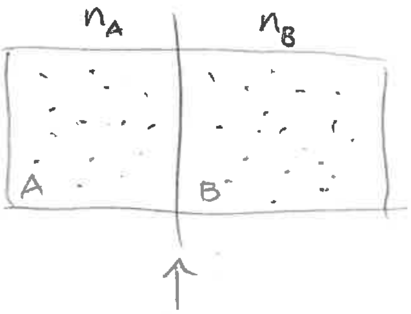
Lecture 18

Canonical loose ends

Entropy of mixing:



(Reversible or irreversible?)

Partition separating two gases.
temperatures T_i and densities n_i, volumes V_i, masses m_i.
Potentially different gases.

How does the entropy change? Initial versus final state:

Final state: obviously the 2 gases mix completely.

$$N = N_1 + N_2 = n_1 V_1 + n_2 V_2$$
$$E = \frac{3}{2} N_1 k_B T_1 + \frac{3}{2} N_2 k_B T_2$$

(a) What is the final temperature? No energy loss in this process.

$$E = \frac{3}{2} N_1 k_B T + \frac{3}{2} N_2 k_B T = \frac{3}{2} k_B T (N_1 + N_2)$$

$$\Rightarrow \boxed{T = \frac{N_1 T_1 + N_2 T_2}{N_1 + N_2}}$$

Now, let us ask about the entropy of these two gases. It is clearly the sum of the entropies of the two gases. Canonical analysis

$$Z = \frac{1}{N_1! N_2!} \left(\prod_{i=1}^{N_1} \frac{d^3q_i \, d^3p_i}{h^3} \right) \left(\prod_{i=1}^{N_2} \frac{d^3q_i \, d^3p_i}{h^3} \right) e^{-\beta \sum_{i=1}^{N_1} \frac{p_i^2}{2m_A} - \beta \sum_{i=1}^{N_2} \frac{p_i^2}{2m_B}}$$

$$= Z_A Z_B$$

$$\Rightarrow F = -k_B T(\ln Z_A + \ln Z_B)$$

$$\Rightarrow S = -\frac{\partial F}{\partial T}\bigg|_{V,N} = S_A + S_B .$$

$$\lambda(T) = \frac{h}{\sqrt{2\pi m k_B T}}$$

The entropy of an ideal gas is given by

$$S(T,N,V) = N k_B \left(\ln \frac{V}{N\lambda^3(T)} + \frac{5}{2} \right) \quad \text{(Sackur-Tetrode)}$$

$$\Rightarrow S_{final} = N_1 k_B \ln \frac{V}{N_1 \lambda_1^3(T)} + N_2 k_B \ln \frac{V}{N_2 \lambda_2^3(T)} + N k_B \frac{5}{2}$$

$$S_{initial} = N_1 k_B \ln \frac{V_1}{N_1 \lambda_1^3(T_1)} + N_2 k_B \ln \frac{V_2}{N_2 \lambda_2^3(T_2)} + N k_B \frac{5}{2}$$

$$S_{mix} = \Delta S = N_1 k_B \ln \frac{V}{V_1} \frac{\lambda_1^3(T_1)}{\lambda_1^3(T)} + N_2 k_B \ln \frac{V}{V_2} \frac{\lambda_2^3(T_2)}{\lambda_2^3(T)}$$

$$= \boxed{N_1 k_B \ln \frac{V T^{3/2}}{V_1 T_1^{3/2}} + N_2 k_B \ln \frac{V T^{3/2}}{V_2 T_2^{3/2}}} \quad \left(\text{Can we check?} \right)$$

Easier case: $T_1 = T_2$ initially ($\Rightarrow T$ same)

$$\boxed{\frac{\Delta S}{k_B} = N_1 \ln \frac{V}{V_1} + N_2 \ln \frac{V}{V_2} > 0 .}$$

Why should we expect $\Delta S \geq 0$? Well,

$$T \Delta S \geq \Delta Q_{rev} = 0$$

and this is not reversible!

Intuition? The case with two different temperatures is also positive.

What happens if the two gases are the same? Then, we need to be careful because

$$Z \neq Z_1 Z_2 \quad \left(\text{which has } \frac{1}{N_1! N_2!}\right),$$

in fact Z is what you know:

$$Z = \frac{1}{N!}\frac{V}{\lambda^3} \Rightarrow S = N k_B\left(\ln\frac{1}{n\lambda^3} + \frac{5}{2}\right)$$

$$\Rightarrow S_f - S_i = N k_B\left(\ln\frac{1}{n\lambda^3} + \cancel{\frac{5}{2}}\right) - N_1 k_B\left(\ln\frac{1}{n\lambda^3} + \cancel{\frac{5}{2}}\right) - N_2 k_B\left(\ln\frac{1}{n\lambda^3} + \cancel{\frac{5}{2}}\right)$$

$$= \ln\frac{1}{n\lambda^3}\left(N - N_1 - N_2\right) = 0 \quad (\text{as expected}).$$

What happens if we treat gaseous atoms as distinguishable?

$$Z = V/\lambda^3$$

$$= \frac{N!}{N!}\frac{V}{\lambda^3} \Rightarrow F = F_{\text{ideal}}^{(\text{indist.})} - k_B T \ln N!$$

$$\Rightarrow S = S_{\text{ideal}}^{(\text{indist.})} + \underbrace{k_B\left(N\ln N - N\right)}_{\text{should be higher}}$$

OR $k_B \ln N!$

If we repeat the entropy of mixing calculation, we get:

$$\frac{\Delta S}{k_B} = \cancel{k_B\left(N\ln N - \cancel{N} - N_1 \ln N_1 + \cancel{N_1} - N_2 \ln N_2 + \cancel{N_2}\right)}$$

$$= \cancel{k_B\left(N\ln N - N_1 \ln N_1 - N_2 \ln N_2\right)} \neq 0$$

$\Big($suppose $N_1 = N_2 = N/2$, get $N\ln N - \frac{N}{\cancel{2}}\ln\frac{N}{2}\cdot\cancel{2}\Big)$

$= N(\ln 2)$.

$$\boxed{\frac{\Delta S}{k_B} = \ln\frac{N!}{N_1! N_2!} \neq 0}$$

Makes no physical sense!

This is called the Gibbs paradox.

(*) Discussion from Kardar?

Classical stuff - in principle distinguishable - we can put it on a computer and track it.
Quantum argument - OK but there's a classical world out there and we can distinguish particles when they're not quantum mechanically coherent with each other.

Equipartion theorem

Consider a Hamiltonian of the form

$$H = \sum_{i=1}^{M} \frac{1}{2}\alpha_i p_i^2 + \frac{1}{2}\beta_i q_i^2$$

We call this a quadratic Hamiltonian and refers to a case where the energy depends on the squares of the canonical coordinates and momenta, where the canonical positions and momenta satisfy Hamilton's eqns.

$$\dot{q}_i = \frac{\partial H}{\partial p_i}$$

$$\dot{p}_i = -\frac{\partial H}{\partial q_i}$$

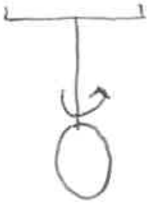
Examples:

Free particle, $H = \frac{p^2}{2m} = \frac{p_x^2 + p_y^2 + p_z^2}{2m}$

Oscillator, $H = \frac{1}{2}\frac{p^2}{m} + \frac{1}{2}m\omega^2 q^2$

Rigid rotor, $H = \frac{L^2}{2I}$ (angular momentum, angle)

Torsional oscillator, $H = \frac{L^2}{2I} + \frac{1}{2}K\theta^2$



EM field $H = \int d^3x \; \frac{\epsilon_0}{2}E^2(x) + \frac{1}{2\mu_0}B^2(x)$ (electric & magnetic fields)

All to say, it's common. The equipartition theorem says the following; the average energy associated with each quadratic degree of freedom is $\frac{1}{2}k_B T$.

Proof: $Z = \prod_i \sqrt{\frac{2\pi}{\alpha_i\beta}}\sqrt{\frac{2\pi}{\beta_i\beta}} \Rightarrow \ln Z = \sum_{i=1}^{N}\left(\ln\sqrt{\frac{(2\pi)^2}{\alpha_i\beta_i}} + \ln\frac{1}{\beta}\right)$

$= \beta\text{-ind. sum} + \overset{-N\ln\beta}{N\ln 1/\beta}$

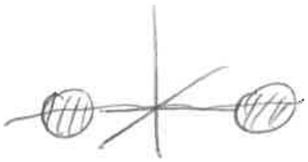
$$\Rightarrow \langle E\rangle = -\frac{\partial}{\partial\beta}\ln Z$$

$$= -\frac{\partial}{\partial\beta}(-N\ln\beta)$$

$$= \frac{N}{\beta} = Nk_BT$$

Note that $N = \#$ a terms + $\#$ b terms. If say b vanishes like for ideal gas, get ½. So we see that T emerges directly as a measur

Ideal gas: 3 DoFs per particle

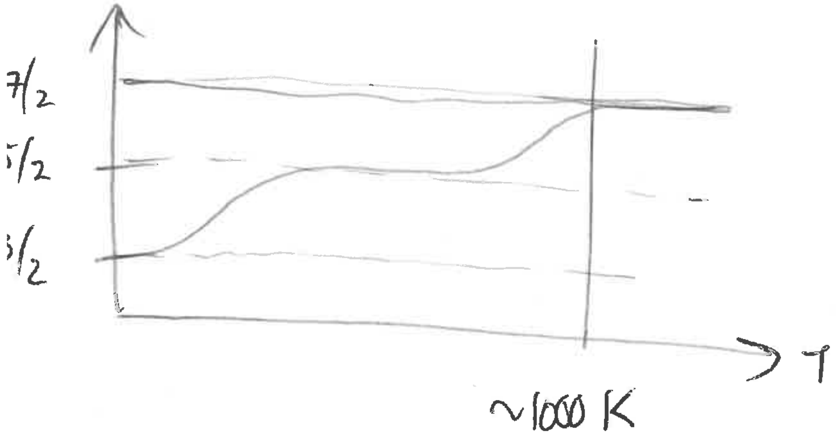


Diatomic mol

$$\rightarrow \begin{array}{ccc} 3 \text{ trans}, & 2 \text{ rot}, & 1 \text{ vib} \\ \downarrow & \downarrow & \downarrow \\ 3/2\, kT & kT & kT \end{array} \longrightarrow 7/2\, Nk_BT$$

C_v

$$C_v = 7/2\, Nk_B$$



Temp. for vibs to heat up.

Correction due to quantum mechanics.

Bohr van Leeuwen theorem

Consider a gas of charged particles where

$$H = \sum_i \frac{p_i^2}{2m_i} + \underbrace{U(q_1, \dots, q_N)}_{\substack{\text{interactions \& potential energy to} \\ \text{assemble the } n \text{ charges in some} \\ \text{configuration}}}$$

$$\left(\text{e.g. } U = \sum_{i \neq j} \frac{q_i q_j}{8\pi \varepsilon_0 r_{ij}}\right)$$

If we place these particles in a magnetic field, then we can write the resulting Hamiltonian from E&M as

$$\sum_i \frac{(p_i - q_i A(r_i))^2}{2m_i} + U$$

with $A(r_i)$ the vector potential such that

$$B(r) = \nabla \times A(r).$$

In principle, the B-field should affect the thermodynamic properties of the system. For example, it could magnetize the system, leading to $M(B)$, or even change other thermodynamic properties.

The van Leeuwen theorem states that this is not the case, and it is very straightforward to prove.

$$Z = \frac{1}{N!} \int \prod_{i=1}^{N} \frac{d^3p_i \, d^3q_i}{h^3} \, e^{-\beta\left(\sum_i \frac{(p_i - q_i A_i)^2}{2m_i} + U(\{q\})\right)}$$

$$= \frac{1}{N! h^{3N}} \int \prod_{i=1}^{N} d^3q_i \, e^{-\beta U} \int \prod_{i=1}^{N} d^3p_i \, e^{-\beta \sum_i \frac{(p_i - e_i A(q_i))^2}{2m}}$$

Take $p_i \to p_i - e_i A(r_i)$ for each i

$$\Rightarrow Z = \frac{1}{N! h^{3N}} \int \prod_{i=1}^{N} d^3 q_i \, e^{-\beta U} \int \prod_{i=1}^{N} d^3 p_i \; e^{-\sum_i \beta p_i^2/2m_i}$$

$$= \left(V/\lambda^3\right)^N \frac{1}{N!} \cdot \underbrace{\int \left(\prod_{i=1}^{N} d^3 q_i\right) e^{-\beta U}}_{\text{Not A-dependent!}}$$

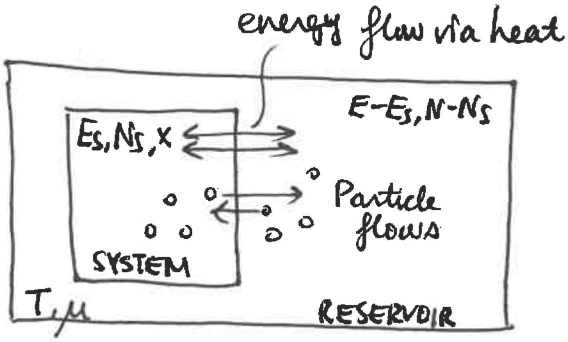
No magnetism.

Assuming atom has mag. moment is gm. Orbital moment.

Grand Canonical Ensemble

Reminder

Ensemble	What is fixed	Probability
MicroCanonical	E, x, N	$p(\mu_s) = \frac{1}{\Omega}\delta(E - H(\mu))$
Canonical	T, x, N	$p(\mu_s) = \frac{1}{Z} e^{-\beta H(\mu)}$
Grand canonical	T, x, μ	$p(\mu_s) = \frac{1}{Q} e^{-\beta(H(\mu_s) - \mu N)}$



<u>Strategy</u>: same as canonical case. Start in microcanonical ensemble of S+R and trace out the reservoir.

$$p(\underset{\substack{\uparrow \\ N_s \\ \text{particles}}}{\mu_s}, \underset{\substack{\uparrow \\ N-N_s \\ \text{particles}}}{\mu_R}) = \frac{1}{\Omega_{SR}}\,\delta\left(E - H_S^{N_s}(\mu_s) - H_R^{N-N_s}(\mu_R)\right)$$

$$p(\mu_s, N_s) = \underbrace{\sum_{\mu_R}{}'}_{\substack{\text{sum fixing res. to have} \\ N-N_s \text{ particles}}} p(\mu_s, \mu_R) = \frac{1}{\Omega_{SR}} \sum_{\mu_R}{}' \delta\left(E - H_S^{N_s}(\mu_s) - H_R^{N-N_s}(\mu_R)\right)$$

$$= \frac{1}{\Omega_{SR}}\,\Omega_R\left(E - H_S^{N_s}(\mu_s), N - N_s\right) \sim \exp\left[\frac{1}{k_B}\left(S_R(E_s, N_s) - \frac{H_s^{N_s}}{T} - N_s \frac{\partial S}{\partial N}\bigg|_E\right)\right]$$

$dE = 0 \Rightarrow T\,dS + \mu\, dN = 0$

$$\Rightarrow \left.\frac{\partial S}{\partial N}\right|_E = -\mu/T$$

$$\Rightarrow \boxed{p(\mu_s, N_s) \sim e^{-\beta H_s(\mu_s) + \beta \mu N_s} = \frac{1}{Q}\, e^{-\beta H_s(\mu_s) + \beta \mu N_s}}$$

grand canonical distribution

grand partition function.

$N \gg N_s^*$

$$Q = \sum_{N_s=0}^{\infty} {\sum_{\mu_s}}' e^{-\beta H_s(\mu_s) + \beta \mu N_s}$$

$$= \boxed{\sum_{N_s=0}^{\infty} e^{\beta \mu N_s} Z(T, x, N_s)}\,.$$

$$p(N_s) = {\sum_{\mu_s}}' \frac{1}{Q}\, e^{-\beta H_s(\mu_s) + \beta \mu N_s}$$

$$= \boxed{\frac{Z(T, x, N_s)}{Q(T, x, \mu)}\, e^{\beta \mu N_s}}$$

Recall for thermodynamic systems that $F(T, x, N) = -k_B T \ln Z \Rightarrow$

$$p(N_s) \sim e^{-\beta\left(F(T, x, N_s) - \mu N_s\right)} \equiv e^{-\beta \underbrace{\mathcal{G}(T, x, N_s)}_{\text{grand potential}}}.$$

As in canonical case, this is optimized by min of $F - \mu N$.

N_* such that $\boxed{\left.\frac{\partial F}{\partial N}\right|_{N_*} = \mu}$.

The second derivative is given by $\left.\frac{\partial^2 F}{\partial N^2}\right|_{N_*} = \left.\frac{\partial \mu}{\partial N}\right|_{N_*}$

$$p(N_s) \sim e^{-\beta \mathcal{Y}(N_*) - \frac{1}{2}\frac{\partial(\beta\mu)}{\partial N_*}(N-N_*)^2}$$

$$\sigma_N^2 = \frac{\partial N_*}{\partial(\beta\mu)} .$$

Can also be seen via:

$$\langle N^2 \rangle = \frac{1}{Q}\frac{\partial^2 Q}{\partial(\beta\mu)^2}$$

$$\sigma_N^2 = \langle N^2\rangle - \langle N\rangle^2 = \underbrace{\frac{1}{Q}\frac{\partial^2 Q}{\partial(\beta\mu)^2}}_{} - \frac{1}{Q^2}\left(\frac{\partial Q}{\partial(\beta\mu)}\right)^2$$

$$= \underbrace{\frac{1}{Q}\frac{\partial}{\partial(\beta\mu)}\frac{\partial Q}{\partial(\beta\mu)}}_{}$$

$$= \frac{\partial}{\partial(\beta\mu)}\left(\frac{1}{Q}\frac{\partial Q}{\partial(\beta\mu)}\right) + \frac{1}{Q^2}\left(\frac{\partial Q}{\partial(\beta\mu)}\right)^2$$

Isothermal compressibility connection?

$$\boxed{\sigma_N^2 = \frac{\partial}{\partial(\beta\mu)}\frac{\partial \ln Q}{\partial(\beta\mu)} = \frac{\partial^2 \ln Q}{\partial(\beta\mu)}} = \frac{\partial\langle N\rangle}{\partial(\beta\mu)} .$$

Ideal gas in GCE

$$Q = \sum_{N=0}^{\infty} e^{\beta\mu N} Z(T,x,N)$$

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

$$= \exp\left[e^{\beta\mu}\frac{V}{\lambda^3}\right]$$

$$N = \frac{\partial \ln Q}{\partial(\beta\mu)} = e^{\beta\mu}V/\lambda^3 \Rightarrow n\lambda^3 = e^{\beta\mu} \Rightarrow \boxed{\mu = k_B T \ln n\lambda^3} .$$

$$\frac{\partial N}{\partial(\beta\mu)} = e^{\beta\mu} V/\lambda^3 = N$$

$\sigma_N^2 = \langle N \rangle$ [Poisson → var rel. → 0 as $N \to \infty$].

Ensemble equivalence.

Unified picture of ensembles

$p(E, N) = ?$

$$\frac{\partial}{\partial p_i}\left(-k_B \sum_i p_i \ln p_i - \lambda_0 \left(\sum_i p_i - 1\right) - \lambda_1 \left(\sum_i \epsilon_i p_i - E\right) - \lambda_2 \left(\sum_i N_i p_i - N\right)\right) = 0$$

$$\Rightarrow -k_B(\ln p_i + 1) - \lambda_0 - \lambda_1 \epsilon_i - \lambda_2 N_i = 0$$

$$\Rightarrow \ln p_i + 1 = \frac{-k_B(\tilde{\lambda}_0 + \tilde{\lambda}_1 \epsilon_i + \tilde{\lambda}_2 N_i)}{k_B}$$

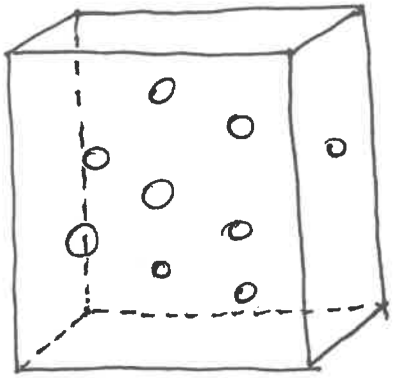
$$\Rightarrow p_i = \exp\left[-(1+\tilde{\lambda}_0) - \tilde{\lambda}_1 \epsilon_i - \tilde{\lambda}_2 N_i\right]$$

$$= \frac{1}{Q} \exp\left[-\underbrace{\tilde{\lambda}_1}_{\beta} \epsilon_i - \underbrace{\tilde{\lambda}_2}_{-\beta\mu} N_i\right]$$

$$= \frac{1}{Q} \exp\left[-\beta(\epsilon_i - \mu N_i)\right]$$

$$Q = \sum_i e^{-\beta(\epsilon_i - \mu N_i)} = \sum_N e^{\beta\mu N} Z(N).$$

Interactions



Ad nauseum: ideal gas

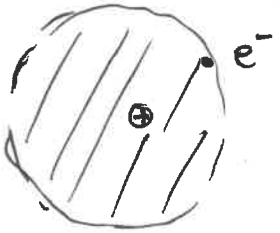
$$H = \sum_i \frac{p_i^2}{2m}$$

In equilibrium, have $PV = Nk_BT$ and all other things that you know.

Reality more complicated by interactions:

Two neutral atoms have electrical forces despite their neutrality

Quantum mechanics leads to a fluctuating dipole



$$|e\,\Delta x| \sim |d|.$$

Which creates an induced dipole in a neighboring atom, which always leads to an attraction

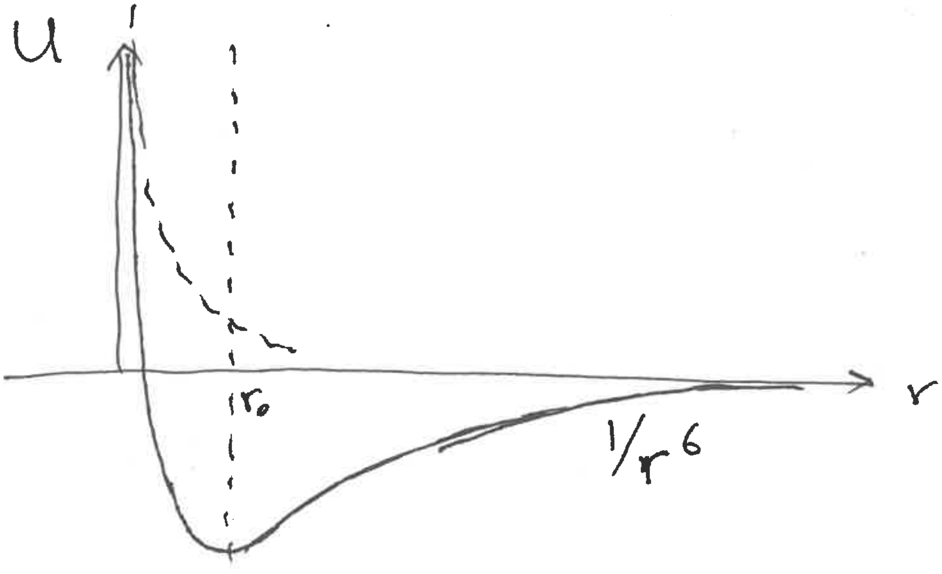
$$U_{dip} = \frac{(p_1\cdot p_2) - (p_1\cdot\hat{R})(p_2\cdot\hat{R})}{4\pi\epsilon_0 R^3}.$$

Since $p_2 \sim \overset{\text{polarizability.}}{\overset{\downarrow}{\alpha_2}} E_{2,1} \sim \frac{\alpha_2}{R^3}$

$$U_{dip} \sim -\frac{C_6}{R^6}.$$

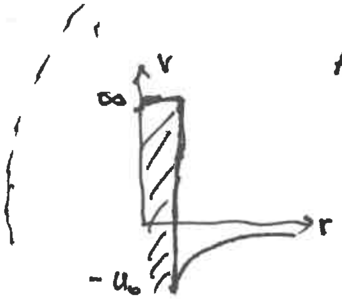
Thus, at long distances, two neutral atoms attract and this attraction gets stronger as atoms get closer.

When atoms get very close, their electron shells repel each other very strongly and effectively diverges.



Different models for this interaction. A famous one is the Lennard-Jones potential

$$U = A\left[\left(\frac{\sigma}{r}\right)^{12} - \left(\frac{\sigma}{r}\right)^{6}\right].$$



Another that we will use is

$$\left\{ V(r) = \begin{cases} \infty & r < r_0 \quad \text{(hard sphere)} \\ -u_0\left(\frac{r}{r_0}\right)^6 & r > r_0 \quad \text{(vdW)} \end{cases} \right\}$$

Now suppose that we have N such molecules interacting through this interatomic potential. Then the total potential energy depends on the configurations $\{q\}$ as

$$V(\{q\}) = V(q_1, q_2, \dots, q_N) = \sum_{i>j} V(q_i - q_j)$$

$$= \sum_{i>j} V(|q_i - q_j|)$$

$$= \frac{1}{2}\sum_{i\neq j} V(|q_i - q_j|).$$

In principle, the way to address the thermodynamic properties such as the equation of state is clear. Compute Ω, Z, Q (etc.) and take derivatives. As an example, let us consider Z.

$$Z(T,V,N) = \frac{1}{N!}\int \prod_{i=1}^{N} \frac{d^3q_i\, d^3p_i}{h^3}\, e^{-\beta H} = \frac{1}{N!\,h^{3N}}\int \prod_{i=1}^{N} d^3p_i\, d^3q_i\; e^{-\beta\sum_{i=1}^{N}\frac{p_i^2}{2m} - \beta V(\{q\})}$$

Cluster expansion

Starting point:

$$Z = \frac{1}{h^{3N} N!} \int \prod_{i=1}^{N} d^3 q_i \, d^3 p_i \; e^{-\beta \left(\sum_{i=1}^{N} \frac{p_i^2}{2m} + \sum_{i>j} \overset{V(q_{ij})}{\widetilde{V_{ij}}} \right)}$$

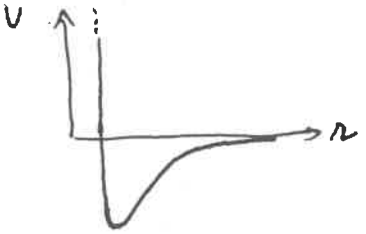
$$= \frac{1}{N! \, \lambda^{3N}} \underbrace{\int \left(\prod_{i=1}^{N} d^3 q_i \right) e^{-\sum_{i>j} \beta V_{ij}}}_{\text{analytically intractable.}}$$

Perturbation scheme for weak interactions. If βV small (weak int., high T), could try

$$e^{-\beta V} = 1 + (-\beta V) + \frac{1}{2}(-\beta V)^2 + \frac{1}{3!}(-\beta V)^3 + \dots$$

The issue however is that for $r < r_0$, V_{ij} diverges.

$$V(r) = \begin{cases} -u_0 \left(\frac{r_0}{r} \right)^6 & r > r_0 \\ +\infty & r \leq r_0 \end{cases}$$



Therefore integrals involving V also diverge. A better perturbation parameter is

$$f_{ij} = e^{-\beta V_{ij}} - 1 \quad \begin{cases} \text{Small when } +\beta u_0 \text{ small} & r > r_0 \\ -1 & r < r_0 \end{cases}$$

Let us use that then, and express

$$Z = \frac{1}{N! \, \lambda^{3N}} \int \left(\prod_{i=1}^{N} d^3 q_i \right) \prod_{\alpha > \beta = 1}^{N} (1 + f_{\alpha\beta}) .$$

Let's now analyze this in more detail. This looks complicated but we can write out a small example for a hypothetical small # particles.

$N=2 : \int d^3q_1 d^3q_2 \, (1+f_{\underline{12}})$ Note label permutation

$N=3 : \int d^3q_1 d^3q_2 d^3q_3 \, (1+f_{12})(1+f_{13})(1+f_{23})$ $\left(\begin{matrix}\text{ignoring} \\ N!\,\lambda^{3N}\end{matrix}\right)$:

$$= \int d^3q_1 d^3q_2 d^3q_3 \, \left(1+ f_{12} + \underbrace{f_{13} + f_{23} + f_{12}f_{13} + f_{12}f_{23} + f_{13}f_{23}}_{\text{already ok.}} + f_{12}f_{13}f_{23}\right)$$

$N=4 = \int d^3q_1 d^3q_2 d^3q_3 d^3q_4 \, (1+f_{12})(1+f_{13})(1+f_{14})(1+f_{23})(1+f_{24})(1+f_{34})$

$$= \int d^3q_1 d^3q_2 d^3q_3 d^3q_4 \, \Big| 1 + (f_{12}+f_{13}+f_{14}+f_{23}+f_{24}+f_{34})$$

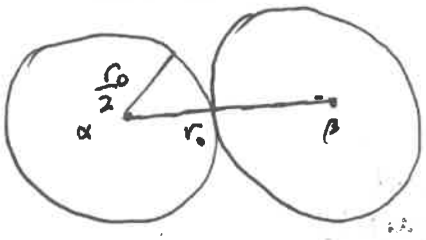
64 terms.

Maybe worth enumerating

$$\left\{\begin{aligned}
&+ (f_{12}f_{13} + f_{12}f_{14} + f_{12}f_{23} + f_{12}f_{24} + f_{12}f_{34} \\
&\quad + f_{13}f_{14} + f_{13}f_{23} + f_{13}f_{24} + f_{13}f_{34} \\
&\quad + f_{14}f_{23} + f_{14}f_{24} + f_{14}f_{34} \\
&\quad + f_{23}f_{24} + f_{23}f_{34} \\
&\quad + f_{24}f_{34}) \\
&+ (20 \text{ terms w/ } 3 \text{ fs}) \ldots \\
&+ (15 \text{ terms w/ } 4 \text{ fs}) \\
&+ 6 \text{ terms w/ } 5 \text{ fs} \\
&+ 1 \text{ term w/ } 6 \text{ fs})
\end{aligned}\right.$$

Cluster expansion motivated by the following observation

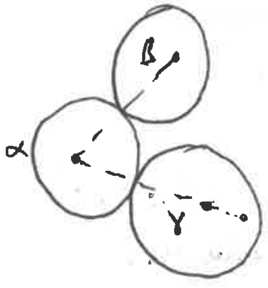
$f_{\alpha\beta}$ is "large" (-1) when $|r_\alpha - r_\beta| \leq r_0$ (effective atomic radius).



Otherwise it goes to zero as $V \to 0$ or $T \to \infty$. A term like

$f_{\alpha\beta} f_{\alpha\gamma}$ is doubly small $O(\beta V)^2$ unless

$|r_\alpha - r_\beta| \leq r_0, |r_\alpha - r_\gamma| \leq r_0$



Representing something like a three body collision which should be an unlikely event for a dilute gas which we're trying to address.

Meanwhile again, a term like

$f_{\alpha\beta} f_{\delta\gamma}$ is meaningful when $r_{\alpha\beta} < r_0$ & $r_{\delta\gamma} < r_0$

consider skipping.

$f_{\alpha\beta} f_{\delta\gamma} \sim 1$ if $\alpha\beta$ & $\delta\gamma$ collide

(βV) if $\alpha\beta$ OR $\delta\gamma$ collide

$(\beta V)^2$ if neither

$f_{\alpha\beta} f_{\alpha\gamma} \sim 1$ if α collides with β and V, βV if α-β close but not α-γ or v.v.

$(\beta V)^2$ otherwise.

The intuition is that p(2 particles collide) >> p(3 particles collide) and so is (2 particles collide in 2 places) vs. (3 particles collide)

$$\binom{N}{2} = \frac{N!}{2(N-2)!} = \frac{N(N-1)}{2} \quad (n\Omega)^2$$

$$\binom{N}{3} = \frac{N(N-1)(N-2)}{6} \quad (n\Omega)^3$$

So we neglect all terms where an index appears more than once.

$$\int \prod_{i=1}^{N} d^3q_i \prod_{\beta>\alpha} (1 + f_{\alpha\beta})$$

$$= \int \prod_{i=1}^{N} d^3q_i \sum_{k=0}^{N/2} S_k \; .$$

N labels.

S_k = sum of products of K f's where no index is shared

	4 particles	3 particles
$S_0 = 1$		
$S_1 = \sum_{\alpha>\beta} f_{\alpha\beta}$	$f_{12}+f_{13}+f_{23}+f_{14}+f_{24}+f_{34}$	$f_{12}+f_{13}+f_{23}$
e.g. $S_2 =$	$f_{12}f_{34} + f_{13}f_{24} + f_{14}f_{23}$	0

Now we need to integrate S_K.

Typical S_K:

$$f_{12} f_{34} f_{56} \cdots f_{2k-1,2k}$$

Integral is

$$\int d^3q_1 \cdots d^3q_N \; f_{12} f_{34} f_{56} \cdots f_{2k-1,2k}$$

$$= \underbrace{\left(\int d^3q_1 d^3q_2 \, f_{12}\right)\left(\int d^3q_3 d^3q_4 \, f_{34}\right) \cdots \left(\int d^3q_{2k-1} d^3q_{2k} \, f_{2k-1,2k}\right)}_{\text{all these integrals are the same}} \int d^3q_{2k+1} \cdots d^3q_N$$

$$= I^k V^{N-2k}.$$

$$I = \int d^3q_1 d^3q_2 \, f(|q_1 - q_2|) = \int d^3Q \, d^3q_{12} \, f(|q_{12}|)$$

$$= V \underline{\int 4\pi r^2 dr \, f(r)} \equiv V b.$$

$$\Rightarrow \quad I^k V^{N-2K} = V^{N-k} b^k.$$

Then

$$S_K = V^{N-k} b^k \times \left(\begin{array}{l} \text{\# terms where I can make k pairings} \\ \text{with all different indices} \end{array} \right)$$

· · · · · · · · · · · · · N

~~N(N-1) ... (N-2k)~~ $\binom{N}{2k}$ ways to grab 2K indices.

Pairing them up corresponds to their permutations: $\dfrac{(2k)!}{k!\,2^k}$

$$\Rightarrow \quad S_k = \binom{N}{2k} \frac{(2k)!}{2^k\, k!}\, V^{N-k} b^k$$

$$= \frac{N!}{(N-2k)!\,\cancel{(2k)!}} \quad \frac{\cancel{(2k)!}}{2^k\, k!}\, V^{N-k}\, b^k$$

$$= \frac{N!}{(N-2k)!\, 2^k \cdot k!}\, V^{N-k}\, b^k$$

$$= \frac{N!\, V^N}{(N-2k)!\, k!} \left(\frac{b}{2V} \right)^k$$

Putting it all together, we have

$$\cancel{Z = \frac{1}{h^{3N} N}}$$

$$Z = \frac{V^N}{\cancel{N!}\, \lambda^{3N}} \sum_{k=0}^{N/2} \frac{\cancel{N!}}{(N-2k)!\, k!} \left(\frac{b}{2V} \right)^k$$

$$= \tilde{V}^N \sum_{k=0}^{N/2} \frac{1}{(N-2k)!\, k!} \left(\frac{b}{2V} \right)^k$$

Easier as grand partition

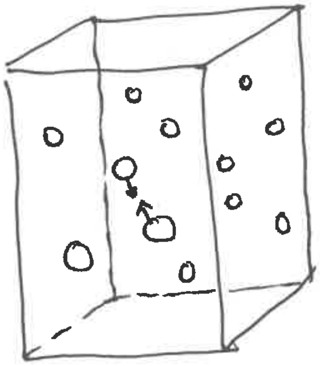
$$Q = \sum_{N=0}^{\infty} e^{\beta \mu N}\, \tilde{V}^N \sum_{k=0}^{N/2} \frac{1}{(N-2k)!\, k!} \left(\frac{b}{2V} \right)^k$$

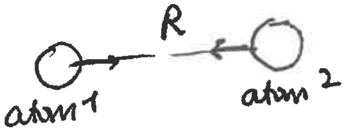
$$= \sum_{k=0}^{\infty} \sum_{N=2k}^{\infty} e^{\beta \mu N}\, \tilde{V}^N \frac{1}{(N-2k)!\, k!} \left(\frac{b}{2V} \right)^k$$

$$= \sum_{k=0}^{\infty} \left(\sum_{N=0}^{\infty} \frac{e^{\beta \mu N}\, \tilde{V}^N}{N!} \right) \frac{e^{2\beta\mu k}\, \tilde{V}^{2k}}{k!} \left(\frac{b}{2V} \right)^k$$

$$= \exp\left[e^{\beta\mu} \frac{V}{\lambda^3} \right] \sum_{k=0}^{\infty} \frac{1}{k!} \left(e^{2\beta\mu} \frac{bV}{2\lambda^6} \right)^k = \boxed{\exp\left[e^{\beta\mu} \frac{V}{\lambda^3} \right] \exp\left[e^{2\beta\mu} \frac{bV}{2\lambda^6} \right]}$$

Review of previous lecture





$$V(r) = \begin{cases} \infty & r \leq r_0 \\ -u_0\left(\frac{r_0}{r}\right)^6 & r > r_0 \end{cases}$$

$$N! Z = \int \prod_{i=1}^{N} \frac{d^3p_i\, d^3q_i}{h^3} e^{-\beta H} = \frac{1}{N!\,\lambda^{3N}} \int \prod_{i=1}^{N} d^3q_i \; e^{-\beta \sum_{i>j} V(\underbrace{r_{ij}}_{|q_i - q_j|})}$$

Cluster expansion

$$e^{-\beta \sum_{\alpha>\beta} V(r_{\alpha\beta})} \equiv \prod_{\alpha>\beta=1}^{N} e^{-\beta V(r_{\alpha\beta})} \equiv \prod_{\alpha>\beta=1}^{N} (1 + \overbrace{f_{\alpha\beta}}^{(e^{-\beta V_{\alpha\beta}}-1)})$$

C.E. approx. lowest order - ignore terms like $f_{12} f_{13}$ where an index repeats as it corresponds to a correction coming from 3 body coll. Suppressed by $n V_{atom}$ rel. 2-body coll.

$\downarrow$ Math/algebra

$$\boxed{\begin{aligned} Q &= \exp\left[e^{\beta\mu}\frac{V}{\lambda^3}\right] \exp\left[\frac{bV}{2\lambda^6} e^{2\beta\mu}\right] \\ b &= \int dr\, 4\pi r^2 \left(e^{-\beta V(r)} - 1\right) \\ \lambda &= \frac{h}{\sqrt{2\pi m k_B T}} \end{aligned}}$$

Evaluation of b

$$b = \int_0^{r_0} dr\; 4\pi r^2 (\underset{\substack{V=\infty \\ e^{-\beta V}=0}}{\underset{\uparrow}{e^{-\beta V(r)}}} - 1) + \int_{r_0}^{\infty} dr\; 4\pi r^2 (e^{-\beta V(r)} - 1)$$

$$= \int_0^{r_0} dr\; 4\pi r^2 (-1) + \int_{r_0}^{\infty} dr\; 4\pi r^2 \left(e^{\beta u_0 \left(\frac{r_0}{r}\right)^6} - 1\right).$$

Since we are interested in small corrections anyway, we will consider $\beta u_0 \ll 1$ although it is not strictly necessary.

$$b = -\frac{4}{3}\pi r_0^3 + \underbrace{4\pi \beta u_0 \int_{r_0}^{\infty} dr\, \frac{r_0^6}{r^4}}_{\underbrace{4\pi \beta u_0 r_0^6 \left(-\frac{1}{3r_0^3}\Big|_{r_0}^{\infty}\right)}_{= \frac{4\pi}{3} r_0^3 (\beta u_0)}}$$

$$\Rightarrow b = \frac{4\pi}{3} r_0^3 (\beta u_0 - 1)$$

$$= \underset{\substack{\uparrow \\ \text{8x atomic} \\ \text{volume}}}{\Omega} (\beta u_0 - 1)$$

Equation of state:

$$PV = -\mathcal{G} = k_B T \ln Q$$

$$\Rightarrow \frac{PV}{k_B T} = e^{\beta\mu} \frac{V}{\lambda^3} + e^{2\beta\mu} \frac{bV}{2\lambda^6}$$

$$\tilde{p} = e^{\beta\mu}/\lambda^3 + e^{2\beta\mu} \frac{b}{2\lambda^6}.$$

We want to relate to n.

$$N = \frac{\partial \ln Q}{\partial(\beta\mu)} = \frac{e^{\beta\mu}V}{\lambda^3} + \frac{\cancel{2}e^{2\beta\mu}bV}{\cancel{2}\lambda^6}$$

$$\Rightarrow n = \frac{e^{\beta\mu}}{\lambda^3} + \frac{e^{2\beta\mu}b}{\lambda^6}.$$

We want $p(n,T)$. [e.g: $p = nk_BT$]. To express p in terms of n, define $x = e^{\beta\mu}/\lambda^3$ $\Rightarrow$

$$\tilde{p} = x + \frac{1}{2}bx^2 \qquad\qquad x = \frac{e^{\beta\mu}}{\lambda^3} \geq 0.$$

$$n = x + bx^2$$

$$\hookrightarrow bx^2 + x - n = 0$$

$$\Rightarrow x = \frac{-1 \pm \sqrt{1+4bn}}{2b}$$

$bn \sim n\Omega \sim nV_{atom} \ll 1$ (assuming βu_0 not too large) $\Rightarrow$

$$\sqrt{1+4bn} \approx 1 + \frac{1}{2}(4bn) \underbrace{- \frac{1}{8}(4bn)^2}_{\text{need this to get corr. to ideal gas law.}} + \ldots$$

only sensible root

$$\Rightarrow x = \frac{-1 \oplus 1 + \frac{1}{2}(4bn) - \frac{1}{8}(4bn)^2}{2b}$$

$$= n - bn^2$$

$$\Rightarrow \tilde{p} = \frac{p}{k_BT} \approx n - bn^2 + \frac{1}{2}bn^2 + O(n^3).$$

$$= n - \frac{1}{2}bn^2$$

Putting it all together, we get:

$$p = n k_B T - \frac{1}{2} n k_B T \cdot \underbrace{(bn)}_{(\Omega \beta u_0 - \Omega) n}$$

$$-\frac{1}{2} n \cancel{k_B} T \Omega \cancel{\beta} u_0 n + \frac{1}{2} n k_B T \Omega n$$

$$= n k_B T + \frac{1}{2} n k_B T n \Omega - \frac{1}{2} n^2 \Omega u_0$$

$$\approx \frac{n k_B T}{1 - \frac{n\Omega}{2}} - \frac{1}{2} \Omega u_0 n^2$$

$$\equiv \boxed{\frac{N k_B T}{V - N b_{vdW}} - a_{vdW} \left(\frac{N}{V}\right)^2} \,, \quad \underbrace{b_{vdW} = \frac{\Omega}{2} \,, \quad a_{vdW} = \frac{1}{2} \Omega u_0}_{\text{NOT SAME } b, \text{ Sorry!!}}$$

Or

$$\underline{\underline{\left[p + a_v \left(\frac{N}{V}\right)^2\right] \left[V - N b_v\right] = N k_B T}}$$

↑ Approximate vdW EoS.

Physics of vdW EoS

A. Magnitude of correction

Set by essentially $(n\Omega) \sim 8n V_{atom}$

Air @ STP, $\Omega \sim 8 \times (\underbrace{2 \cdot 10^{-10} \, m}_{Ar})^3 \sim 10^2 \cdot 10^{-30} \, m^3 \sim 10^{-28} \, m^3$.

Density $n \sim \frac{p}{k_B T} \sim \frac{10^5 \, N/m^2}{5 \cdot 10^{-21} \, J}$ ← 1 atm

$\sim 2 \cdot 10^{25} \, m^{-3}$

$8 n V_{atom} \sim \boxed{2 \cdot 10^{-3} \text{ @ STP}} \ll 1$

Hence, ideal gas law is accurate to about 1 pt. in 1000 @ STP.

Breaks down when

$$\frac{n u_0 \Omega}{k_B T} \sim 1$$ (Interactions too strong or atoms too close).

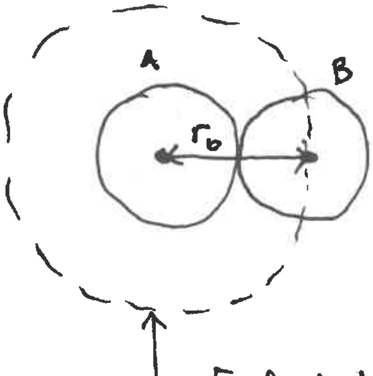
Why increasing pressure & lowering T condenses things.

B. Origin of terms

$$(P + a n^2)(V - \underline{\underline{N b}}) = N k_B T.$$

Excluded volume: Consider a hard-core gas with potential

$$V(r) = \begin{cases} \infty & r \le r_0 \\ 0 & r > r_0 \end{cases}$$



Excluded volume for placing atom B:

$$\Omega = \frac{4}{3}\pi r_0^3 = 8 \times \text{atom volume}.$$

$$Z = \frac{1}{N!\lambda^{3N}} \int \left(\prod_{i=1}^{N} d^3 q_i\right) \eta(\underbrace{\{q\}}_{q_1 q_2 \cdots q_N})$$

$\eta(\{q\}) = 0$ if any 2 particle positions $|q_\alpha - q_\beta| < r_0$.

$$\int \left(\prod_{i=1}^{N} d^3 q_i\right) = V(V-\Omega)(V-2\Omega)\cdots(V-(N-1)\Omega)$$

$$\ln (V)(V-\Omega)\cdots(V-(N-1)\Omega)$$

$$\ln V-k\Omega$$
$$=\ln V\left(1-\frac{k\Omega}{V}\right)$$
$$\approx \ln V-\frac{k\Omega}{V}$$

$$\approx \sum_{k=0}^{N-1} \ln V - \frac{k\Omega}{V}$$

$$= N\ln V - \frac{(N-1)N\Omega}{2V}$$

$$\approx N\ln V - N\,\frac{N\Omega}{2V}$$

$$\approx N\ln\left(V-\frac{N\Omega}{2}\right) \qquad \left(\frac{N\Omega}{V} \ll 1\right).$$

$$\Rightarrow e^{\ln V(V-\Omega)\cdots(V-(N-1)\Omega)}$$
$$\approx V(V-\Omega)\cdots(V-(N-1)\Omega)$$
$$=\left(V-\frac{N\Omega}{2}\right)^N$$

$$\Rightarrow Z = \frac{\left(V-\frac{N\Omega}{2}\right)^N}{N!\,\lambda^{3N}}$$
$$=\frac{1}{N!}\left[\frac{V-N\Omega/2}{\lambda^3}\right]^N$$

$$F = -K_BT\left(N\ln\frac{V-N\Omega/2}{\lambda^3} - N\ln N + N\right)$$

$$\boxed{P = -\frac{\partial F}{\partial V} = \frac{NK_BT}{V-\frac{N\Omega}{2}}}$$

(b). Reduced potential due to attraction.

Review of Lecture 22

$$Q = \exp\left[e^{\beta\mu}\frac{V}{\lambda^3}\right]\exp\left[e^{2\beta\mu}\frac{bV}{2\lambda^6}\right] \; ; \; b = \int dr\, 4\pi r^2 \left(e^{-\beta V(r)} - 1\right)$$

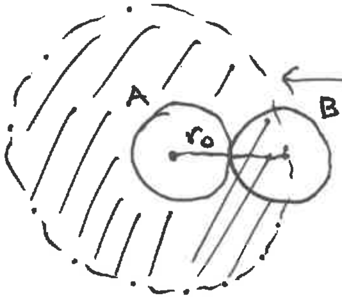
$$p = \frac{Nk_BT}{V - Nb} - a\left(\frac{N}{V}\right)^2 \qquad V(r) = \begin{cases} +\infty & r \leq r_0 \\ -u_0\left(\frac{r_0}{r}\right)^6 & r > r_0 \end{cases}$$

$$b = \frac{\Omega}{2} = \frac{1}{2}\underbrace{\left(\frac{4}{3}\pi r_0^3\right)}_{\text{excluded volume}}$$

$$a = \frac{u_0\Omega}{2}$$

Hard-core gas

$$V(r) = \begin{cases} +\infty & r \leq r_0 \\ 0 & \text{else} \end{cases}$$



atom A "excludes" a volume Ω for atom B.

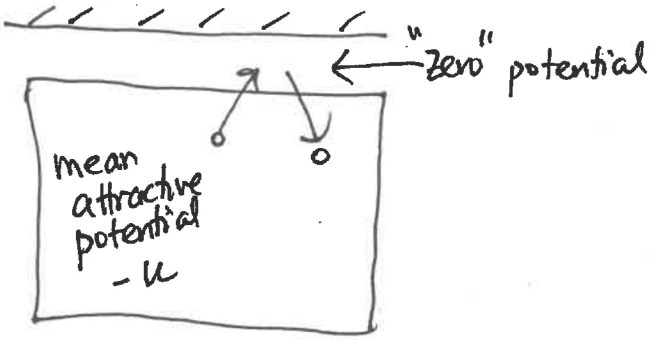
$$Z = \frac{1}{N!\lambda^{3N}}\left[V(V-\Omega)(V-2\Omega)\cdots(V-(N-1)\Omega)\right]$$

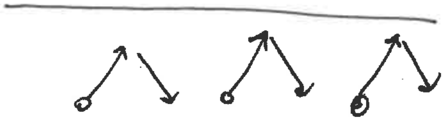
$$\approx \frac{(V - N\Omega/2)^N}{N!\lambda^{3N}}$$

$$\Rightarrow p = -\frac{\partial F}{\partial V}\bigg|_{T,N} = \underbrace{\frac{Nk_BT}{V - Nb}}_{\text{explains one term of vdW.} \to \text{comes from repulsion.}} .$$

Other term comes from attraction.

I Pressure comes from collisions with walls





Flux $\sim nv$

Rate of coll $\sim nvA$

Impulse $\sim mv$

$$\Rightarrow F = \frac{\text{Impulse}}{\text{time}} \sim mv^2 n A$$

$$p = F/A \sim mv^2 n$$

$$\sim n k_B T.$$

v reduced by leaving attractive potential

$$\frac{1}{2} mv(2\delta v) \sim u$$

$$\Rightarrow \Delta v \sim \frac{u}{mv}$$

$$u = \sum_j V(r_j)$$

$$\sim \int_{r_0}^{\infty} d^3 r \, n \, V(r)$$

$$\sim n \cdot \int 4\pi r^2 dr \, V(r)$$

$$\sim n u_0 \Omega$$

$$\Rightarrow \cancel{\Delta v \sim} \quad \Rightarrow \Delta p \sim \frac{n \cancel{v} \cancel{A} \cdot \cancel{m} u / \cancel{m} \cancel{v}}{\cancel{A}} \sim n^2 u_0 \Omega$$ and <u>is negative</u>.

Mean-field theory of condensation

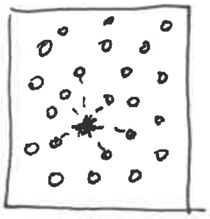
Previously: expanded partition function of vdW gas to get correction to ideal gas law in a way consistent with vdW equation of state:

$$P = \frac{Nk_BT}{V-Nb_{vdW}} - a\left(\frac{N}{V}\right)^2 .$$

Today: Use another powerful technique, called mean-field theory to get vdW eqn. as well as qualitatively understand the condensation transition.

Idea: Treat system as an effective system of non-interacting particles. Hard spheres in an effective potential set by all other atoms.

Physics



$$U = \frac{1}{2}\sum_{i\neq j} V(r_{ij}) = \frac{1}{2}\int d^3r\, d^3r'\, n(r)V(r-r')n(r')$$

$$n(r) = \sum_i \delta(r-r_i) \rightarrow \text{Treat as average density.}$$

If we treat the atoms as a homogenized blob of uniform density n, then

$$U = \frac{1}{2}\int d^3r\, d^3r'\, n(r)n(r')V(r-r')$$

If we treat the density as constant, then

$$U = \frac{1}{2}n^2\int d^3r\, d^3r'\, V(r-r')$$

$$= \frac{1}{2}n^2 V\int 4\pi r^2 V(r)\, dr$$

$$\equiv -\frac{1}{2}n^2 V u_0 ; \quad u_0 > 0$$

$\int d^3r\, d^3r'\, f(r-r')$:

$\Rightarrow R \equiv r$

$u \equiv r - r'$

Jacobian det is 1. $\Rightarrow$

$= \int_V d^3R \int_{-\infty}^{\infty} d^3u\, f(u).$

$$\Rightarrow Z = \frac{1}{N!\lambda^{3N}}\int\left(\prod_{i=1}^N d^3q_i\right) e^{-\beta U\{q\}}$$

$$\rightarrow \frac{1}{N!\lambda^{3N}}\int\left(\prod_{i=1}^N d^3q_i\right) \overbrace{\eta(q_1\cdots q_N)}^{\text{no overlaps}} e^{+\frac{1}{2}\beta n^2 u_0 V}$$

$$= \frac{\left(V-\frac{N\Omega}{2}\right)^N}{N!\lambda^{3N}} e^{\frac{1}{2}\beta n^2 u_0 V}$$

The pressure is given by

$$p = -\frac{\partial F}{\partial V}\Big|_{T,N},$$ where

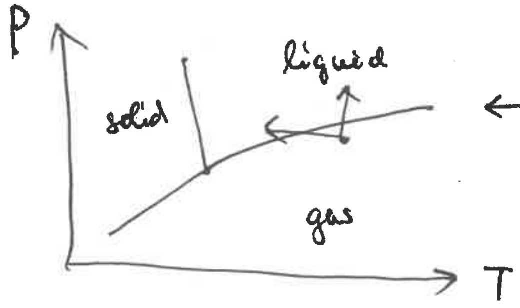
$$F = -k_B T\left(N\ln\left(V - \frac{N\Omega}{2}\right) + \frac{1}{2}\beta n^2 u_0 V - \ln N!\,\lambda^{3N}\right)$$

$$\frac{\partial F}{\partial V}\Big|_{T,N} = -k_B T\left(\frac{N}{V - \frac{N\Omega}{2}} - \frac{1}{2}\frac{\beta u_0 N^2}{V^2}\right)$$

$$\boxed{p = \frac{N k_B T}{V - \frac{N\Omega}{2}} - \frac{1}{2}u_0\left(\frac{N}{V}\right)^2}$$ (vdW EoS)!

This <u>very</u> simplistic picture, surprisingly, recovers the vdW EoS. Indeed, it is very unclear that fluctuations in positions can be neglected over a volume $\frac{4}{3}\pi r_0^3$ containing only a few atoms.

Nevertheless, the vdW mean-field theory qualitatively recovers other things. We know physically, as we crank up the pressure or lower temperature, the gas will condense into a liquid phase.



← The transition is first order, and is associated with <u>discontinuities</u> in the first derivatives in the free energy.

$$V = \frac{\partial G}{\partial p}\Big|_{T,N}$$

Volume changes discontinuously, or equivalently, density. Can we see this? Yes, let us treat the system in the GCE and ask about $p(N)$, the probability of N particles, or equivalently $p(n)$ since density is fixed.

↑ Changes in the mode/mean that are discontinuous will signal a phase transition.

$$\cancel{p(N) = e^{-\beta\Omega(N)}}$$

$$=$$

Recall from GCE: $$p(N) = \frac{e^{\beta\mu N} Z(T,V,N)}{Q} = \frac{1}{Q}e^{\beta\mu N}\frac{\left(V - \frac{N\Omega}{2}\right)^N}{N!\,\lambda^{3N}}e^{\frac{1}{2}\beta u_0 \frac{N^2}{V^2}V}$$

Further recall that when $N \gg 1$, the probability will be very tightly centered around the N that maximizes the distribution. Or, since V is fixed, the maximizing n, denoted n_*. To find n_* corresponding to the density of the gas, consider

$$p(N) = \exp\left[\beta\mu N + N\ln\left(V-\frac{N\Omega}{2}\right) - N\ln N + N - N\ln\lambda^3 + \frac{1}{2}\beta u_0 n^2 V\right]$$

$$= \exp\left[N\underbrace{(\beta\mu + 1 - \ln\lambda^3)}_{\Delta} + N\ln\left(n^{-1}-\frac{\Omega}{2}\right) + \frac{1}{2}\beta u_0 n^2 V\right]$$

$$= \exp\left[V\left\{n\Delta + n\ln\left(\frac{1}{n}-\frac{\Omega}{2}\right) + \frac{1}{2}\beta u_0 n^2\right\}\right]$$

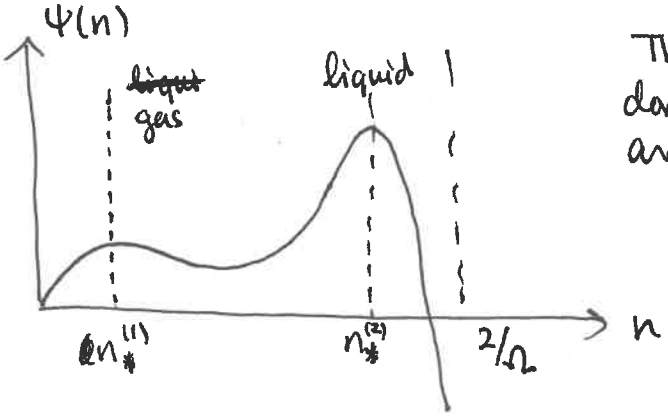
n_* satisfies

$$\Delta + \ln\left(\frac{1}{n_*}-\frac{\Omega}{2}\right) + \cancel{n_*}\,\frac{-\frac{1}{\cancel{n_*^2}}}{\frac{1}{n_*}-\frac{\Omega}{2}} + \beta u_0 n_* = 0$$

$$\Rightarrow \boxed{\Delta + \ln\left(n_*^{-1}-\frac{\Omega}{2}\right) - \frac{1}{1-n_*\Omega/2} + \beta u_0 n_* = 0}$$

$$\Rightarrow \Delta = -\ln\left(n_*^{-1}-\frac{\Omega}{2}\right) + \frac{1}{1-n_*\Omega/2} - \beta u_0 n_*$$

Consider $\Psi(n) \equiv n\Delta + n\ln\left(\frac{1}{n}-\frac{\Omega}{2}\right) + \frac{1}{2}\beta u_0 n^2$. If we plot it for some Δ, βu_0, it can look like



The phase where $\Psi(n_*)$ is larger dominates by the "saddle point" argument.

$$p(N) = \exp\left[V\Psi(n)\right]$$

Thermodynamic limit $N\to\infty \Rightarrow$ n which maximizes $\Psi(n)$ dominates exponentially. Can also be seen as $V\to\infty$ if density held fixed.

Maybe more clear if we write it as:

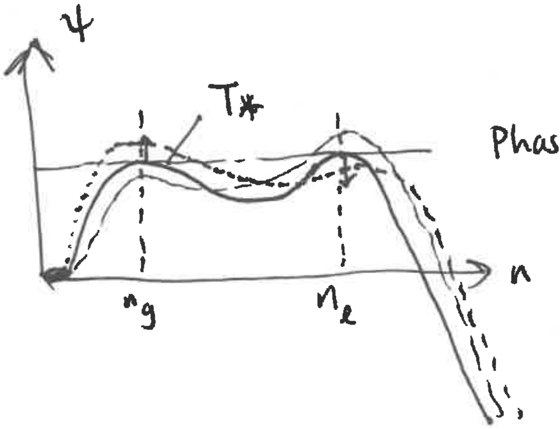
$$p(N) = \exp\left[N \underset{\sim\sim\sim\sim\sim\sim\sim\sim\sim\sim\sim\sim}{\left\{\Delta + \ln\left(n^{-1} - \frac{\Omega}{2}\right) + \frac{1}{2}\beta u_0 n\right\}}\right]$$

The function scales like N and so
it is like # N_A ~~and m~~ and we are
maximizing over #. Consider

$$e^{N_A} \text{ vs. } e^{(1+\epsilon)N_A}$$

Ratio is $e^{\epsilon N_A} \gg 1$ for reasonable ϵ.

For different parameters (β) we could get



Phases compete.

as measured by density

Phase changes discontinuously with some parameter like T.

$T < T_*$: liquid (n_e is realized)
$T > T_*$: gas. (n_g is realized).

As M → ∞, if we have $e^{V\Psi(n_g)+V\Psi(n_e)}$, their ratio is

$$e^{V(\Psi(n_g)-\Psi(n_e))}\begin{cases}0\\ \infty\end{cases} \text{as } V\to\infty$$

The transition is infinitely sharp. Why?

$$Q = \sum_N e^{V\Psi(N)} = \sum_n e^{V\Psi(n)}$$

$$\approx e^{V\Psi(n_g)+V\Psi(n_e)} \rightarrow \begin{cases} e^{\beta V P_{gas}} & n_g \text{ dom.} \\ e^{\beta V P_{liq}} & n_e \text{ dom.}\end{cases}$$

~~But $e^{V\Psi(N_*)} \approx Q \Rightarrow V\Psi(N_*) = \frac{PV}{k_B T} = \beta PV$.~~

An infinitely sharp & discontinuous P.T. occurs only in infinite systems in the thermodynamic limit.

Review of Lecture 23

Mean-field theory of van der Waals gas:

$$p(N) = \frac{e^{\beta\mu N} Z(N)}{Q}$$

Each atom is in an attractive potential set by all other atoms, neglect fluctuations in density and use the average:

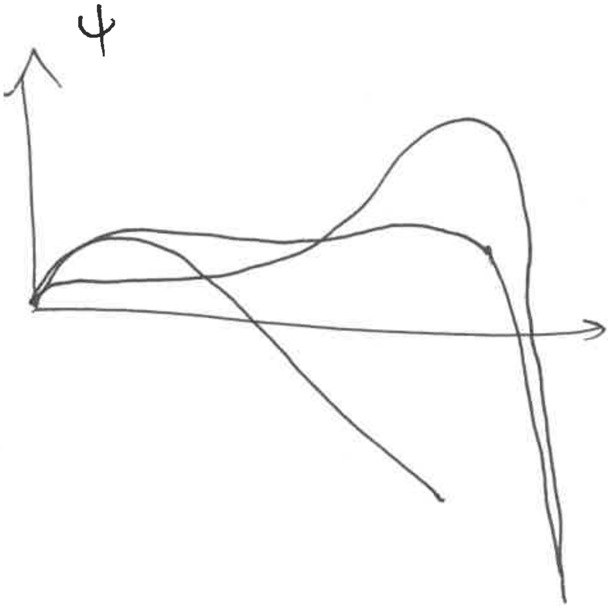
$$U = \frac{1}{2}\int d^3r\, d^3r'\, n(r) V(r-r') n(r')$$

$$\rightarrow \frac{1}{2} n^2 V \underbrace{\int d^3r\, V(r)}$$

$$= \int d^3r\, 4\pi r^2 \cdot V(r) \equiv -u.$$

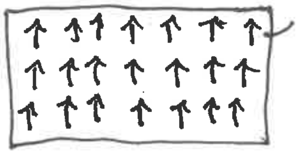
$$Z = \frac{\left(V - \frac{N\Omega}{2}\right)^N}{N!\,\lambda^{3N}}\, e^{\frac{1}{2}\beta n^2 V u} \Rightarrow \text{vdW eqn.}$$

$$p(N) = \frac{1}{Q} e^{\beta\mu N} \frac{\left(V - \frac{N\Omega}{2}\right)^N}{N!\,\lambda^{3N}} \cdot e^{\frac{1}{2}\beta u \frac{N^2}{V^2} V}$$



Mean-field theory of magnetism

Consider as a simple model of a magnet like iron:



electron spins either up or down.

The ferromagnetic order corresponds to all spins being aligned one way or another. As we raise the temp. beyond a critical temperature T_c, the system becomes non-magnetic and only has a net magnetic moment when a magnetic field is applied. In principle such effects may be understood by applying equilibrium statistical mechanics to the Hamiltonian

$$H = \sum_{i,j} J_{ij}\, \underbrace{S_i}_{\substack{\text{spin of}\\ i\text{th electron}}} \cdot S_j$$

position dependent coupling strength; could be long ranged $\sim \frac{1}{R_{ij}^3}$.

We will consider a toy-version of this model called the Ising model,

$$H_{\text{Ising}} = -\sum_{\langle i,j\rangle} J_{ij}\, \underbrace{\sigma_i}_{\pm 1} \cdot \sigma_j$$

(spin up or down; no rotation)

($-J \Rightarrow$ parallel spins lower energy)

- 1D: exactly soluble
- 2D: soluble, but tour-de-force
- 3D: still subject of research

Using MFT, one may solve this problem in any dimension. The core idea is to treat each spin as being in a magnetic field set by all other spins — setting the Hamiltonian to:

$$H_{\text{Ising}}^{\text{MFT}} = -\sum_i \mu B_{\text{eff}}\, \sigma_i \qquad \equiv \gamma B_{\text{eff},i}$$

B_{eff} may be expressed via $\quad -\sum_i \sigma_i \underbrace{\sum_{j} J_{ij}\sigma_j}$

$$H = -\sum_i \sigma_i \gamma B_{\text{eff},i}$$

$$B_{\text{eff}} = \sum_j J_{ij} \langle\sigma\rangle$$

$$\equiv A\langle\sigma\rangle$$

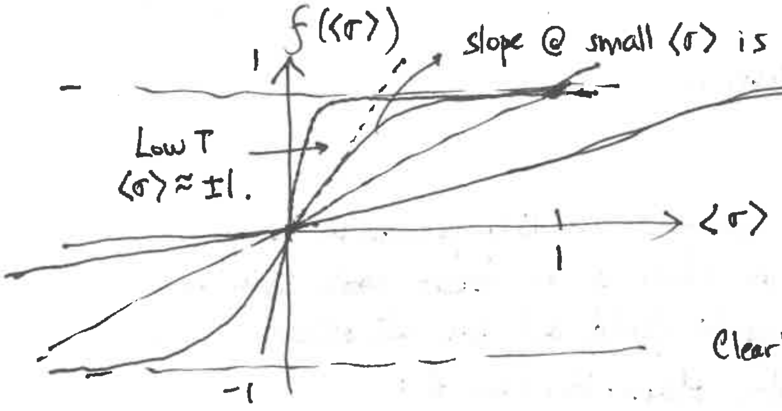
$$\Rightarrow H = -\underbrace{\gamma A}_{\text{"}\mu B\text{"}} \sum_i \langle\sigma_i\rangle$$

We know for N independent spins in a B-field

$$\langle\sigma\rangle = \tanh \beta\mu B$$

$$= \tanh \beta\cancel{\mu} A\gamma\langle\sigma\rangle$$

Value of $\langle\sigma\rangle$ and B_{eff} determined by soln. to this eqn.



slope @ small $\langle\sigma\rangle$ is $\beta A\gamma = \frac{A\gamma}{k_B T}$.

Only $\langle\sigma\rangle = 0$ solves.
No mean spin.

Clearly if $\beta A\gamma < 1$, no ~~nontrivial~~ finite $\langle\sigma\rangle$.

$$\boxed{k_B T > A\gamma}$$

For $A\gamma > k_B T \Rightarrow T < \frac{A\gamma}{k_B} \equiv T_c$. $\langle\sigma\rangle$ small $\Rightarrow$

$\tanh \frac{A\gamma}{k_B T}$

$$\langle\sigma\rangle \approx \beta A\gamma\langle\sigma\rangle - \frac{1}{3}(\beta A\gamma)^3\langle\sigma\rangle^3 \quad \approx 1$$

$$\Rightarrow \langle\sigma\rangle\left(1 - \frac{T_c}{T}\right) = -\frac{1}{3}\left(\frac{T_c}{T}\right)^3\langle\sigma\rangle^3 \Rightarrow \left(\frac{T}{T_c}\right)^2\left(1 - \frac{T}{T_c}\right)3 = \langle\sigma\rangle^2$$

$$\boxed{\langle\sigma\rangle = \pm\sqrt{3\left(1 - \frac{T}{T_c}\right)}}$$

Mean-field Ising review

$$H = \sum_{ij} J_{ij} \sigma_i \sigma_j$$

$$\equiv \sum_i \sigma_i \sum_j J_{ij} \sigma_j$$

Change

$$\sum_j J_{ij} \sigma_j \rightarrow \ominus \gamma B_{\text{eff},i}$$

~~$\equiv -\sum_i \sigma_i \gamma B_{\text{eff},i}$~~

~~$B_{\text{eff},i} \rightarrow \langle B_{\text{eff},i} \rangle = \sum_j J$~~

$$\sum_j J_{ij} \sigma_j \longrightarrow \sum_j J_{ij} \langle \sigma_j \rangle$$

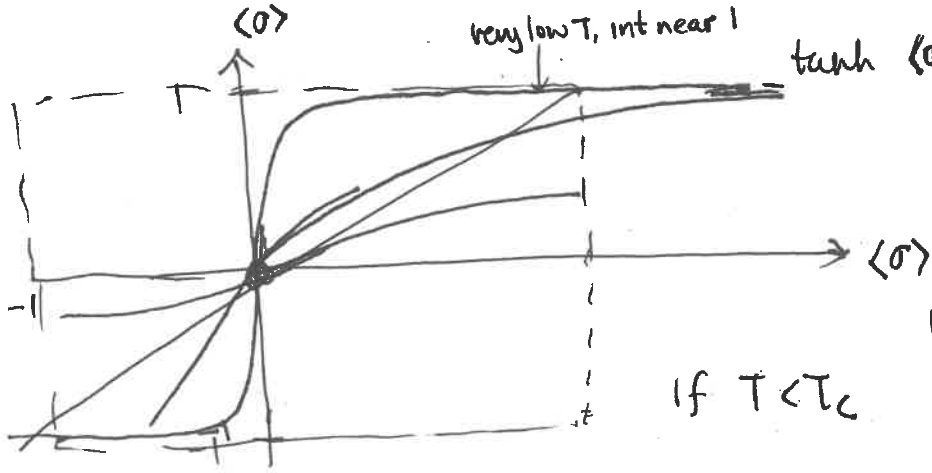
$$\equiv \sum_j J_{ij} \langle \sigma \rangle \equiv \langle \sigma \rangle (-\gamma)$$

$$\Rightarrow H = -\gamma \langle \sigma \rangle \sum_i \sigma_i$$

Compare to $H = -\mu B \sum_i \sigma_i$

$$\langle \sigma \rangle = \tanh \beta \mu B$$

$$\Rightarrow \langle \sigma \rangle = \tanh \beta \gamma \langle \sigma \rangle$$



$$k_B T > \gamma \Rightarrow T > \frac{\gamma}{k_B} \equiv T_c$$

Only intersection is @ $\langle \sigma \rangle = 0$, no mean magnetization (paramagnet).

if $T < T_c$

$\pm \langle \sigma \rangle$ both solns - spontaneous symmetry breaking.

Mean magnetization

$T \lesssim T_c \quad (T = T_c - \epsilon).$

$\langle\sigma\rangle$ small

$$\Rightarrow \langle\sigma\rangle \approx \beta\gamma\langle\sigma\rangle - \frac{1}{3}(\beta\gamma\langle\sigma\rangle)^3$$

$\langle\sigma\rangle \neq 0$

$$\Rightarrow (1-\beta\gamma) = -\frac{1}{3}(\beta\gamma)^2\langle\sigma\rangle^2$$

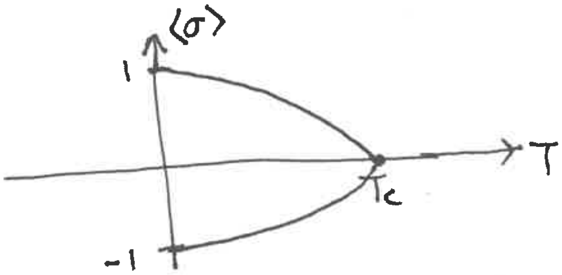
$$\beta\gamma = \frac{T_c}{T}$$

$$\Rightarrow \left(\frac{T_c}{T}-1\right)\cdot 3\cdot\left(\frac{T}{T_c}\right)^2 = \langle\sigma\rangle^2$$

$$\Rightarrow 3\frac{T}{T_c}\left(1-\frac{T}{T_c}\right)$$

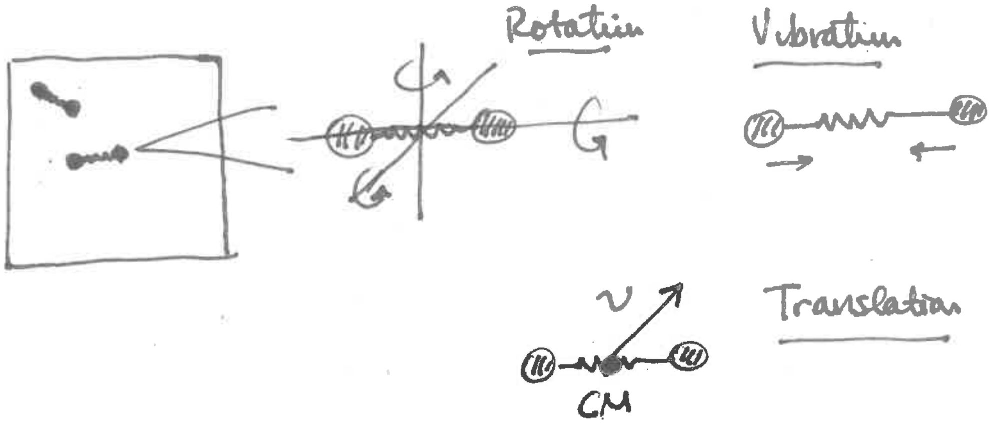
$$\approx 3\left(1-\frac{T}{T_c}\right)$$

$$\Rightarrow \langle\sigma\rangle \approx \pm\sqrt{3}\,\underbrace{\sqrt{1-\frac{T}{T_c}}}_{T<T_c,\ \text{positive arg.}}$$



Failures of classical statistical mechanics

Let us consider the SM of a gas of molecules.



Classical treatment

$$H = \sum_{i=1}^{N} \frac{p_i^2}{2m} + V(\{q\})$$

In mechanical equilibrium, a configuration of positions $\{q_0\}$ (up to rotation & translation). Therefore

$$(\nabla V)(\{q_0\}) = 0$$

$$V(\{q\}) = V(\{q_0\}) + \frac{1}{2}\sum_{i\alpha, j\beta} (q_{i\alpha} - q_{0,i\alpha})(q_{j\beta} - q_{0,j\beta}) \left.\frac{\partial^2 V}{\partial q_{i\alpha}\partial q_{j\beta}}\right|_{q_{0,i\alpha}\, q_{0,j\beta}}$$

i, j: atoms $1, \ldots, N$

α, β: components $1, \ldots, d$ ($= 3$ in 3 dimensions).

The expansion coefficient $\frac{\partial^2 V}{\partial q_{i\alpha}\partial q_{j\beta}} \equiv \mathcal{D}_{i\alpha, j\beta}$ is the dynamical matrix, and is simply the matrix version of spring constants. To see this, let us consider the EOM for the system.

$$\frac{\partial H}{\partial p_{i\alpha}} = \dot{q}_{i\alpha}, \; -\frac{\partial H}{\partial q_{i\alpha}} = \dot{p}_{i\alpha} \implies \begin{array}{l} \dot{q}_{i\alpha} = p_{i\alpha}/m_i \\ \dot{p}_{i\alpha} = -\sum_{j\beta} \mathcal{D}_{i\alpha,j\beta}(q_{j\beta} - q_{0,j\beta}) \end{array}$$

Define displacements

$$u_{i\alpha} = q_{i\alpha} - q_{0,i\alpha}, \text{ so that}$$

$$\dot{u}_{i\alpha} = \dot{q}_{i\alpha} \Rightarrow p_{i\alpha} = m_i \dot{u}_{i\alpha}$$

$$\Rightarrow m_i \ddot{u}_{i\alpha} = -\sum_{j\beta} \mathcal{D}_{i\alpha,j\beta}\, u_{j\beta}$$

$$\Rightarrow M\ddot{u} = -\mathcal{D}u$$

$$M = \begin{pmatrix} m_1^{-1} & & & & & & & & \\ & m_1^{-1} & & & & & & & \\ & & m_1^{-1} & & & & & & \\ & & & m_2^{-1} & & & & & \\ & & & & m_2^{-1} & & & & \\ & & & & & m_2^{-1} & & & \\ & & & & & & \ddots & & \\ & & & & & & & m_N^{-1} & \\ & & & & & & & & m_N^{-1} \\ & & & & & & & & & m_N^{-1} \end{pmatrix}, \quad M_{i\alpha,j\beta} = \delta_{\alpha\beta}(m_i \delta_{ij})$$

To solve this linear problem, we expand in normal modes.

$$u_{i\alpha}(t) = \mathrm{Re}\sum_n \underset{\uparrow\ \text{complex amplitude}}{u_{n,i\alpha}}\, e^{-i\omega_n t}$$

The u_n satisfy:

$$-M\omega_n^2 u_n = -\mathcal{D}u_n$$

$$\Rightarrow \boxed{\mathcal{D}u_n = M\omega_n^2 u_n} \longleftarrow$$ This is called a generalized eigenvalue problem (because of the constant matrix in the RHS).

To convert the generalized eigenvalue problem into a conventional one, we do:

$$\boxed{u_n \equiv M^{-1/2} w_n}$$

Normal eigenvalue problem.

$$\Rightarrow \mathcal{D}M^{-1/2} w_n = M\omega_n^2 M^{-1/2} w_n \Rightarrow \boxed{(M^{-1/2}\mathcal{D}M^{-1/2})\, w_n = \omega_n^2 w_n}$$

Since $(M^{-1/2} D M^{-1/2})^T = M^{-1/2} D^T M^{-1/2}$

$= M^{-1/2} D M^{-1/2}$ (commutativity of 2nd derivatives)

$M^{-1/2} D M^{-1/2}$ is a real, symmetric matrix and therefore by the spectral thm. from QM, we may say that the eigenvalues

$$\boxed{\omega_n^2 \text{ are real}}$$

(They can be negative, implying mechanical instability. We'll ignore that here)

and that the eigenvectors are <u>orthogonal</u>

also real $\rightarrow$

$$\boxed{W_m^T W_n \equiv \underbrace{(W_m, W_n)}_{\text{inner product}} = \delta_{mn}}.$$

In general 3N (or dN) eigenvalues & eigenvectors, not nece. distinct, some $\omega_n = 0$.

~~$\Rightarrow (M^{+1/2} w_m, M^{+1/2} w_n) = \delta_{mn}$~~

~~$\Rightarrow (w_m, M^{+1} w_n) - \sum_{i\alpha} W_{m,i\alpha}$~~

$$\Rightarrow (M^{1/2} u_m, M^{1/2} u_n) = (u_m, M u_n) = \delta_{mn}$$

$$\delta_{mn} = \sum_{i\alpha, j\beta} u_{m,i\alpha} \underbrace{M_{i\alpha, j\beta}}_{m_i \delta_{ij} \delta_{\alpha\beta}} u_{n,j\beta}$$

$$= \boxed{\sum_{i\alpha} m_i u_{m,i\alpha} u_{n,i\alpha}}$$

$u_{m,i\alpha}$

We may use orthogonality to express the Hamiltonian in terms of the eigenvectors.

$$\mathcal{L} = \sum_{i\alpha} \frac{1}{2} m_i \dot{u}_{i\alpha}^2 - \frac{1}{2} \sum_{j\beta} u_{i\alpha} u_{j\beta} D_{i\alpha, j\beta}$$

(Lagrangian $\rightarrow$ Hamiltonian)

$u_{i\alpha} = u_{i\alpha}(t) = M^{-1/2} w_{i\alpha}(t)$

$$\Rightarrow \mathcal{L} = \sum_{i\alpha} \frac{1}{2} \dot{w}_{i\alpha}^2 - \frac{1}{2} \sum_{j\beta} w_{i\alpha} w_{j\beta} \tilde{D}_{i\alpha, j\beta}, \quad \tilde{D} = M^{-1/2} D M^{-1/2}$$

$$\mathcal{L} = \frac{1}{2}\dot{W}^T W - \frac{1}{2} W^T \tilde{D} W^T .$$

Change of basis to eigenbasis:

$$\tilde{D} = S^T \Omega^2 S$$

$$\Omega^2 = \mathrm{diag}\left(\omega_1^2, \omega_2^2, \ldots, \omega_{dN}^2\right).$$

~~Define $\xi =$~~

New basis

$$\dot{W}^T \dot{W} = \dot{W}^T S^T S \dot{W} \equiv \dot{Q}^T \dot{Q}$$

$$W^T \tilde{D} W = W^T S^T \Omega^2 S W \equiv Q^T \Omega^2 Q$$

$$\Rightarrow \mathcal{L} = \frac{1}{2}\dot{Q}^T Q - \frac{1}{2} Q^T \Omega^2 Q$$

Q is the displacement expressed in terms of dN eigenmodes, components Q_n, $n=1,\ldots,dN$.

$$H = \dot{Q}^T \dot{Q} - \mathcal{L} \qquad (\dot{Q} = P)$$

$$= \frac{1}{2} P^T P + \frac{1}{2} Q^T \Omega^2 Q$$

$$= \sum_{n=1}^{dN} \frac{P_n^2}{2} + \frac{1}{2}\omega_n^2 Q_n^2$$

(dN uncoupled oscillators!)

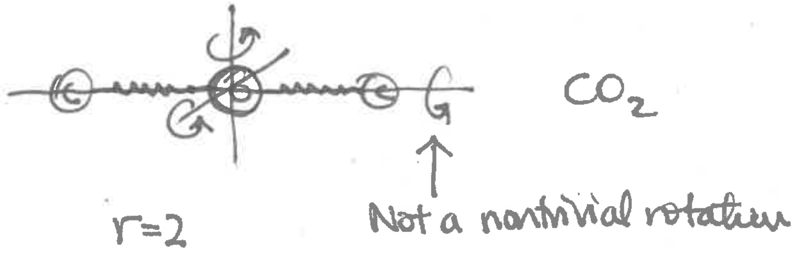
Equipartition theorem tells us that

$$\langle E \rangle = \frac{1}{2} k_B T \cdot (M_p + M_q)$$

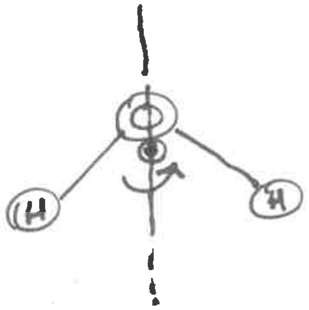
$$= \frac{1}{2} k_B T (3N + 3N - \underset{\substack{\uparrow \\ \text{translations}}}{3} - \underset{\substack{\uparrow \\ \text{rotations}}}{r}) = \boxed{\frac{1}{2} k_B T (6N - 3 - r)}$$

$$C_V = \frac{N}{2} k_B (6N - 3 - r)$$

Example :

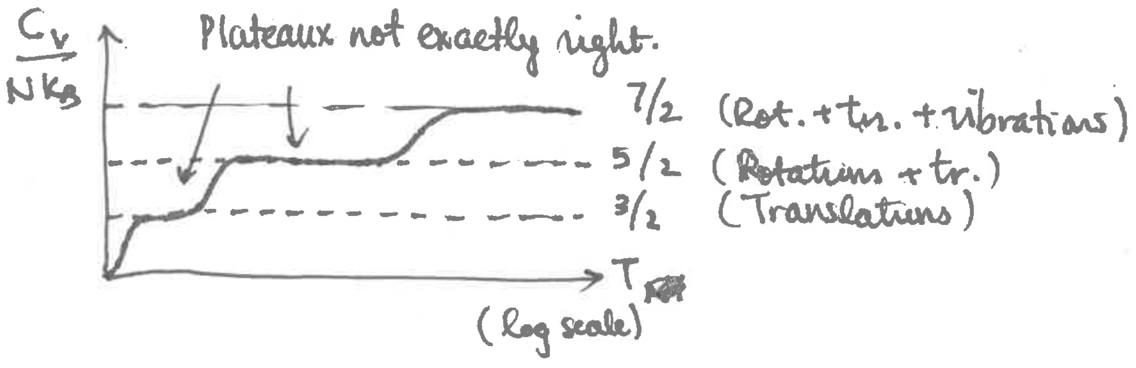


$$\langle E \rangle = \frac{1}{2} k_B T \left(6 \cdot 3 - 3 - 2\right) = \frac{13 k_B T}{2}, \quad C_V = \frac{13}{2} N k_B .$$



$r = 3$
$N = 3$, $\quad C_V = 6 N k_B$.

Prediction: T-independent specific heat.



Quantum treatment of molecular specific heat

$$H = \underbrace{\frac{P_{CM}^2}{2M} + \frac{L^2}{2I}}_{\text{CoM and rot. DoFs split out.}} + \sum_{n=1}^{N_v} \frac{P_n^2}{2} + \frac{1}{2}\omega_n^2 Q_n^2$$

Not same dims as trans. H. Should I absorb M?

Quantize this Hamiltonian. The rotations depend on the type of molecule & so we will do the simplest thing, a rigid rotor.

$$H = \underbrace{\frac{P_{CM}^2}{2M}}_{H_{tr}} + \underbrace{\frac{L^2}{2I}}_{H_{rot}} + \underbrace{\sum_{n=1}^{N_v} \frac{P_n^2}{2} + \frac{1}{2}\omega_n^2 Q_n^2}_{H_{vib}}$$

Since these three motions are independent, we have

$$|\psi\rangle = \underbrace{|\psi_t\rangle \otimes |\psi_r\rangle \otimes}_{\text{tensor product}} |\psi_v\rangle$$

$$H|\psi\rangle = E|\psi\rangle$$
$$= (E_t + E_r + E_v)|\psi\rangle$$

$$E_t = \frac{p^2}{2M} = \frac{\hbar^2 K^2}{2M}. \qquad \left(\frac{P^2}{2M}|\hbar K\rangle = \frac{\hbar^2 K^2}{2M}|\hbar K\rangle \right)$$

Translation

Rotation

~~Vibration~~

$$\frac{L^2}{2I}|l,m\rangle = \frac{\hbar^2 l(l+1)}{2I}|l,m\rangle$$

$$\langle \hat{\Omega}|l,m\rangle = Y_{lm}(\hat{\Omega})$$

Vibration

H_{vib} : Define

$$\left.\begin{aligned} P_n &= i\,(a_n^\dagger - a_n)/\sqrt{2}\cdot\sqrt{\hbar\omega_n} \\ Q_n &= (a_n + a_n^\dagger)/\sqrt{2}\cdot\sqrt{\frac{\hbar}{\omega_n}} \end{aligned}\right\} [a_m, a_n^\dagger] = \delta_{mn}$$

$$\frac{P_n^2}{2} = \frac{1}{2}\cdot\frac{\cancel{i}}{\cancel{2}}\cdot(-1)\left(a_n^{\dagger 2} + a_n^2 - a_n^\dagger a_n - a_n a_n^\dagger\right)\cdot\frac{\hbar\omega_n}{2}$$

$$\frac{1}{2}\omega_n^2 Q_n^2 = \frac{1}{2}\frac{\hbar}{2\cancel{\omega_n}}\omega_n^{\cancel{2}}\left(a_n^{\dagger 2} + a_n^2 + a_n^\dagger a_n + a_n a_n^\dagger\right)$$

$$\frac{P_n^2}{2} + \frac{1}{2}\omega_n^2 Q_n^2 = \frac{\hbar\omega_n}{4}\left(2a_n^\dagger a_n + 2a_n a_n^\dagger\right) = \frac{\hbar\omega_n}{4}\left(4a_n^\dagger a_n + 2\right) = \boxed{\hbar\omega_n\left(a_n^\dagger a_n + \frac{1}{2}\right)}$$

$$H_{vib} = \sum_{n=1}^{N_v} \hbar\omega_n (a_n^\dagger a_n + 1/2)$$

$$E_{vib} = E_{vib}(n_1, \dots, n_{N_v})$$

$$= \boxed{\sum_{n=1}^{N_v} \hbar\omega_n \left(n_n + \frac{1}{2}\right)}$$

$$\Rightarrow \boxed{E = E(K, l, m, \{n\}) = \frac{\hbar^2 K^2}{2M} + \frac{\hbar^2 l(l+1)}{2I} + \sum_{n=1}^{N_v} \hbar\omega_n \left(n_v + \frac{1}{2}\right)}$$

At this level, the N! still has to be taken/added by hand.

$$\boxed{Z = Z_{tr} Z_{rot} Z_{vib}} = \frac{1}{N!}\left(Z_{1,tr} Z_{1,rot} \cancel{Z_{1,vib}}\right)^N \underbrace{Z_{1,vib}^N}$$

~~already multi-particle~~

Prescription of QSM in canonical ensemble – simply use quantum energies.

Example:

$$Z_{1,tr} = \sum_K e^{-\beta \frac{\hbar^2 K^2}{2m}}$$

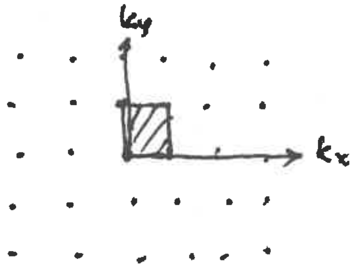
$$\sum_K = \frac{V}{(2\pi)^3} \int d^3k \longrightarrow \text{Box quantization}$$

Wave functions of a free particle

$e^{ik\cdot r}$ → Boundary conditions, PBC

$$k_x L = 2m\pi$$

$$\Rightarrow k = \frac{2\pi}{L}(m_x, m_y, m_z)$$



$$(\Delta k)^3 = \left(\frac{2\pi}{L}\right)^3 \Rightarrow \sum_k = \frac{L^3}{(2\pi)^3} \sum_k (\Delta k)^3$$

$$= \frac{V}{(2\pi)^3} \int d^3k$$

$$\Rightarrow Z_{1,tr} = \frac{V}{(2\pi)^3}\int d^3K \; e^{-\frac{\beta\hbar^2K^2}{2m}}$$

$$= \frac{V}{(2\pi)^3}\left(\frac{2\pi m k_B T}{\hbar^2}\right)^{3/2}$$

$$= \frac{V}{(2\pi)^3}\left(\frac{(2\pi)^3 m k_B T}{h^2}\right)^{3/2}$$

$$= \frac{V}{(2\pi)^3}\,(2\pi)^3\left(\frac{2\pi m k_B T}{h^2}\right)^{3/2}$$

$$= \frac{V}{\lambda^3(T)}$$

$$Z_{1,rot} = \sum_{\ell=0}^{\infty}\sum_{m=-\ell}^{\ell} e^{-\beta\frac{\hbar^2\ell(\ell+1)}{2I}} = \sum_{\ell=0}^{\infty}(2\ell+1)\,e^{-\theta_{rot}\ell(\ell+1)}$$

$T \to \infty$

$$Z \approx \int_0^\infty d\ell(2\ell+1)\,e^{-\theta_{rot}\ell(\ell+1)} \qquad \Big|\; d(\ell^2+\ell) = (2\ell+1)\,d\ell$$

$$= \int_0^\infty du \; e^{-\theta_{rot}u}.$$

$$= \frac{-1}{-\theta_{rot}} = \frac{1}{\theta_{rot}} = \frac{2Ik_BT}{\hbar^2}$$

$\underline{T \to 0}$

$$\approx 1 + 3e^{-\theta_{rot}\cdot 2} + 5e^{-\theta_{rot}\cdot 6} + \dots$$

$$\approx 1 + 3e^{-2\theta_{rot}}$$

$$Z_{1,vib} = \prod_n Z_{1,vib}^{(n)}$$

$$Z_{1,vib}^{(n)} = \sum_m e^{-\beta\hbar\omega_n(m+\frac{1}{2})} = e^{-\frac{\beta\hbar\omega_n}{2}}\frac{1}{1-e^{-\beta\hbar\omega_n}}$$

$$Z_{vib} = e^{-\frac{\beta\hbar}{2}\sum_n\omega_n}\cdot\prod_n\frac{1}{1-e^{-\beta\hbar\omega_n}}$$

The energy is then given by

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

$$= \langle E_{tr}\rangle + \langle E_{rot}\rangle + \langle E_{vib}\rangle$$

$$\langle E_{tr}\rangle = \frac{3}{2}Nk_BT \quad (\text{all } T)$$

$$\ln Z \sim -\ln\beta \Rightarrow -\frac{\partial \ln Z}{\partial\beta} = 1/\beta .$$

$$\langle E_{rot}\rangle = \begin{cases} k_BT & \text{high } T \quad \hookleftarrow \\ \frac{-3e^{-2\theta_{rot}}\cdot -2\frac{\hbar^2}{2I}}{1+3e^{-2\theta_{rot}}} & \text{low } T \end{cases}$$

$$= \begin{cases} k_BT & \text{high } T \\ 6\frac{\hbar^2}{2I}e^{-2\theta_{rot}} & \text{low } T \end{cases}$$

$$\langle E_{vib}\rangle = \begin{cases} \frac{1}{2}k_BT\cdot \overset{M_q+M_p}{\widetilde{2\cdot}}\, N_\nu & \text{high } T \\ \sum_{n=1}^{N_\nu}\frac{\hbar\omega_n}{2}\left(1+2e^{-\beta\hbar\omega_n}\right) & \text{low } T \end{cases}$$

$\Rightarrow$ The heat capacity @ high T is

$$C_V = \frac{\partial E}{\partial T} = \frac{3}{2}Nk_B + Nk_B + \overset{\swarrow 1}{N_\nu}Nk_B$$

$$= Nk_B\,\frac{3+2+2}{2}$$

$$= \boxed{\frac{7}{2}Nk_B} .$$

$$\frac{\partial}{\partial\beta}\ln\prod_n e^{-\frac{\beta\hbar\omega_n}{2}}\frac{1}{1-e^{-\beta\hbar\omega_n}}$$

$$= \frac{\partial}{\partial\beta}\sum_n -\frac{\beta\hbar\omega_n}{2} - \ln\frac{1}{1-e^{-\beta\hbar\omega_n}}$$

$$= -\sum_n \frac{\hbar\omega_n}{2} - \frac{+e^{-\beta\hbar\omega_n}\hbar\omega_n}{1-e^{-\beta\hbar\omega_n}}$$

$$= -\frac{\hbar\omega_n}{2}\sum_n 1 + \frac{2}{e^{\beta\hbar\omega_n}-1}$$

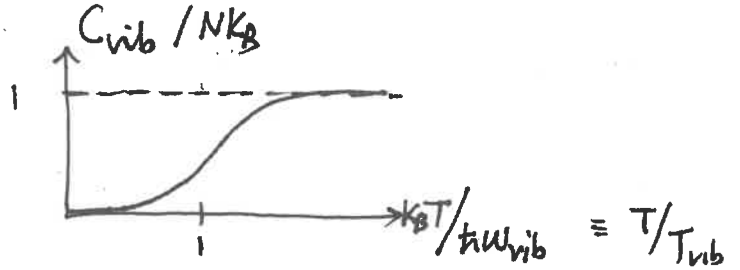
$$= -\frac{\hbar\omega_n}{2}\sum_n \frac{e^{\beta\hbar\omega_n}+1}{e^{\beta\hbar\omega_n}-1}$$

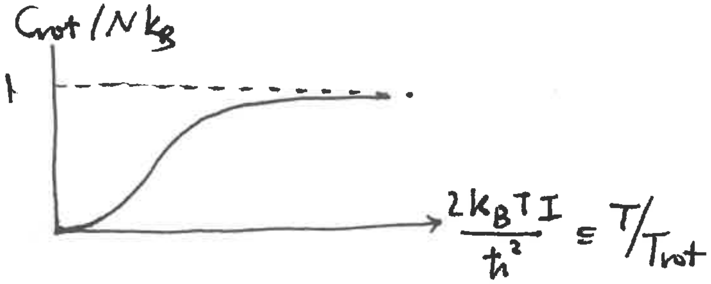
$$= -\frac{\hbar\omega_n}{2}\sum_n \coth\frac{\beta\hbar\omega_n}{2} .$$

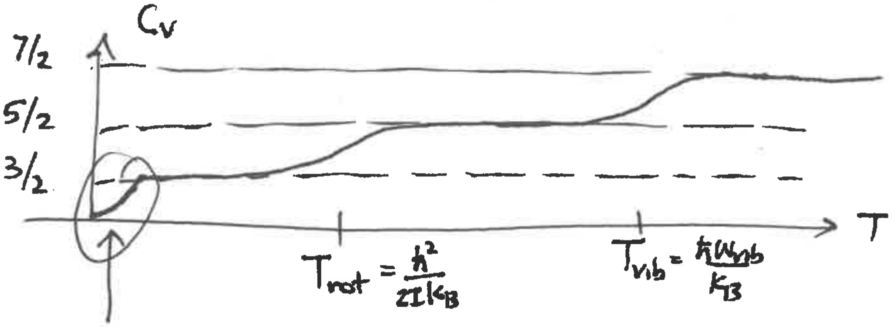
\## $\omega_0 = \omega_{vib}$

Suppose (as is typically the case):

$$\frac{\hbar^2}{2I} \ll \hbar\omega_{vib}$$

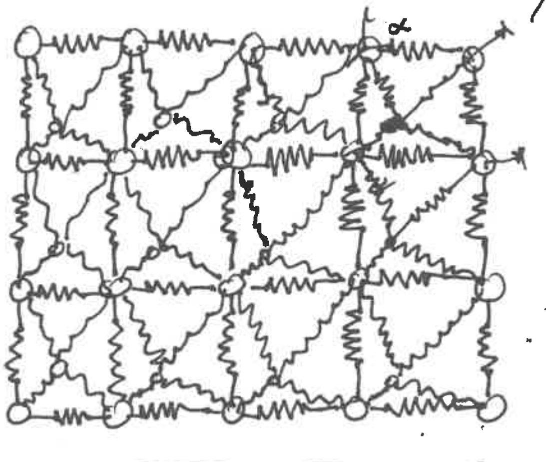






Requires consideration of particle statistics.

Phonons



→ displacements defined on a discrete lattice

normal modes of an ordered lattice

Classical picture

$$m_i \ddot{u}_{i\alpha} = -\sum_{j\beta} \mathcal{D}_{i\alpha,j\beta}\, u_{j\beta}$$

Same as the molecular case. Dynamical matrix <u>much</u> more structured for the ordered lattice.

$$\mathcal{D}_{i\alpha,j\beta} = \frac{\partial^2 V}{\partial q_{i\alpha}\partial q_{j\beta}}$$

i, j are associated with sites R, R' in the ordered lattice (and basis sites κ, κ')

e.g: $R = la\hat{x} + ma\hat{y} + na\hat{z}$.
(cubic lattice).

$$\mathcal{D}^{\kappa,\kappa'}_{\alpha\beta}(R,R') = \frac{\partial^2 V}{\partial q_\alpha(R_\kappa)\,\partial q_\beta(R'_{\kappa'})} \leftarrow$$

This can only depend on R − R' because of translation invariance.

We may therefore write the EOM as

$$m_{\kappa}(R_\kappa)\,\ddot{u}_\alpha(R_\kappa) = -\sum_{R',\beta,\kappa'} \overbrace{D^{\kappa\kappa'}_{\alpha\beta}(R,R')}^{=D^{\kappa\kappa'}_{\alpha\beta}(R-R')}\, u_\beta(R'_{\kappa'})$$

Since u is defined on a discrete and ordered lattice of points, we may represent it via a discrete Fourier transform:

$$u_\alpha(R) = \frac{1}{N}\sum_k e^{ik\cdot R}\, u_\alpha(k).$$

k must of course be discrete [If we apply PBC, we have say for a cubic system (L_x, L_y, L_z) - dim

$$k = 2\pi\left(\frac{m_x}{L_x}, \frac{m_y}{L_y}, \frac{m_z}{L_z}\right)$$] ← Consider not mentioning.

We thus have, for $W = m^{1/2}u$:

$$\ddot{w}_\alpha(R) = -\sum_{R',\beta,\kappa'} m^{-1/2}(R_\kappa)\, D^{\kappa\kappa'}_{\alpha\beta}(R-R')\, m^{-1/2}(R'_{\kappa'})\, w_\beta(R')$$

To simplify things, reserving the real treatment for a solid state physics class, we consider the case of all masses being the same and no basis, such that

$$m\ddot{u}_\alpha(R) = -\sum_{R'} D_{\alpha\beta}(R-R')\, u_\beta(R')$$

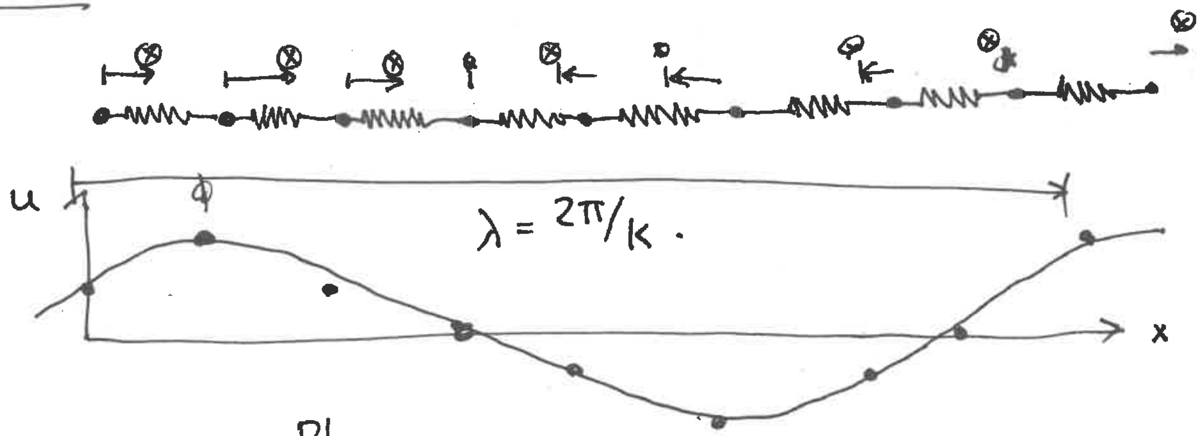
$$\Rightarrow \frac{m}{N}\sum_k e^{ik\cdot R}\,\ddot{u}_\alpha(k) = -\frac{1}{N^2}\underbrace{\sum_{R',k,k'} e^{ik\cdot(R-R')}\, e^{ik'\cdot R'}}_{\sum_{R'} e^{-ik\cdot R' + ik'\cdot R'} = N\delta_{k,k'}} D_{\alpha\beta}(k)\, u_\beta(k')$$

$$\Rightarrow \boxed{m\ddot{u}_\alpha(k) = -D_{\alpha\beta}(k)\, u_\beta(k)}$$ or u_n, 3 for each k.

Eigenvectors $\xi(k)$ satisfy $\boxed{m\omega^2(k)\,\xi_\alpha(k) = D_{\alpha\beta}(k)\,\xi_\beta(k)}$

How many ks? Basis has to have same info as in linear transform so this is 3N.

Interpretation: displacement wave



Phonon wave

By precisely the same argument as in the molecular case we may write

$$H = \sum_{n,k} \frac{P_n^2(k)}{2} + \frac{1}{2}\omega_n^2(k)\, Q_n^2(k)$$

Can ignore 0 modes since only 3+r out of 3N. Classical specific heat is simply

$$C_V = \partial_T \frac{k_B T}{2}(3N + 3N) = \boxed{3Nk_B}$$

(equipartition, independent of shape of solid)

Quantum mechanically, we get

$$E = \sum_{n,k} \frac{\hbar\omega_n(k)}{2}\left(1 + \frac{2}{e^{\beta\hbar\omega_n(k)} - 1}\right)$$

$$C_V = \sum_{n,k} \frac{\hbar\omega_n(k)}{\cancel{2}}\, \frac{\cancel{-1}\cdot\cancel{2}\cdot e^{\beta\hbar\omega_n(k)}\hbar\omega_n(k)\cdot\cancel{-}\frac{1}{k_BT^2}}{(e^{\beta\hbar\omega_n(k)} - 1)^2}$$

$$= \boxed{k_B \sum_{n,k}\left(\frac{\hbar\omega_n(k)}{k_BT}\right)^2 \frac{e^{\beta\hbar\omega_n(k)}}{(e^{\beta\hbar\omega_n(k)} - 1)^2}}$$

At very high temperatures, we get that

$$e^{\beta\hbar\omega_n(k)} \approx 1 + \beta\hbar\omega_n(k)$$

$$\Rightarrow C_V = k_B \sum_{n,k} \left(\frac{\hbar\omega_n(k)}{k_BT}\right)^2 \frac{1}{\left(\frac{\hbar\omega_n(k)}{k_BT}\right)^2}$$

$$= k_B \cdot \sum_{n,k} 1 = \boxed{3Nk_B}.$$

At low temperatures, we get that

$$\frac{e^{\beta\hbar\omega_n(k)}}{\left(e^{\beta\hbar\omega_n(k)}-1\right)^2} \approx e^{-\beta\hbar\omega_n(k)} \quad \text{for} \quad \hbar\omega_n(k) \gg k_BT.$$

As $T \to 0$, only zero frequency modes contribute. Higher freq. ones are screened out and we can ignore zone-boundaries.

$$C_V \approx k_B \sum_n \frac{V}{(2\pi)^3} \int d^3k \left(\frac{\hbar\omega_n(k)}{k_BT}\right)^2 \frac{e^{\beta\hbar\omega_n(k)}}{\left(e^{\beta\hbar\omega_n(k)}-1\right)^2}.$$

To say anything further, we need to understand $\omega_n(k)$ – the phonon dispersion relation at small k. This is governed by

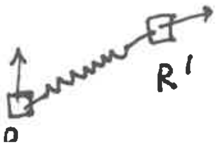
$$D_{\alpha\beta}(k).$$

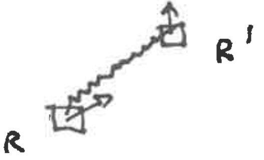
First of all, we can show that $D_{\alpha\beta}$ is even. It follows from inversion symmetry. In other words, if the crystal is the same when I take

~~$D_{\alpha\beta}(R)$ real $\Rightarrow$ $D_{\alpha\beta}(k) = D^*_{\alpha\beta}(-k)$~~.

$R \to -R$, then it follows that $D(R) = D(-R)$. Therefore

$$\underset{\substack{\| \\ D(K)}}{\sum_R e^{-ik\cdot R} D(R)} = \underset{\substack{\| \\ D(-K)}}{\sum_R e^{-ik\cdot R} D(-R)}$$





$$\boxed{D(K) = D(-K)}$$

Therefore $\mathcal{D}$ must be an even function of k. For small k

$$\mathcal{D}_{\alpha\beta}(k) \approx \mathcal{D}_{\alpha\beta}(0) + \frac{1}{2} k^T \underbrace{\mathcal{D}''_{\alpha\beta}(0)}_{\left.\frac{\partial^2 \mathcal{D}(k)}{\partial k_i \partial k_j}\right|_{k=0}} k$$

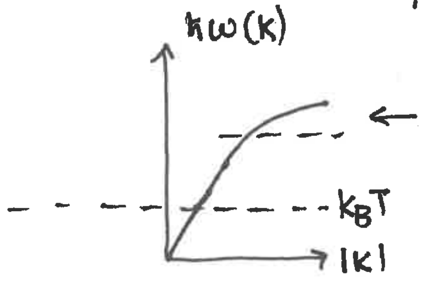
Further $\mathcal{D}(k=0) = 0$ because $k=0$ corresponds to a translation.

~~$\mathcal{D}(k=0) = \sum_R e^{-i0\cdot R} \mathcal{D}(R) = \sum_R \mathcal{D}(R)$~~

Therefore $\mathcal{D}_{\alpha\beta}(k) \approx \frac{1}{2} k^T \mathcal{D}''_{\alpha\beta}(0)\, k$. We consider a toy model of a bulk solid which is <u>isotropic</u> such that

$$\mathcal{D}''_{\alpha\beta} = \mathcal{D}_0 \delta_{\alpha\beta} \Rightarrow -\frac{1}{2} k^T \mathcal{D}'' k = -\frac{\mathcal{D}_0}{2}(k\cdot k)$$

$$\Rightarrow \omega(k) = \underbrace{\sqrt{\frac{\mathcal{D}_0}{2m}}}_{\text{speed of sound.}} |k| \equiv v|k|$$



← where Taylor approx. of 2nd order ~~series~~ isn't accurate. But for low T, this can be neglected.

Thus $$C_V = 3k_B \frac{V}{(2\pi)^3} \int d^3k \left(\frac{\hbar v|k|}{k_BT}\right)^2 \frac{e^{\frac{\hbar v|k|}{k_BT}}}{\left(e^{\frac{\hbar v|k|}{k_BT}} - 1\right)^2}$$

Define $x = \frac{|k|}{k_BT/\hbar v}$ or $x = \beta\hbar v|k|$

Such that

$$C_v = \frac{3Vk_B}{(2\pi)^3}\int 4\pi\left(\frac{x}{\beta\hbar v}\right)^2\left(d\left(\frac{x}{\beta\hbar v}\right)\right)(x)^2\frac{e^x}{(e^x-1)^2}$$

$$= \frac{3Vk_B}{2\pi^2}\left(\frac{k_BT}{\hbar v}\right)^3\int_0^\infty dx\,\frac{x^4e^x}{(e^x-1)^2}$$

From this, we may already see that $C \sim T^3$. The standard way to do this however is to go back to the energy:

$$\underset{\substack{\uparrow\\ \text{T-ind.}}}{E - E_{zp}} = \sum_{n,k}\frac{\hbar\omega_n(k)}{e^{\beta\hbar\omega_n(k)}-1}$$

$$= 3\frac{V(4\pi)}{(2\pi)^3}\int dk\,k^2\,\frac{(\beta\hbar vk)/\beta}{e^{\beta\hbar vk}-1}$$

$$= \frac{3V}{2\pi^2}\frac{1}{(\beta\hbar v)^3\beta}\underbrace{\int_0^\infty dx\,\frac{x^3}{e^x-1}}_{\substack{\text{standard tabulated integral}\\ =\pi^4/15}}$$

$$= \frac{3V\pi^4}{30\pi^2}\frac{(k_BT)^4}{(\hbar v)^3}$$

$$\Rightarrow C_v = \frac{2\pi^2}{5}V\cdot\frac{k_B^3T^3}{(\hbar v)^3}k_B$$

$$= \boxed{\frac{2\pi^2}{5}V\left(\frac{k_BT}{\hbar v}\right)^3k_B} \longrightarrow \text{in agreement with observations}.$$

Scaling argument: at temperature T, only modes with $\hbar\omega < k_BT$ contribute in an equi-partition way.

Blackbody radiation

Nick Rivera

Contents

In this lecture, we will consider the statistical mechanics of the electromagnetic field itself. Suppose that we are in vacuum. We know that it is possible for electromagnetic waves to propagate in vacuum in a manner consistent with Maxwell's equations. Recall that in free-space, Maxwell's equations for the electric field $\mathbf{E}(\mathbf{r}, t)$ are simply

$$\nabla^2\mathbf{E}(\mathbf{r}, t) - \frac{1}{c^2}\frac{\partial^2}{\partial t^2}\mathbf{E}(\mathbf{r}, t) = 0, \tag{1}$$

admitting complex plane-wave solutions of the form

$$\mathbf{E}(\mathbf{r}, t) = A_{\mathbf{k},\hat{\mathbf{e}}_\mathbf{k}} e^{i\mathbf{k}\cdot\mathbf{r}-i\omega_k t}\hat{\mathbf{e}}_\mathbf{k}. \tag{2}$$

In this solution, $A_{\mathbf{k},\hat{\mathbf{e}}_\mathbf{k}}$ is the complex amplitude, $\mathbf{k}$ is the wavevector, $\omega_k = ck$ is the corresponding frequency with $k \equiv |\mathbf{k}|$ and $\hat{\mathbf{e}}_\mathbf{k}$ is a polarization vector. The polarization vector is constrained by Gauss' law to satisfy $\mathbf{k}\cdot\hat{\mathbf{e}}_\mathbf{k} = 0$.

An arbitrary spatiotemporal electric field may be expanded in these plane-wave solutions as

$$\mathbf{E}(\mathbf{r}, t) = \sum_{\mathbf{k},\hat{\mathbf{e}}_\mathbf{k}} A_{\mathbf{k},\hat{\mathbf{e}}_\mathbf{k}} e^{i\mathbf{k}\cdot\mathbf{r}-i\omega_k t}\hat{\mathbf{e}}_\mathbf{k}. \tag{3}$$

In what follows, we will consider the light to be confined to a large cubic box of length L and impose periodic boundary conditions on the electromagnetic field. The boundary conditions do not matter when describing local thermodynamic properties, as they did not for phonons, but this is a useful device for counting electromagnetic modes. Using these periodic boundary conditions, the allowed wavevectors satisfy

$$\mathbf{k} = \frac{2\pi}{L}(m_x, m_y, m_z), \tag{4}$$

where $m_{x,y,z}$ are integers.

Let us now assuming that light is in thermal equilibrium at temperature T. We defer for later the question of *how* light might be in a thermal equilibrium state. The partition function of the electromagnetic field is simply $Z = \sum_\mu e^{-\beta H(\mu)}$ where μ are the allowed microstates and H is the Hamiltonian. The Hamiltonian is simply given by the electromagnetic field energy as

$$H = \frac{\epsilon_0}{2}\int d^3r\, \mathbf{E}(\mathbf{r}, t)^2 + c^2\mathbf{B}(\mathbf{r}, t)^2, \tag{5}$$

where $\mathbf{B}(\mathbf{r}, t)$ is the magnetic field corresponding to the electric field. This is a quadratic Hamiltonian corresponding to a linear wave system, and therefore, we expect that we can write the Hamiltonian in terms of normal coordinates as

$$H = \frac{1}{2}\sum_{\mathbf{k},\hat{\mathbf{e}}_\mathbf{k}} P^2_{\mathbf{k},\hat{\mathbf{e}}_\mathbf{k}} + \omega_k^2 Q^2_{\mathbf{k},\hat{\mathbf{e}}_\mathbf{k}}. \tag{6}$$

I will omit the derivation of how this form is arrived at, since it does not matter for our purposes. We may perform a quantization of the electromagnetic field Hamiltonian by defining creation and annihilation operators, leading to the same result as for phonons.

$$H = \sum_{\mathbf{k},\hat{\mathbf{e}}_\mathbf{k}} \hbar\omega_k a^\dagger_{\mathbf{k},\hat{\mathbf{e}}_\mathbf{k}} a_{\mathbf{k},\hat{\mathbf{e}}_\mathbf{k}}. \tag{7}$$

In other words, the electromagnetic field in vacuum is simply a collection of oscillators: one for each mode which is labeled by a wavevector and a polarization state. If there are N_v possible wavevectors (this value is countably infinite, but assume we apply a wavevector cutoff), then there are $2N_v$ possible electromagnetic modes with the factor of 2 arising from polarization degeneracy.

With this, we may at once write the partition function as

$$Z = \prod_{\mathbf{k},\hat{\mathbf{e}}_\mathbf{k}} \frac{e^{-\frac{1}{2}\beta\hbar\omega_k}}{1 - e^{-\beta\hbar\omega_k}}. \tag{8}$$

Its logarithm is

$$\ln Z = -\sum_{\mathbf{k},\mathbf{e}_\mathbf{k}} \left(\frac{1}{2}\beta\hbar\omega_k + \ln(1 - e^{-\beta\hbar\omega_k})\right). \tag{9}$$

Notice that due to polarization degeneracy, there is no dependence of the summand on the polarization vector and so this may also just be written as

$$\ln Z = -2\sum_{\mathbf{k}} \left(\frac{1}{2}\beta\hbar\omega_k + \ln(1 - e^{-\beta\hbar\omega_k})\right). \tag{10}$$

From this, we may calculate the internal energy of photons in the thermal equilibrium state as

$$E = -\frac{\partial \ln Z}{\partial \beta} = \sum_{\mathbf{k}} \hbar\omega_k + 2\sum_{\mathbf{k}} \frac{\hbar\omega_k}{e^{\beta\hbar\omega_k} - 1} \equiv E_{\text{z.p.}} + 2\sum_{\mathbf{k}} \frac{\hbar\omega_k}{e^{\beta\hbar\omega_k} - 1}. \tag{11}$$

The term $E_{\text{z.p.}} \equiv \sum_{\mathbf{k}} \hbar\omega_k$ is an infinite constant that has no effect on the thermodynamic properties of the system. The second term may be evaluated by converting the sum into an integral in the same manner we did for phonons, leading to

$$E - E_{\text{z.p}} = \frac{2V}{(2\pi)^3} \int d^3k \frac{\hbar ck}{e^{\beta\hbar ck} - 1} = \frac{V}{\pi^2} \int_0^\infty dk\, k^2 \frac{\hbar ck}{e^{\beta\hbar ck} - 1}, \tag{12}$$

where I have used the spherical symmetry in the integrand to reduce the three dimensional integral to a one-dimensional one. Making the change of variables $x = \beta\hbar ck$ yields

$$E - E_{\text{z.p}} = \frac{V}{\pi^2} \left(\frac{k_B T}{\hbar c}\right)^3 k_B T \int_0^\infty dx \frac{x^3}{e^x - 1} = \frac{V\pi^2}{15} \left(\frac{k_B T}{\hbar c}\right)^3 k_B T. \tag{13}$$

The energy is proportional to the volume (as is expected from extensivity) and is quartic in the system temperature.

The corresponding pressure may be derived the the derivative of the free energy as

$$P = \frac{k_B T}{V} \ln Z = -\frac{1}{(2\pi)^3} \int d^3k\, \hbar\omega_k + 2k_B T \ln(1 - e^{-\beta\hbar\omega_k}) \equiv P_{\text{z.p}} - \frac{1}{(2\pi)^3} \int d^3k\, 2k_B T \ln(1 - e^{-\beta\hbar\omega_k}). \tag{14}$$

The first term is an infinite constant which does not lead to any mechanical response in vacuum because only pressure differences lead to forces. This is a uniform (albeit infinite) pressure. In systems which have material boundaries, the pressure will vary spatially but the infinite part will always cancel out. The second term may be evaluated as

$$P - P_{\text{z.p.}} = -\frac{k_B T}{\pi^2} \int_0^\infty dk\, k^2 \ln(1 - e^{-\beta\hbar\omega_k}) = -\frac{k_B T}{\pi^2} \left(\frac{k_B T}{\hbar c}\right)^3 \int_0^\infty dx\, x^2 \ln(1 - e^{-x}). \tag{15}$$

We may re-express the logarithmic integral by writing $x^2 = \frac{1}{3}\frac{d}{dx}x^3$ and integrating by parts. The boundary terms vanish and we may write

$$P - P_{\text{z.p.}} = \frac{k_B T}{3\pi^2} \left(\frac{k_B T}{\hbar c}\right)^3 \int_0^\infty dx \frac{x^3}{e^x - 1} = \frac{E - E_{\text{z.p}}}{3V} = \frac{\pi^2}{45} \left(\frac{k_B T}{\hbar c}\right)^3 k_B T. \tag{16}$$

I. RADIATION BY A BLACKBODY

Consider thermalized radiation as a photon gas. The thermalized radiation, as we know has an energy given by

$$E = \frac{2V}{(2\pi)^3} \int d^3k \frac{\hbar\omega_k}{e^{\beta\hbar\omega_k} - 1}, \tag{17}$$

where I am omitting the zero-point energy. We may write this in terms of photon frequencies and directions of propagation via

$$E = \frac{2V}{(2\pi)^3 c^3} \int d\Omega d\omega \, \omega^2 \frac{\hbar\omega}{e^{\beta\hbar\omega} - 1}, \tag{18}$$

and we could say the energy of photons per unit frequency and per unit solid angle is given by

$$\frac{1}{V}\frac{dE}{d\omega d\Omega} = \frac{1}{4\pi^3 c^3}\frac{\hbar\omega^3}{e^{\beta\hbar\omega} - 1}. \tag{19}$$

This quantity can be thought of as an energy density per unit frequency and per unit solid angle of direction. Let us now imagine the following: suppose we have thermalized photons existing in some volume. If the boundary of that volume allows light to pass through it, then there is an energy flux out of that volume. Let us evaluate that. Consider a gas of photons in a volume. The energy passing per unit area per unit time through the boundary (energy flux), Φ, is given by

$$\Phi = \int_0^{2\pi} d\phi \int_0^{\pi/2} d\theta \sin\theta \int_0^{\infty} d\omega \frac{1}{V}\frac{dE}{d\omega d\Omega} \times c\cos\theta = \pi \int d\omega \, \frac{1}{4\pi^3 c^2}\frac{\hbar\omega^3}{e^{\beta\hbar\omega} - 1} = \frac{\pi^2\hbar}{60c^2}\left(\frac{k_B T}{\hbar}\right)^4. \tag{20}$$

Defining the so-called Stefan-Boltzmann constant $\sigma \equiv \frac{\pi^2 k_B^4}{\hbar^3 c^2}$, we find

$$\Phi = \sigma T^4, \tag{21}$$

such that the power exiting the material volume becomes $\sigma A T^4$ with A the surface area of the boundary.

Now, you may have noticed that I did not necessarily say that the power radiated out of a body at temperature T is given by $P = \sigma A T^4$. I just said that if we have thermalized photons in a volume enclosed by a boundary of area A, they would transmit an energy per unit time given by $\sigma A T^4$. Indeed, that power P is only radiated by an *blackbody*, an idealized system that is capable of absorbing all radiation incident on it (hence why it is called a blackbody: it would scatter none of the incident light back to you and thus look black). It follows from a principle of optics called *reciprocity* that any light *generated* inside the body must be radiated out.

Therefore, if we have our material body in equilibrium with the radiation field at temperature T, the absorbed radiation would be given by the *influx* of photons from outside of the material, which by our previous argument is $\sigma A T^4$. However, this must *also* be equal to the *outflux* of photons from the body: otherwise, we would not be describing equilibrium. Therefore the light radiated by our body must have a power $\sigma A T^4$. This radiation is typically called *blackbody radiation.*

If our body is not a perfect absorber of incident radiation, it is called an *grey body*, and must emit less than a blackbody (because its emission is still equal to its absorption in equilibrium). It emits less by a factor ε that is called the *emissivity*.

Bosons and Fermions

Suppose we have N particles, however we define that:

- N electrons
- N atoms

In QM, we may write a wavefunction for the entire state of the system $|\psi\rangle$. Let us think about the simple case of two free particles (identical):

$$H = \frac{p_1^2}{2m} + \frac{p_2^2}{2m}$$

The eigenfunctions satisfy

$$H|\psi_{1,2}\rangle = E|\psi_{1,2}\rangle \, ,$$

and it is reasonably clear that since the particles are not interacting, the eigenstates should be

$$\underbrace{|k_1, k_2\rangle}_{\substack{\text{one particle plane} \\ \text{wave w/ wavevector} \\ k_1 \text{ and one w/} \\ \text{wavevector } k_2}}$$

with corresponding energy

$$E(k_1, k_2) = \frac{\hbar^2 k_1^2}{2m} + \frac{\hbar^2 k_2^2}{2m} .$$

In general, for N identical non-interacting particles, with Hamiltonian

$$H = \sum_{i=1}^{N} H_i^{(1)}$$

where $H^{(1)}|\psi_n\rangle = \epsilon_n|\psi_n\rangle$, with n denoting a complete set of quantum numbers. For example, if I had N hydrogen atoms, n would be the $\underset{(n)}{\text{principal}}$, $\underset{(l)}{\text{orbital}}$, $\underset{(m)}{\text{magnetic}}$, and $\underset{(s)}{\text{spin}}$ quantum numbers. Or (nlm).

We could write an n-particle wavefunction as

$$|m_1, m_2, \ldots, m_N\rangle$$

where particle 1 is in a quantum state with quantum numbers n_1, particle 2 is in a state with q-numbers n_2, so on.

The discussion thus far has treated the ~~two~~ particles as distinguishable - however in quantum mechanics, that is not really the case. Particles are in fact <u>indistinguishable</u>, and there are constraints on the wavefunction imposed by that. Deriving this from "first principles" is the subject of the spin-statistics theorem of quantum field theory and so for us, we'll need to take this on faith. To state these constraints, we must introduce the permutation operator P.

There are two types of constraints on particles in 3 dimensions:

<u>Bosons</u>: $P|\psi\rangle = |\psi\rangle$, <u>Fermions</u>: $P|\psi\rangle = -|\psi\rangle$. (SKIP).

P is a permutation operator and does the following:

$$P(i_1 i_2, \ldots i_N)\,|m_1, m_2, \ldots, m_N\rangle$$

$$= |m_{i_1}, m_{i_2}, \ldots, m_{i_N}\rangle$$

For example

state with particle 1 w/ q. number n_1 and particle 2 w/ q. number n_2.

$$P(12)\,|m_1 m_2\rangle = |m_1 m_2\rangle$$

$$P(21)\,|m_1, m_2\rangle = |m_2, m_1\rangle$$

← puts particle 1 in a state with q. number $\underline{\underline{n_2}}$ and particle 2 in a state w/ q. number $\underline{\underline{n_1}}$ - we have interchanged them.

However, if the particles are <u>indistinguishable</u>, then we cannot say there is any physical difference between

$$|m_1, m_2\rangle \longleftrightarrow |m_2, m_1\rangle$$

Both describe a state where one particle is in state n_1 and the other in n_2.

Thus, we require

$$P|\psi\rangle = e^{i\varphi}|\psi\rangle$$

since a w.f. is equivalent to itself under global phase multiplication.

$$\langle A\rangle = \langle\psi|A|\psi\rangle$$

$$\rightarrow \langle\psi|e^{-i\varphi} A\, e^{i\varphi}|\psi\rangle = \langle A\rangle .$$

all expectation values of Hermitian operators (observables) are preserved.

In 3D, the SST turns out to restrict

$$\begin{tikzcd} & +1 \text{ (Bosons)} \\ e^{i\varphi} \arrow[ur] \arrow[dr] & \\ & -1 \text{ (Fermions)} \end{tikzcd}$$

In say 2D, more general phases $\varphi \neq 0, \pi$ are possible, corresponding to <u>anyons</u>.

Bosons: $P|\psi\rangle = |\psi\rangle$ for any P (spin integer particles) → photons, He-4 nucleus, coll. exc. like phonons

Fermions: $P|\psi\rangle = -|\psi\rangle$ for any P. (half-integer spin particles) ↳ electrons, nucleons, He-3.

This restriction implies that a state of two free particles such as

$|k_1, k_2\rangle$ is not valid for bosons or fermions.

For Bosons, a properly (symmetrized) wavefunction is:

$$|\psi_{12}\rangle = \mathcal{N}\left(|k_1, k_2\rangle + |k_2, k_1\rangle\right)$$

$$P(21)|\psi_{12}\rangle = \mathcal{N}\left(|k_2, k_1\rangle + |k_1, k_2\rangle\right) = |\psi_{12}\rangle .$$

For fermions, a properly antisymmetrized wavefunction is:

$$|\psi_{12}\rangle = \mathcal{N}\left(|k_1, k_2\rangle - |k_2, k_1\rangle\right).$$

This has enormous implications for statistical mechanics as it strongly constrains the allowed states. To help us understand the ramifications, we need to discuss the occupation # representation of identical particle states.

Occupation number representation

Clearly, we cannot say what particle is in ~~one~~ what state, when the particles are indistinguishable. We can however say <u>how many</u> particles are in what state. In both the B and F examples, I could specify the state by saying:

- How many particles are in what state
- If they are bosons or fermions.

$$|\psi\rangle = |\underset{\substack{\uparrow\\ \text{state}\\ 1}}{n_1}, \underset{\substack{\uparrow\\ \text{state}\\ 2}}{n_2}, \underset{\substack{\uparrow\\ \text{state}\\ 3}}{\overset{\substack{\text{number of particles in}\\ \text{the state.}\\ \downarrow}}{n_3}}, \ldots\rangle$$

Example: Bosons $\quad |2k_1, k_2\rangle \leftarrow$ Needs to be symmetric under <u>all</u> interchanges.

$$|\psi^B_{123}\rangle = \mathcal{N}\underline{\left(|k_1,k_1,k_2\rangle + |k_1,k_2,k_1\rangle + |k_2,k_1,k_1\rangle\right)}$$

$$a_1^{\dagger 2} a_2^{\dagger}|0\rangle = \sqrt{2}\,|2,1\rangle$$

This wavefunction is not possible for <u>fermions</u>. Why?. Consider $P(12)$ on the state ~~$|k_1,k_1,k_2\rangle$~~

~~$|k_1,k_1,k_2\rangle \longrightarrow |k_1,k_1,k_2\rangle$~~

$$|\psi^F_{123}\rangle = \mathcal{N}\left(\alpha|k_1,k_1,k_2\rangle + \beta|k_1,k_2,k_1\rangle + \gamma|k_2,k_1,k_1\rangle\right).$$

It must be antisymmetric under any interchange:

$$P(12)|\psi^F_{123}\rangle = -|\psi^F_{123}\rangle = \mathcal{N}\left(\alpha|k_1,k_1,k_2\rangle + \beta|k_2,k_1,k_1\rangle + \gamma|k_1,k_2,k_1\rangle\right)$$

Since each state is an independent basis state, we require:

$$\begin{aligned} \alpha &= -\alpha \\ \beta &= -\gamma \\ \gamma &= -\beta \end{aligned} \quad \Rightarrow \alpha = 0.$$

Similar logic with $P(23)$ and $P(13)$ immediately shows $\beta = \gamma = 0$ and

$|\psi^F_{123}\rangle = 0$. (There is no state).

More generally, no fermionic state can have 2 particles in the same eigenstate. This is called the Pauli exclusion principle.

Summarizing

The allowed states of bosons are

$$|\psi\rangle = |n_1, n_2, \ldots\rangle, \quad n_i = 0, 1, 2, \ldots, \infty$$

while the allowed states of fermions are

$$|\psi\rangle = |n_1, n_2, \ldots\rangle, \quad n_i = 0, 1.$$

The corresponding energies, given a Hamiltonian $H = \sum_i H_i^{(1)}$ w/ eigenenergies ϵ_m, are

$$\boxed{E = \sum_m n_m \epsilon_m}$$

subject to constraints on occupation #s above.

Quantum statistical mechanics of bosons and fermions

The program is the same as before: compute Z or Q.

$$Z = \sum_{n_1, n_2, \ldots}' e^{-\beta \sum_m n_m \epsilon_m} \delta_{n_1 + n_2 + \cdots = N}$$

restricted sum. $0 \to \infty$ (B)
$0 \to 1$ (F).

$$Z_N = \sum' e^{-\sum_m \beta n_m \epsilon_m} \delta_{\sum_m n_m = N}$$

The constraint makes the sum hard. Go to GCE and calculate

$$\mathcal{Q} = \sum_{N=0}^{\infty} e^{\beta\mu N} Z_N$$

$$= \sum_{N=0}^{\infty} \sum_{n_1,n_2,\ldots}^{\prime} e^{-\beta\sum_m n_m\epsilon_m} \delta_{\sum_m n_m, N}\, e^{\beta\mu N}$$

$$= \sum_{n_1,n_2,\ldots}^{\prime} e^{-\beta\sum_m n_m\epsilon_m}\, e^{\beta\mu\sum_m n_m}$$

$$= \sum_{n_1,n_2,\ldots}^{\prime} e^{-\sum_m \beta(\epsilon_m-\mu)\, n_m}$$

$$= \prod_m \left(\sum_{n_i}^{\prime} e^{-\beta(\epsilon_m-\mu)\, n_i} \right)$$

$$= \boxed{\begin{cases} \prod_m \dfrac{1}{1-e^{-\beta(\epsilon_m-\mu)}} \\ \prod_m \left(1+e^{-\beta(\epsilon_m-\mu)}\right) \end{cases}}$$

Bosons $\sum_{n_i}^{\prime} = \sum_{n_i=0}^{\infty}$

Fermions

We can write the two cases as one by introducing $\eta = +1$ (bosons)
$\quad\quad -1$ (fermions)

~~$\Rightarrow \mathcal{Q} = \prod_m \left(1+e^{-\beta(\epsilon_m-\mu)}\right)^{-\eta}$~~

~~The thermodynamics of non-interacting bosons and fermions may be developed as:~~

~~$\ln \mathcal{Q} = -\eta \sum_m \ln\left(1+e^{-\beta(\epsilon_m-\mu)}\right)$.~~

~~The mean # particles follows from~~

~~$\langle N \rangle = \dfrac{\partial \ln \mathcal{Q}}{\partial(\beta\mu)} = -\eta \sum_m \dfrac{}{\left(1+e^{-\beta(\epsilon_m-\mu)}\right)}$~~

$$\boxed{Q = \sum\left(1-\eta e^{-\beta(\epsilon_m-\mu)}\right)^{-\eta}}$$

The thermodynamics is generated by

$$\boxed{\ln Q = -\eta \sum_m \ln\left(1-\eta e^{-\beta(\epsilon_m-\mu)}\right).}$$

The mean particle # follows as:

$$\frac{\partial \ln Q}{\partial(\beta\mu)} = \langle N\rangle = -\eta \sum_m \frac{-\eta e^{-\beta(\epsilon_m-\mu)}}{1-\eta e^{-\beta(\epsilon_m-\mu)}}$$

$$= \sum_m \frac{1}{e^{\beta(\epsilon_m-\mu)}-\eta} = \sum_m n_m$$

mean # particles in state m. follows from linearity & non-interacting.

$$\boxed{n_m \equiv \begin{cases} \dfrac{1}{e^{\beta(\epsilon_m-\mu)}-1} \\[2ex] \dfrac{1}{e^{\beta(\epsilon_m-\mu)}+1} \end{cases}}$$

Bosons **Bose-Einstein distribution**

Fermions **Fermi-Dirac distribution**

The mean energy is given by

$$\langle E\rangle = \sum_m n_m \epsilon_m$$

$$= \boxed{\sum_m \frac{\epsilon_m}{e^{\beta(\epsilon_m-\mu)}-\eta}}$$

Note that the chemical potential is ~~ex~~implicitly determined by:

$$\boxed{N = \sum_m \frac{1}{e^{\underset{\uparrow}{\beta}(\underset{\uparrow}{\epsilon_m}-\mu)}-\underset{\uparrow}{\eta}} = N(\mu,T). \Rightarrow \mu=\mu(T,N).}$$

Known

AEP 4230: Corrections to the ideal gas law from quantum statistics

Nick Rivera; dated November 14, 2025

We wish to find an approximate equation of state for non-interacting bosons and fermions at high temperature, in the absence of an external potential. In other words, corrections to the ideal gas law. The discussion here follows from Kardar Section 7.4. on the non-relativistic gas.

Consider non-interacting particles in a cubic box of length L and volume V. The single-particle eigenstates are momentum eigenstates $|\mathbf{k}\rangle$ with energy $\epsilon_k = \frac{\hbar^2 k^2}{2m}$. If we impose periodic boundary conditions, then the allowed wavevectors are $\mathbf{k} = \frac{2\pi}{L}(m_x, m_y, m_z)$ with $m_{x,y,z}$ integers.

We know that in the grand canonical ensemble, we have

$$\langle N \rangle = \sum_{\mathbf{k}} \frac{1}{e^{\beta(\epsilon_k - \mu)} - \eta}, \tag{1}$$

which would allow us for example to find the chemical potential $\mu(T, \langle N \rangle)$ in terms of the average number of particles.

The equation of state itself will follow from

$$\frac{PV}{k_B T} = \ln Q = -\eta \sum_{\mathbf{k}} \ln(1 - \eta e^{-\beta(\epsilon_k - \mu)}). \tag{2}$$

The leading correction to the ideal gas law at high-temperature is expected to be small because we know that the ideal gas law works well. Thus, it must be proportional to a small parameter. That small parameter is

$$z = e^{\beta\mu}. \tag{3}$$

[This was written with the incorrect sign in the exponent in class]. For a classical gas, we have

$$\mu = k_B T \ln n\lambda^3, \tag{4}$$

[where, this too, was originally written with the wrong sign]. Therefore in the classical regime, the *fugacity* z is given as $z = n\lambda^3 \ll 1$. This can be computed to be on the order of 10^{-8} for typical gases at room temperature. This parameter tells us how many particles "fit" in the volume defined by the deBroglie wavelength λ^3 and is a quantumness parameter. λ is essentially the length scale over which a particle can be thought of as a quantum wave, and so if more than one particle is in that volume, the identicality of particles becomes relevant. For example, since fermions cannot be in the same state, they also cannot be in the same position, and so if their quantum wavefunctions start to overlap, new physics should "kick in".

Writing the number of particles in terms of z gives

$$\langle N \rangle = \sum_{\mathbf{k}} \frac{1}{z^{-1} e^{\beta(\epsilon_k)} - \eta} = \sum_{\mathbf{k}} \frac{z e^{-\beta\epsilon_k}}{1 - \eta z e^{-\beta\epsilon_k}}. \tag{5}$$

We may write this in a Taylor series in z, anticipating that $z \ll 1$, as

$$\langle N \rangle = \sum_{\mathbf{k}} z e^{-\beta\epsilon_k} \sum_{s=0}^{\infty} (\eta z e^{-\beta\epsilon_k})^s. \tag{6}$$

We may re-arrange the sums as

$$\langle N \rangle = \sum_{s=0}^{\infty} z(\eta z)^s \sum_{\mathbf{k}} e^{-(s+1)\beta\epsilon_k}. \tag{7}$$

Converting the sum into an integral, and evaluating the Gaussian integrals which follow, yields [1]

$$\langle N\rangle = \frac{zV}{\lambda^3}\sum_{s=0}^{\infty}\frac{(\eta z)^s}{(s+1)^{3/2}} = \frac{V}{\lambda^3}\left(z + \frac{\eta}{2^{3/2}}z^2 + \frac{1}{3^{3/2}}z^3 + \frac{\eta}{4^{3/2}}z^4 + \dots\right). \tag{8}$$

Similarly, for the pressure, we can use the expansion $\ln(1-x) = -\sum_{s=1}^{\infty}\frac{x^s}{s}$ to retrieve [2]:

$$\frac{PV}{k_BT} = \eta\sum_{\mathbf{k}}\sum_{s=1}^{\infty}\frac{1}{s}(\eta z e^{-\beta\epsilon_{\mathbf{k}}})^s = \sum_{s=1}^{\infty}\eta\frac{(\eta z)^s}{s}\sum_{\mathbf{k}}e^{-s\beta\epsilon_{\mathbf{k}}} = \frac{V}{\lambda^3}\sum_{s=1}^{\infty}\frac{\eta^{s+1}z^s}{s^{5/2}} = \frac{V}{\lambda^3}\left(z + \frac{\eta}{2^{5/2}}z^2 + \frac{1}{3^{5/2}}z^3 + \frac{\eta}{4^{5/2}}z^4 + \dots\right). \tag{9}$$

Summarizing, we have the series expansions in z:

$$n\lambda^3 = \left(z + \frac{\eta}{2^{3/2}}z^2 + \frac{1}{3^{3/2}}z^3 + \frac{\eta}{4^{3/2}}z^4 + \dots\right). \tag{10}$$

and

$$\frac{p\lambda^3}{k_BT} = \left(z + \frac{\eta}{2^{5/2}}z^2 + \frac{1}{3^{5/2}}z^3 + \frac{\eta}{4^{5/2}}z^4 + \dots\right), \tag{11}$$

where $n = \langle N\rangle/V$.

If we keep only the leading order terms linear in z, we get $n\lambda^3 = z = e^{\beta\mu}$ which is the classically expected result from analyzing the ideal gas in the grand canonical ensemble. The pressure then follows as $p = nk_BT$.

The next leading order correction follows from writing

$$n\lambda^3 \approx z + \frac{\eta}{2^{3/2}}z^2 \tag{12}$$

and

$$\frac{p\lambda^3}{k_BT} \approx z + \frac{\eta}{2^{5/2}}z^2. \tag{13}$$

On the practice problems, you are asked to solve these simultaneously. You should get the result that

$$p \approx nk_BT\left(1 - \frac{\eta}{2^{5/2}}(n\lambda^3)\right). \tag{14}$$

The physical content of this equation is that because bosons "like" to be in the same state, they have an effective attraction of a statistical nature: an enhanced statistical tendency to clump together, leading to an attraction that lowers the pressure relative to the non-interacting case (just like the reduced pressure we found when analyzing the classical van der Waals gas!). Meanwhile, for the fermionic case, the pressure is increases because particles *cannot* be in the same location, and therefore there is an effective repulsion between particles leading to *increased pressure*.

Note that relative to Kardar, we have not included the spin degeneracy g. If that is included, the right-hand side of the equations for the particle number and pressure are simply multiplied by g, and the degeneracy parameter becomes $n\lambda^3/g$ rather than $n\lambda^3$.

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[1] make sure you fill in these steps if you do the practice problem!

[2] Again, work through the steps!

Review of previous lecture

Bosons & Fermions in the grand canonical ensemble

$$\boxed{\begin{aligned}
\ln Q_\eta &= -\eta \sum_m \ln\left(1-\eta e^{\beta\mu-\beta\epsilon_m}\right) \\
&\equiv -\eta \sum_m \ln\left(1-\eta z e^{-\beta\epsilon_m}\right) \;;\; z = e^{\beta\mu}. \\
\langle n_m \rangle &= \frac{1}{z^{-1}e^{\beta\epsilon_m}-\eta} \quad \begin{array}{l} \xrightarrow{\eta=+1} \text{Bose-Einstein} \\ \longrightarrow \text{Fermi-Dirac} \end{array} \\
\langle N \rangle &= \sum_m \langle n_m \rangle \longleftrightarrow \mu(\langle N \rangle, T). \\
\langle E \rangle &= \sum_m \epsilon_m \langle n_m \rangle
\end{aligned}}$$

High-temperature : $\mu \approx k_B T \ln n\lambda^3$

$$\boxed{z = e^{\beta\mu} = n\lambda^3 \ll 1}$$

Expand ( ) in z using free particle states

$$\boxed{\begin{aligned}
&|m\rangle = |k\rangle \\
&k = \frac{2\pi}{L}(m_x, m_y, m_z) \\
&\sum_k \rightarrow \frac{V}{(2\pi)^3}\int d^3k
\end{aligned}} \longleftarrow \text{(PBC)}$$

$$\left.\begin{aligned}
n\lambda^3 &= z + \frac{\eta z^2}{2^{3/2}} + \frac{z^3}{3^{3/2}} + \frac{\eta z^4}{4^{3/2}} + \dots \\
\frac{p\lambda^3}{k_B T} &= z + \frac{\eta z^2}{2^{5/2}} + \frac{z^3}{3^{5/2}} + \frac{\eta z^4}{4^{5/2}} + \dots
\end{aligned}\right\} \longrightarrow$$

Lowest-order and next lowest-order corrections

$$\boxed{p = n k_B T \cdot \left(1 - \frac{\eta}{2^{5/2}}(n\lambda^3) + \underset{\substack{\uparrow \\ O(n^2\lambda^6).}}{\dots}\right)}$$

Fermi systems / Fermi gases

Fermion: spin = half integer, $s = 1/2, 3/2, 5/2, \dots$

From theory of angular momentum in QM: states are $|s, m_s\rangle$

$m_s = -s, -s+1, \dots, s-1, s$ (z-projected spin).

$(2s+1)$ states

If H does not depend on spin operators, states have a $(2s+1)$ degeneracy.

Example: N ~~electrons~~ spin ½ particles in a box (a toy model for a metal or a neutron star)

$$H = \sum_i \frac{p_i^2}{2m}$$

Energy eigenstates: $|k, m\rangle$, $k = \frac{2\pi}{L}(m_x, m_y, m_z)$.

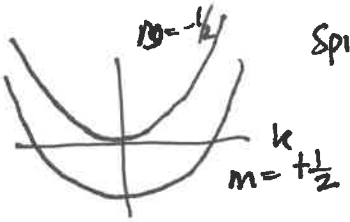
$$E_{k,m} = \frac{\hbar^2 k^2}{2m} \qquad g \equiv 2s+1 \text{ (degeneracy).}$$

On the other hand, if the particles are in a B-field

$$H = \sum_i \frac{p_i^2}{2m} + \sum_i \left(-\frac{\mu B}{\hbar}\right) S_{z,i}$$

Single-particle eigenstates: $|k, m\rangle$ with energy

$$E_{k,m} \frac{\hbar^2 k^2}{2m} - \mu B m.$$



Spin ½

From this, we may derive the mean # particles, the energy, and the pressure. Or if you like, the # density, energy density, and pressure.

The particle density is given by

$$N = \sum_{k,m} \frac{1}{e^{\beta(E_{k,m}-\mu)}+1} = \frac{V}{(2\pi)^3} \int d^3k \sum_m \frac{1}{e^{\beta(E_{k,m}-\mu)}+1}$$

In the absence of a spin potential, we get (i.e; for a free particle gas)

$$n = \frac{g}{(2\pi)^3} \int d^3k \frac{1}{e^{\beta \frac{\hbar^2 k^2}{2m} - \mu} + 1}$$

$$n = \frac{g}{(2\pi)^3}\int 4\pi k^2\, dk \frac{1}{e^{\beta\left(\frac{\hbar^2 k^2}{2m}-\mu\right)}+1}$$

$$x = \frac{\beta\hbar^2 k^2}{2m}$$

$$dx = 2\,\frac{\beta\hbar^2 k}{2m}\, dk$$

~~$= \frac{g}{2\pi^2}\int dk\cdot k\cdot\left(\frac{2m}{\hbar^2}\right)^{3/2}\left(\frac{\hbar}{2m}\right)^{3/2} k$~~

$$= \frac{g}{(2\pi)^3}\,4\pi\int \frac{1}{2}\frac{2m}{\beta\hbar^2}\, dx \left(\frac{2m}{\beta\hbar^2}\right)^{1/2} x^{1/2}\,\frac{1}{e^{\beta x}e^{-\beta\mu}+1}$$

$$= \boxed{\frac{1}{2}\frac{g}{2\pi^2}\left(\frac{2m}{\beta\hbar^2}\right)^{3/2}\int_0^\infty dx\,\frac{\sqrt{x}}{z^{-1}e^{\beta x}+1}}\;, \qquad z \equiv e^{\beta\mu}$$

Low temp. $e^{\beta\mu} \to \infty$.

$$\Rightarrow \boxed{n = \frac{g}{\lambda^3} f^-_{3/2}(z)}$$

The energy is given by:

$$\boxed{\frac{E}{V} = \frac{1}{2}\frac{g}{2\pi^2\beta}\left(\frac{2m}{\beta\hbar^2}\right)^{3/2}\int dx\,\frac{x^{3/2}}{z^{-1}e^{x}+1}} = \boxed{\frac{3}{2}\frac{g k_B T}{\lambda^3} f^-_{5/2}(z)}$$

The pressure is given by

$$PV = k_B T \ln \mathcal{Q}$$

$$P = \frac{k_B T}{\cancel{V}}(+1)\frac{\cancel{V} g}{(2\pi)^3}\int d^3k\, \ln\left(1 + z e^{-\beta\epsilon_k}\right)$$

$$= \frac{g k_B T}{(2\pi)^3}\,4\pi\int \frac{1}{2}\left(\frac{2m}{\beta\hbar^2}\right) dx \left(\frac{2m}{\beta\hbar^2}\right)^{1/2} \ln(1+ze^{-x})$$

$$= \frac{1}{2}\frac{g k_B T}{2\pi^2}\left(\frac{2m}{\beta\hbar^2}\right)^{3/2}\int dx\, x^{1/2}\ln(1+ze^{-x})$$

$$x^{1/2} = \frac{2}{3}\frac{d}{dx}x^{3/2}$$

$$\overset{\text{I.B.P.}}{=} -\frac{g k_B T}{4\pi^2}\left(\frac{2m}{\beta\hbar^2}\right)\cdot\frac{2}{3}\int dx\, x^{3/2}\,\frac{-ze^{-x}}{\underline{1+ze^{-x}}} \qquad \frac{1}{z^{-1}e^{x}+1}$$

$$= \boxed{\frac{2}{3}\frac{E}{V}} = \boxed{\frac{g k_B T}{\lambda^3} f^-_{5/2}(z)}$$

The evaluation of the properties of the Fermi gas is set by integrals of the form

$$f^-_m(z) = \frac{1}{m!}\int_0^\infty dx\; x^m \frac{d}{dx}\left(\frac{-1}{z^{-1}e^x+1}\right)$$

$$= \frac{1}{(m-1)!}\int_0^\infty dx\; \frac{x^{m-1}}{z^{-1}e^x+1}\;.$$

We see that:

$$n = \frac{g}{4\pi^2}\left(\frac{2m}{\beta\hbar^2}\right)^{3/2} f^-_{3/2}(z)\left(\frac{1}{2}\right)! \quad , \qquad \frac{2mk_BT}{\hbar^2} = \frac{8\pi^2 m k_B T}{h^2}$$

$$= \frac{1}{\lambda^2}\cdot 4\pi$$

$$= \frac{(4\cancel{\pi})^{3/2} g}{\cancel{4}\cancel{\pi}^{\cancel{2}}\lambda^3} f^-_{3/2}(z)\,\frac{\sqrt{\cancel{\pi}}}{\cancel{2}}$$

$$= \boxed{\frac{g}{\lambda^3} f^-_{3/2}}$$

while

$$\frac{E}{V} = \frac{g k_B T}{4\pi^2}\left(\frac{2mk_BT}{\beta\hbar^2}\right) f^-_{5/2}(z)\left(\frac{3}{2}\right)!$$

$$= \boxed{\frac{3}{2}\frac{g k_B T}{\lambda^3} f^-_{5/2}(z)}$$

$$\boxed{P = \frac{g k_B T}{\lambda^3} f^-_{5/2}(z)} = \frac{2}{3}\frac{E}{V}$$

So we are tasked with evaluating things like $f^-_\alpha(z)$.

T=0

Before we do that, let's look @ T=0.

$$n = \frac{g}{\lambda^3}\frac{2}{\sqrt{\pi}}\int_0^\infty dx\; \frac{\sqrt{x}}{z^{-1}e^x-1}$$

$\beta \to 0 \Rightarrow$ If $\epsilon < \mu,\; e^{\beta(\epsilon-\mu)} \to 0$

$\epsilon > \mu,\; e^{\beta(\epsilon-\mu)} \to \infty$

$$\Rightarrow n = \frac{2g}{\sqrt{\pi}\lambda^3}\int_0^{x_{max}} dx\,\sqrt{x} = \frac{4g}{3\sqrt{\pi}\lambda^3} x_{max}^{3/2}$$

$$x_{max} = \beta\frac{\hbar^2 k^2}{2m} = \beta\mu \Rightarrow \frac{4g(\beta\mu)^{3/2}}{3\sqrt{\pi}\lambda^3} = n$$

$$n = \left(\frac{2m\mu}{\hbar^2}\right)^{3/2}\cdot\frac{g}{6\pi^2} = \frac{g}{6\pi^2}k_F^3$$

<u>Filling argument</u> : g^- per state until N particles : $N = g\sum_{k<k_m} = \frac{gV}{8\pi^3}\frac{4}{3}\pi k_F^3$

$$\Rightarrow \boxed{n = \frac{g}{6\pi^2}k_F^3}$$

Energy density also from filling

$$E/V = \frac{g}{8\pi^3}\frac{\hbar^2}{2m}\int_0^{k_F} 4\pi k^2 dk\; k^2 = \frac{\hbar^2 k_F^2}{2m}\cdot\frac{g k_F^3}{10\pi^2}$$

$$= \frac{3}{5}n\epsilon_F\,.$$

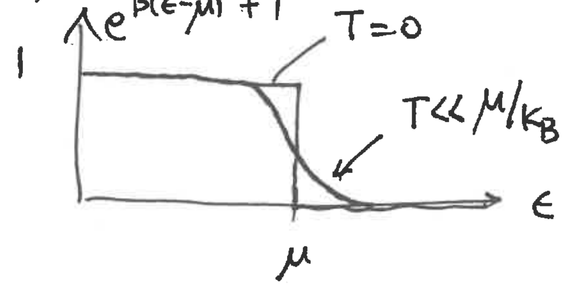
$$\boxed{P = \frac{2}{5}n\epsilon_F}$$ ↶ degeneracy pressure - imagine compression.

Evaluation of $f^-_\alpha(z)$. Could be derived but maybe more convenient to state the Sommerfeld expansion for large z.

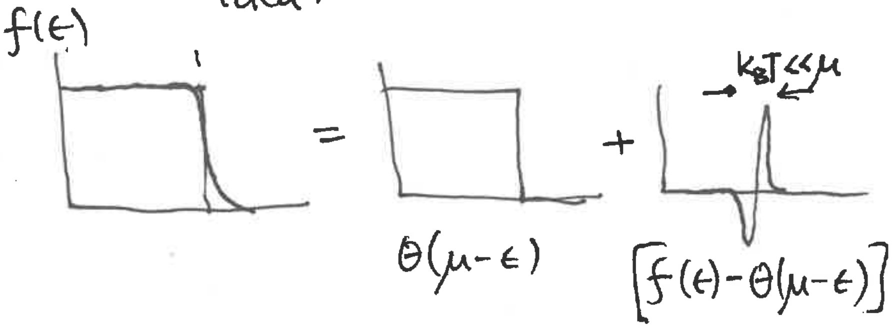
$$f^-_m(z\to\infty) = \frac{(\ln z)^m}{m!}\left[1 + \frac{\pi^2}{6}\frac{m(m-1)}{(\ln z)^2} + \frac{7\pi^4}{360}\frac{m(m-1)(m-2)(m-3)}{(\ln z)^4} + \dots\right]$$

Sommerfeld expansion

$$f(\epsilon) = \frac{1}{e^{\beta(\epsilon-\mu)}+1}$$



Idea:



Now consider an integral like

$$f^-_m(z) = \frac{1}{(m-1)!} \underbrace{\int_0^\infty dx \, \frac{x^{m-1}}{z^{-1}e^x+1}} \qquad \Big| \quad x^{m-1} = \frac{1}{m}\frac{d}{dx}x^m$$

$$\int_0^\infty dx \, \frac{x^{m-1}}{e^{x-\ln z}+1} = \frac{1}{m}\int_0^\infty dx \left(\frac{d}{dx}x^m\right)\frac{1}{z^{-1}e^x+1}$$

$$= -\frac{1}{m}\int_0^\infty dx \; x^m \, \frac{d}{dx} \underbrace{\frac{1}{z^{-1}e^x+1}}_{\text{vanishes @ 0 and } +\infty.}$$

$$\approx -\frac{1}{m}\int_{-\infty}^\infty dx \; x^m \, \frac{d}{dx}\frac{1}{z^{-1}e^x+1}$$

Change variables to $x = t + \ln z \quad (t = x - \ln z)$

$$= -\frac{1}{m}\int_{-\infty}^\infty dt \; (t+\ln z)^m \frac{d}{dt}\frac{1}{e^t+1}$$

$$= -\frac{1}{m}\int_{-\infty}^\infty dt \sum_{\alpha=0}^m \binom{m}{\alpha} t^\alpha (\ln z)^{m-\alpha} \frac{d}{dt}\frac{1}{e^t+1}$$

$$= +\frac{1}{m}\sum_{\alpha=0}^m \binom{m}{\alpha}(\ln z)^{m-\alpha}\,\alpha \underbrace{\int_{-\infty}^\infty dt \, \frac{t^{\alpha-1}}{e^t+1}}_{\text{Use tabulated integrals.}}$$

This can straightforwardly be shown to be

$$f^-_m(z\to\infty) = \frac{(\ln z)^m}{m!}\left[1 + \frac{\pi^2}{6}\frac{m(m-1)}{(\ln z)^2} + \frac{7\pi^4}{360}\frac{m(m-1)(m-2)(m-3)}{(\ln z)^4} + \cdots\right]$$

$$\bar{f}_{3/2}(z) \approx \frac{(\beta\mu)^{3/2}}{\frac{3}{2}\cdot\frac{\sqrt{\pi}}{2}}\left[1+\frac{\pi^2}{6}\frac{\frac{3}{2}\cdot\frac{1}{2}}{(\beta\mu)^2}+\dots\right]$$

$$\Rightarrow n \approx \underbrace{\frac{g}{\lambda^3}(\beta\mu)^{3/2}\frac{4}{3\sqrt{\pi}}}\left(1+\frac{\pi^2}{8}\left(\frac{k_BT}{\mu}\right)^2+\dots\right)$$

$$= \frac{g}{h^3}(2\pi m \cancel{k_BT})^{3/2}\frac{1}{(\cancel{k_BT})^{3/2}}\cdot\mu^{3/2}\cdot\frac{4}{3\sqrt{\pi}}$$

$$= \frac{g}{\underline{(2\pi)}^{3/2}\underline{\hbar}^3}(\cancel{2\pi})^{\cancel{3/2}}\underline{m}^{3/2}\underline{\mu}^{3/2}\cdot\frac{4\cdot\sqrt{2}}{3\sqrt{\pi}\sqrt{2}}$$

$$\left|\ \mu=\frac{\hbar^2k^2}{2m}\right.$$

$$= \left(\frac{2m\mu}{\hbar^2}\right)^{3/2}\cdot\frac{g}{2^{3/2}\pi^{3/2}}\cdot\frac{\cancel{3}\cancel{\sqrt{\pi}}\sqrt{2}}{3\sqrt{\pi}}$$

$$= \left(\frac{2m\mu}{\hbar^2}\right)^{3/2}\cdot\frac{g}{6\pi^2}$$

$$\Rightarrow n = \frac{g}{6\pi^2}\left(\frac{2m\mu}{\hbar^2}\right)^{3/2}\left(1+\frac{\pi^2}{8}\left(\frac{k_BT}{\mu}\right)^2+\dots\right)$$

$$\frac{E}{V} = \left(\frac{2m\mu}{\hbar^2}\right)^{3/2}\cdot\frac{g}{6\pi^2}\cdot\frac{\beta\mu}{(5/2)}\cdot\frac{3}{2}k_BT\left(1+\underset{\frac{\pi^2}{6}\cdot\frac{5}{2}\cdot\frac{3}{2}}{\overset{\frac{5\pi^2}{8}}{\cancel{\frac{5\pi^2}{16}}}}\left(\frac{k_BT}{\mu}\right)^2+\dots\right)$$

To express things completely, we have to find μ and substitute. We will evaluate μ perturbatively in $(k_BT/\varepsilon_F)^2$, which is small as $T\to 0$.

$$\mu=\mu(T=0)+\delta\mu.$$

$\underline{T=0|}$ $\quad n=\frac{g}{6\pi^2}\left(\frac{2m\mu}{\hbar^2}\right)^{3/2} \Rightarrow \mu=\left(\frac{6\pi n}{g}\right)^{2/3}\cdot\frac{\hbar^2}{2m} \equiv \frac{\hbar^2k_F^2}{2m}$

$\mu(T=0)\equiv\varepsilon_F.$ (as expected)

Finite T:

$$\mu = \varepsilon_F + \delta\mu$$

$$\delta\mu \sim \left(\frac{k_BT}{\varepsilon_F}\right)^2 .$$

$$\overbrace{\frac{6\pi^2}{g}n}^{k_F^3} \propto \left(\frac{2m}{\hbar^2}\right)^{3/2} \mu^{3/2}\left(1+\frac{\pi^2}{8}\left(\frac{k_BT}{\mu}\right)^2\right)$$

$$\Rightarrow \frac{\hbar^2k_F^2}{2m} = \varepsilon_F = \mu^{\cancel{3/2}}\left(1+\frac{\pi^2}{\underset{12}{\cancel{8}}}\left(\frac{k_BT}{\mu}\right)^2\right)$$

$$\varepsilon_F = (\varepsilon_F+\delta\mu)\left(1+\frac{\pi^2}{12}\left(\frac{k_BT}{\underset{\uparrow}{\varepsilon_F+\delta\mu}}\right)^2\right)$$

can neglect corr. higher orders

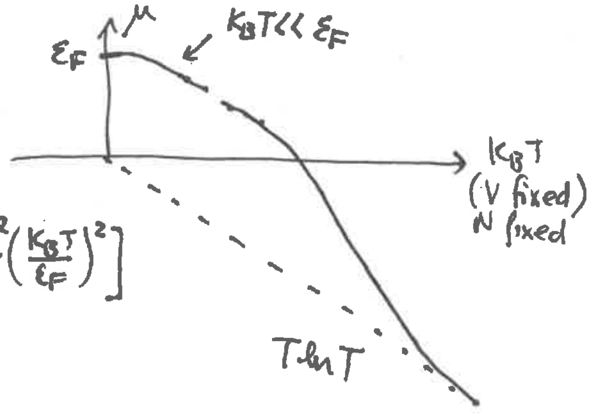
$$\approx \varepsilon_F + \delta\mu + \varepsilon_F\frac{\pi^2}{12}\left(\frac{k_BT}{\varepsilon_F}\right)^2$$

$$\Rightarrow \delta\mu = -\varepsilon_F\frac{\pi^2}{12}\left(\frac{k_BT}{\varepsilon_F}\right)^2$$

$$\Rightarrow \boxed{\mu = \varepsilon_F\left[1-\frac{\pi^2}{12}\left(\frac{k_BT}{\varepsilon_F}\right)^2\right]}$$

T large

$$\mu \to \mu_{cl} = +k_BT\ln n\lambda^3 < 0$$



We can use this to also write down the energy density and get

$$\frac{E}{V} = \frac{n}{1+\frac{\pi^2}{8}\left(\frac{k_BT}{\mu}\right)^2}\cdot\frac{3}{5}\varepsilon_F\left[1-\frac{\pi^2}{12}\left(\frac{k_BT}{\varepsilon_F}\right)^2\right]\left[1+\frac{5\pi^2}{8}\left(\frac{k_BT}{\varepsilon_F}\right)^2\right]$$

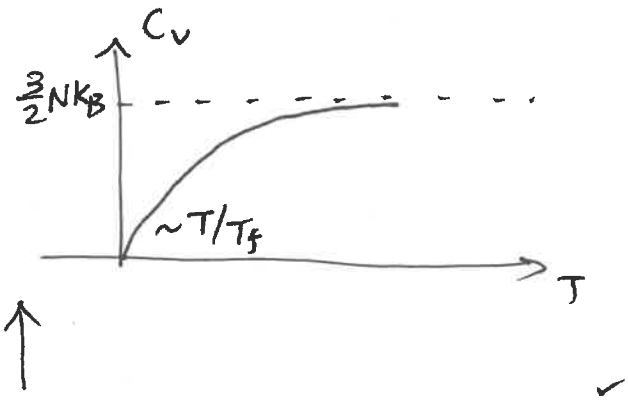
$$\approx \frac{3}{5}n\varepsilon_F\left(1+\pi^2\left(\frac{k_BT}{\varepsilon_F}\right)^2\underbrace{\left(\frac{5}{8}-\frac{1}{8}-\frac{1}{12}\right)}_{\frac{4}{8}-\frac{1}{12}=\frac{5}{12}}\right)$$

$$= \frac{3}{5}n\varepsilon_F\left(1+\frac{5\pi^2}{12}\left(\frac{k_BT}{\varepsilon_F}\right)^2\right) \equiv \boxed{\frac{3}{5}nk_BT_f\left(1+\frac{5\pi^2}{12}\left(\frac{T}{T_f}\right)^2\right)} .$$

And so the heat capacity is given by

$$C_V \approx \frac{3}{5} n k_B \cancel{T_f} \cdot \frac{10\pi^2}{12} \frac{T}{T_f^{\cancel{2}}} V.$$

$$= \boxed{\frac{\pi^2}{2} N k_B \frac{T}{T_f}}.$$



Physically: Only electrons near fermi surface can be promoted

$$\delta\varepsilon = \frac{4\pi k_F^2\, dk}{8\pi^3} \cdot k_B T\, V$$

$$= \frac{k_F^2\, dk}{2\pi^2} k_B T\, V$$

$$\sim \sqrt{\varepsilon_F}\, d\varepsilon \cdot k_B T\, V$$

$$\sim k_B T^2 \Rightarrow C_V \sim T.$$

Can ~~we~~ get the other factors?.

~~Fraction of e^-~~

$$\cancel{\frac{4\pi k_F^2\, dk}{\frac{4}{3}\pi k_F^3} = \frac{3}{k_F} dk}$$

$$\Big|\ 2k_F dk = \frac{2mE_F}{\hbar^2}$$

$$\cancel{= \frac{3}{k_F}\frac{2mE_F}{\hbar^2 k_F} dE}$$

$\sim 3Nk_BT\ (\cdot k_BT)$. where is ~~$1/E_F$~~?

Bose gases

Now we will analyze the Bose gas:

$$\langle n_K \rangle = \frac{1}{e^{\beta(\epsilon_K - \mu)} - 1}$$

$\langle n_K \rangle \geq 0$ requires

$$e^{\beta(\mathcal{E}_K - \mu)} \geq 1$$

$$\Rightarrow \quad \mathcal{E}_K \geq \mu \quad \Rightarrow \boxed{\mu < \min(\mathcal{E}_k)} . \quad (= 0 \text{ for free particle}).$$

Let us examine the chemical potential of the Bose gas as follows:

$$n = \frac{g}{2\pi^2} \int_0^\infty dk \, k^2 \frac{1}{z^{-1} e^{\beta \epsilon_K} - 1}$$

$\beta \frac{\hbar^2 k^2}{2m} = x$

$\Rightarrow \frac{\beta \hbar^2 k dk}{m} = dx$

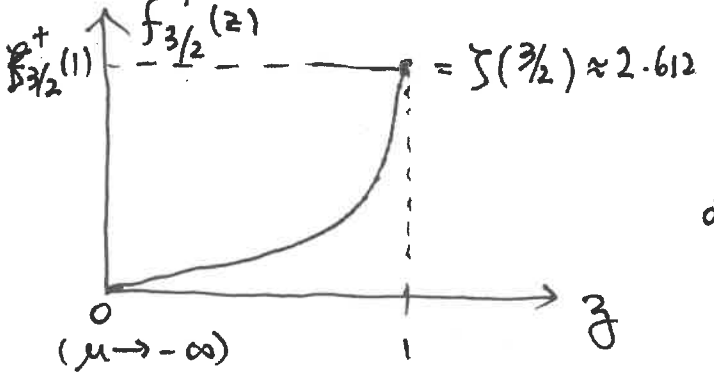
$$= \frac{g}{(2\pi^2)} \int_0^\infty 2 \frac{m \, dx}{2\beta\hbar^2} \left(\frac{2mx}{\beta\hbar^2}\right)^{1/2} \frac{1}{z^{-1}e^x - 1}$$

$$= \frac{g}{4\pi^2} \left(\frac{2m}{\beta\hbar^2}\right)^{3/2} \int_0^\infty dx \frac{\sqrt{x}}{z^{-1} e^x - 1}$$

$z = e^{\beta\mu}$

$$= \frac{g}{\lambda^3} f^+_{3/2}(z).$$

We can integrate $f^+_{3/2}(z)$ as a fn. of z (e.g. numerically) & plot it



$\mu = 0 \Rightarrow z = 1.$

Since $n \sim f^+_{3/2}(z)$, this implies a critical density for which n cannot exceed.

$$n = \frac{g}{\lambda^3} f^+_{3/2}(z) \leq 2.612 \, g/\lambda^3$$

What happens if we try to exceed that density? It's possible only if those particles are placed in the lowest energy state with $k=0$. That is because we could write

$$n = \underbrace{n_x}_{\text{excited}} = \frac{g}{\lambda^3}\int_{0^+}^{\infty} dx \, \frac{\sqrt{x}}{z^{-1}e^{x}-1} .$$

The constraint is then

$$n_x \leq 2.612 \, g/\lambda^3 .$$

At large temperatures, this bound isn't too important since

$$n_x \leq \# \, T^{3/2}$$

$$\lambda(300\text{K}) \sim \frac{h}{m\sqrt{\frac{kT}{m}}} \sim \frac{h}{\sqrt{mkT}} \sim \frac{10^{-34}}{\sqrt{10^{-26}\cdot 10^{-21}}} \sim 10^{-11} \text{ m}$$

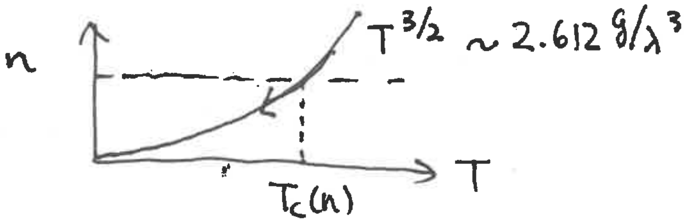
$$n \lesssim 10^{33} \text{ m}^{-3} \gg \text{atomic scale densities} .$$

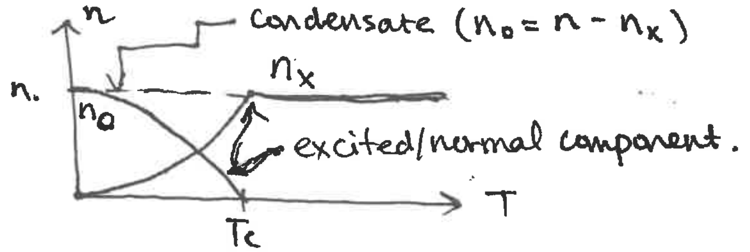
If we lower temperature such that

$$T \leq T_c(n) = \left(\frac{n}{g\zeta_{3/2}} \frac{h^3}{(2\pi m k_B)^{3/2}} \right)^{2/3}$$

$$= \frac{h^2}{2\pi m k_B} \left(\frac{n}{g\zeta^{3/2}} \right)^{2/3}$$

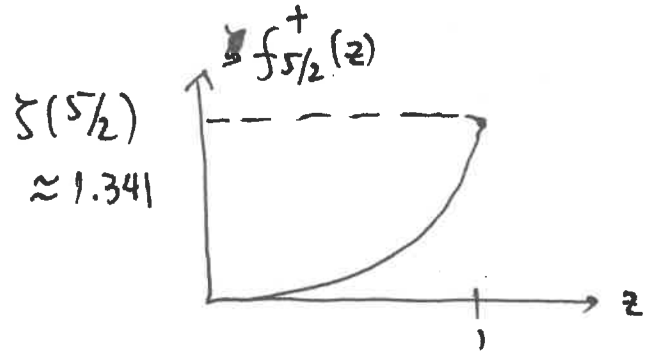
then we reach the limiting density of the excited state.





⊛ When the limiting density is smaller than the total density, the excited state gets "pinned" to the limiting density and the remainder corresponds to a <u>macroscopic occupation</u> of a single (ground state). This is called <u>Bose-Einstein condensation</u>.

Properties of BEC



Pressure:

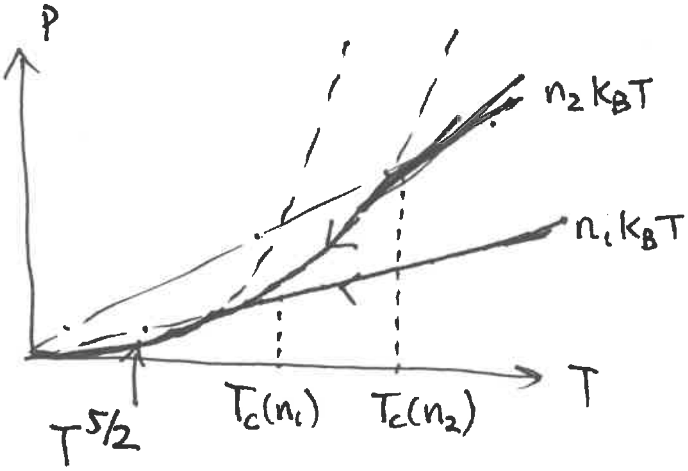
$$P = \frac{g k_B T}{\lambda^3} f^+_{5/2}(z)$$

Below the condensation temperature, we simply get

$$P = \frac{g k_B T}{\lambda^3} \times 1.341$$

independent of density because only excited particles with momentum contribute to pressure.

$\sim T^{5/2}$



high-T classical limit

Gases of same mass but different densities

Let's now think about what happens to the condensate when we lower the specific volume instead

$$v = \frac{V}{N}.$$

While classically, $p = \frac{kT}{v} \Rightarrow \frac{\partial p}{\partial v} = \frac{-kT}{v^2}$.

Condensation happens when

$$n > \frac{g}{\lambda^3} \times 2.612$$

$$\text{or } v < \frac{\lambda^3}{\zeta_{3/2}\, g} \equiv v_*$$

For $v < v_*$, $\left.\frac{\partial p}{\partial v}\right|_T = 0$ since $\left.\frac{\partial p}{\partial n}\right|_T = 0$: In other words, the pressure-volume isotherm is flat. Since the compressibility is given by

$$\kappa_T = -\frac{1}{V}\frac{\partial V}{\partial P} = -\frac{1}{v}\frac{\partial v}{\partial P}$$

the compressibility *diverges*.

The BEC transition combines aspects of first and second-order phase transitions. There is a finite latent heat, given by:

$$\left.\frac{dp}{dT}\right|_{T_c} = \frac{1}{T}\,\frac{S_n - S_0}{v_n - v_0}$$

$$\frac{5}{2}\,\frac{P}{T_c} = \frac{1}{T_c}\,\frac{L}{v}$$

$$\Rightarrow L = \frac{5}{2}\,\frac{\zeta_{5/2}\,\cancel{g}\,k_B T_c}{\cancel{\lambda^3}}\,\frac{\cancel{\lambda^3}}{\cancel{g}\,\zeta_{3/2}} = \frac{5}{2}\,\frac{\zeta_{5/2}}{\zeta_{3/2}}\,k_B T_c$$

$$\approx \boxed{1.28\,k_B T_c}$$

The intuition here is that we have a coexistence between a normal gas of specific volume v and a condensate of zero volume. (*)

Using the identity

$$\frac{d f_m^+(z)}{dz} = \frac{1}{z}\,f_{m-1}^+(z)$$

$$\left|\; -\frac{1}{v}\frac{\partial v}{\partial p} = +\frac{n}{n^2}\frac{\partial n}{\partial p}\right.$$

we have

$$\frac{dP}{dz} = \frac{g k_B T}{\lambda^3}\,\frac{1}{z}\,f_{3/2}^+(z)$$

$$\frac{dn}{dz} = \frac{g}{\lambda^3}\,\frac{1}{z}\,f_{1/2}^+(z)$$

$$\Rightarrow \cancel{\frac{1}{n}\frac{dn}{dp} = K_T = \frac{\frac{5}{3}k_B T\, f_{3/2}^+(z) / f_{1/2}^+(z)\,\lambda^3}{g\, f_{3/2}^+(z)} = \frac{5 k_B T}{3g}\,\lambda^3 f_{1/2}^+(z)}$$

$$K_T = \frac{1}{n}\frac{\partial n}{\partial p}$$

$$= \frac{\lambda^3}{g f_{3/2}(z)} \cdot \cancel{\frac{3}{5}}\,\frac{1}{k_B T}\,\frac{f_{1/2}^+(z)}{f_{3/2}^+(z)}$$

$$= \boxed{\frac{f_{1/2}^+(z)}{n k_B T\, f_{3/2}^+(z)}}$$

, which diverges @ $z=1$ due to $f_{1/2}$ diverging.

The energy of the Bose gas is given by:

$$E = \frac{3}{2} PV = \frac{3}{2} \cdot \frac{g k_B T}{\lambda^3} f^+_{5/2}(z) V$$

$$\sim T^{5/2}. \text{ (when in BEC).}$$

$$C_V = \left.\frac{\partial E}{\partial T}\right|_{V,N} = \frac{3V}{2} \frac{g k_B (2\pi m k_B)^{3/2}}{h^3} \underbrace{\frac{\partial}{\partial T} T^{5/2} f^+_{5/2}}_{\frac{5}{2} T^{3/2} f^+_{5/2} + \underset{T^{3/2}T}{T^{5/2}} \frac{1}{z} f^+_{3/2} \cdot \frac{dz}{dT}}$$

$$\frac{dz}{dT} = \frac{d}{dT} e^{\beta\mu}$$

Since V is constant and N, we have

$$\frac{3}{2T} f^+_{3/2}(z) + \frac{1}{z} f^+_{1/2}(z) \frac{dz}{dT} = 0$$

$$\Rightarrow \frac{T}{z} \frac{dz}{dT} = -\frac{3}{2} \frac{f^+_{3/2}}{f^+_{1/2}}$$

$$\Rightarrow C_V = \frac{5}{2} T^{3/2} f^+_{5/2} + T^{3/2} \left(-\frac{3}{2} \frac{f^{+\,2}_{3/2}}{f^+_{1/2}} \right)$$

$$= T^{3/2} \left(\frac{5}{2} f^+_{5/2} - \frac{3}{2} \frac{f^{+\,2}_{3/2}}{f^+_{1/2}} \right) \cdot \frac{3}{2} \frac{g V k_B (2\pi m k_B)^{3/2}}{h^3}$$

$$\cancel{\frac{3}{2} g \lambda^3 \frac{3}{2}}$$

$$= \frac{3}{2} \frac{gV}{\lambda^3} \left(\frac{5}{2} f^+_{5/2} - \frac{3}{2} \frac{f^{+\,2}_{3/2}}{f^+_{1/2}} \right).$$

$$\frac{C_V}{N k_B} = \frac{15}{4} \frac{g}{n\lambda^3} \zeta_{5/2}$$

$$= \frac{15}{4} \frac{g}{n} \zeta_{5/2} \frac{(2\pi m k_B)^{3/2} T^{3}}{h^3}$$

$$= \frac{15}{4} \frac{\zeta_{5/2}}{\zeta_{3/2}} \left(\frac{T}{T_c} \right)^{3/2}.$$

At $z=1$, we simply get

$$E = \frac{3}{2} \frac{g k_B T}{\lambda^3} \zeta_{5/2} V \Rightarrow \frac{\partial E}{\partial T} = \frac{5}{2} \frac{1}{T} \frac{3}{2} \frac{g k_B T V}{\lambda^3} \zeta_{5/2}$$

$$= \frac{15}{4} \frac{g k_B V}{\lambda^3} \zeta_{5/2} = \frac{15}{4} k_B \cdot \frac{g V (2\pi m k_B)^{3/2}}{h^3} \zeta_{5/2} T^{3/2}$$

$$\boxed{\frac{1}{N k_B} C_V = \frac{15}{4} \left(\frac{T}{T_c} \right)^{3/2} \frac{\zeta_{5/2}}{\zeta_{3/2}}}$$: Low temp, understandable from disp. reln.

$$k_B T \sim \frac{\hbar^2 k^2}{2m}$$

$$\Rightarrow k \sim T^{1/2}$$

Volume of states $\sim T^{3/2}$

Energy $\sim T^{5/2} \longrightarrow C \sim T^{3/2}$.