omega}{kT} \gg 1$ low T

$E \approx \frac{\hbar\omega}{2} \neq 0$!

zero point energy.