

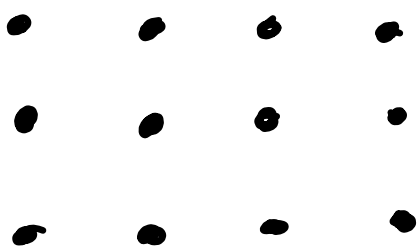
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Last time:

We found that for 1D quantum harmonic oscillator

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

Specific heat of Solids:



The atoms will vibrate (move around) their equilibrium position at the crystal lattice size. Since the movement is small we will assume that it is harmonic.

For the crystal

$$H(P, Q) = T(P_i) + V_{ij}(Q_i, Q_j)$$

$3N$ P_i 's and $3N$ Q_i 's $N = \#$ of atoms.

$$V_{ij} = V_0 + \underbrace{\frac{\partial V}{\partial Q_i}}_0 \bigg|_0 Q_i + \frac{1}{2} \underbrace{\frac{\partial^2 V}{\partial Q_i \partial Q_j}}_{\text{Tensor}} Q_i Q_j$$

because V_0
is the equilibrium
position

We can define new coordinates:

$$p_i = \sum_j a_{ij} P_j \quad q_i = \sum_j b_{ij} Q_j$$

$\{p_i, q_i\}$ are the $6N$ normal coordinates.

In this new basis the tensor $\frac{\partial^2 V}{\partial Q_i \partial Q_j}$ is

diagonal, $\{p_i, q_i\}$ are the normal coordinates that "decouple" the oscillators.

Now

$$E = \sum_{i=1}^{3N} \left(\underbrace{\frac{p_i^2}{2m}}_{\text{K.E.}} + \underbrace{\frac{1}{2} K_i q_i^2}_{\text{P.E.}} \right)$$

K_i : elastic constants.

If T is high (room temperature):

we can use equipartition of energy:

$$\bar{E} = 3N \left[\left(\frac{1}{2} kT \right) \times 2 \right] = 3NkT$$

If $N = N_a$ then

$$\bar{E} = 3 \underbrace{N_a k}_{R} T = 3RT$$

then

$$C_V = \left. \frac{\partial \bar{E}}{\partial T} \right|_V = 3R \quad \text{constant.}$$

$C_V \approx 3R$ at room temperature but eventually C_V decreases as T gets lower.

For low T we can see that $\lim_{T \rightarrow 0} C_V = 0$.

$$C_V = \left. \frac{\partial Q}{\partial T} \right|_V = T \left. \frac{\partial S}{\partial T} \right|_V \quad \therefore \quad dS = \frac{C_V}{T} dT$$

$$\int_0^T dS = \int_0^T \frac{C_V(T')}{T'} dT'$$

$$S(T) - S(0)$$

Since $\lim_{T \rightarrow 0} S(T) - S(0) = 0$ then $C_V(T)$ has to go to 0 as T goes to zero so that $\frac{C_V(T)}{T}$ does not diverge.

Then to study low T we need to use the quantum mechanical formulation.

Notice that k_i are different for each oscillator but Einstein made the approximation that $k_i = m\omega^2$ for all i .

This means that we need to consider $3N_a$ independent 1D oscillators.

Using the result for \bar{E} that we got last time:

$$\bar{E} = 3 N_a \hbar \omega \left(\frac{1}{2} + \frac{1}{e^{\beta \hbar \omega} - 1} \right)$$

$$\beta = 1/kT$$

$$\frac{\partial \beta}{\partial T} = -\frac{1}{kT^2}$$

$$C_v = \left. \frac{\partial \bar{E}}{\partial T} \right|_v = \left. \frac{\partial \bar{E}}{\partial \beta} \right|_v \left. \frac{\partial \beta}{\partial T} \right|_v =$$

$$= -\frac{1}{kT^2} 3 N_a \hbar \omega \frac{(-\hbar \omega) e^{\beta \hbar \omega}}{(e^{\beta \hbar \omega} - 1)^2} =$$

$$= \frac{3 N_a \overset{R}{k} (\hbar \omega)^2 e^{\beta \hbar \omega}}{k^2 T^2 (e^{\beta \hbar \omega} - 1)^2} = 3 R \left(\frac{\theta_E}{T} \right)^2 \frac{e^{\theta_E/T}}{(e^{\theta_E/T} - 1)^2}$$

$$\theta_E = \frac{\hbar \omega}{k} \text{ Einstein's temperature}$$

Limits of c_v :

$$c_v = 3R \left(\frac{\theta_E}{T} \right)^2 \frac{e^{\theta_E/T}}{(e^{\theta_E/T} - 1)^2}$$

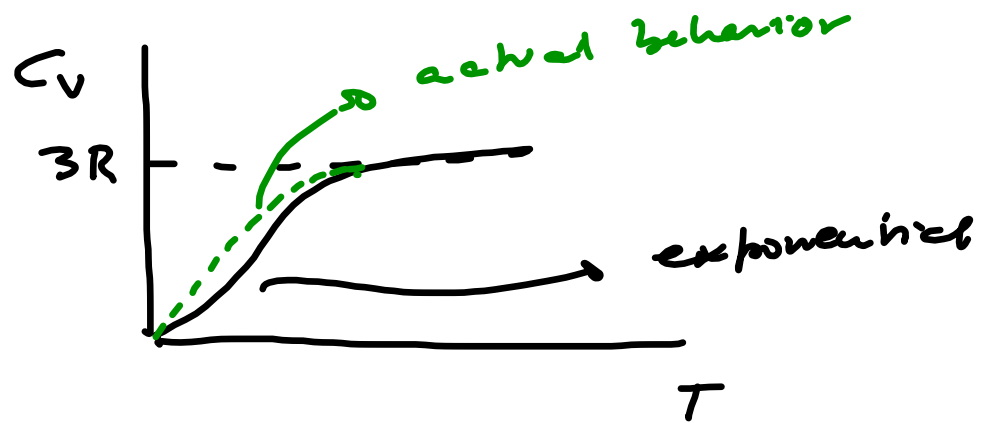
For $\theta_E \ll T$ (means high T)

$$c_v = 3R \left(\frac{\theta_E}{T} \right)^2 \frac{1}{\left(1 - \frac{\theta_E}{T} + \dots \right)^2} \cong 3R \quad \text{classical result.}$$

For $\theta_E \gg T$ (low T)

$$c_v = 3R \left(\frac{\theta_E}{T} \right)^2 e^{-\theta_E/T}$$

it goes to zero
with $T \rightarrow 0$ as
expected.

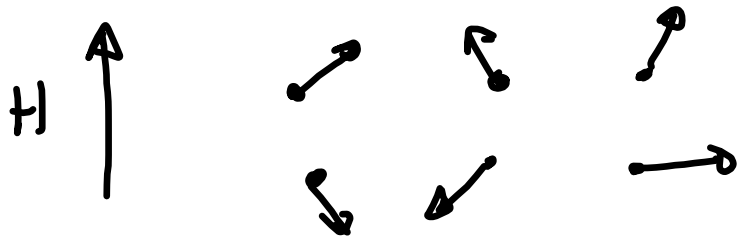


In real
crystals $C_v \propto T^3$
not exponentially.

This issue was
solved by Debye
by assuming different
frequencies for the
oscillators.

Paramagnetism

Consider N particles with arbitrary spin J in a magnetic field $\vec{H} = (0, 0, H)$.



N non-interacting
"spins".

$\vec{\mu}$: magnetic moment.

$$\mathcal{E} = -\vec{\mu} \cdot \vec{H}$$

magnetic energy of each atom.

$$\vec{\mu} = g \mu_B \vec{J}$$

$$\mu_B = \frac{e \hbar}{2 m c}$$

Bohr's magneton
 m : electron mass
 g : Landé factor ~ 1 .

$$\mathcal{E} = -g\mu_0 \vec{J} \cdot \vec{H} \equiv -g\mu_0 J_z H$$

$$J_z = m \quad \text{with} \quad -J \leq m \leq J$$

$2J+1$ values
of m .

$$\mathcal{E}_m = -g\mu_0 m H$$

are the
possible
magnetic
energies of
each atom.

If $J=3$
 $m = -3, -2, -1, 0, 1, 2, 3$.

In the canonical formalism

$$P_m \propto e^{-\beta \mathcal{E}_m} = e^{\beta \overbrace{g\mu_0 m}^{\mu_z} H}$$

Then we can find

$$\langle \mu_z \rangle = \frac{\sum_{m=-J}^J e^{\beta g \mu_0 H m} (g \mu_0 m)}{\sum_{m=-J}^J e^{\beta g \mu_0 H m}} = \frac{1}{\beta} \frac{\partial \ln Z_a}{\partial H} \quad (1)$$

$$\eta = g \mu_0 H \beta = \frac{g \mu_0 H}{kT} \quad (3)$$

Define

$$Z_a = \sum_{m=-J}^J e^{\beta g \mu_0 H m} = \sum_{m=-J}^J e^{\eta m} = \underbrace{\sum_{m=-J}^J e^{\eta m}}_{\text{geometric series}} = \frac{e^{-\eta J} - e^{\eta(J+1)}}{1 - e^{\eta}} = \frac{e^{-\eta(J+\frac{1}{2})} - e^{\eta(J+\frac{1}{2})}}{e^{-\eta/2} - e^{\eta/2}} = \frac{\sinh[(J+\frac{1}{2})\eta]}{\sinh \eta/2} \quad (2)$$

partition function for one single atom

Plugging (3) in (2) and (2) in (1), we find that

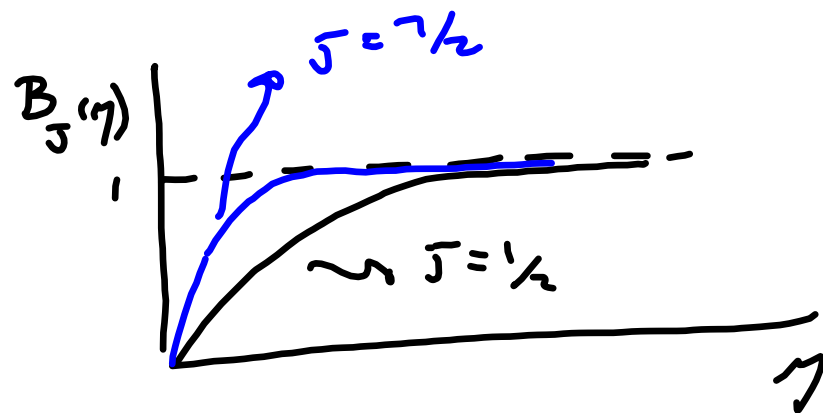
$$\begin{aligned}
 \langle \mu_z \rangle &= \frac{1}{\beta} \frac{\partial \ln Z_a}{\partial H} = \frac{1}{\beta} \frac{\partial \ln Z_a}{\partial \gamma} \frac{\partial \gamma}{\partial H} = \\
 &= \frac{g \mu_0}{kT} kT \left[\frac{(J+\frac{1}{2}) \cosh (J+\frac{1}{2}) \gamma}{\sinh (J+\frac{1}{2}) \gamma} - \frac{\frac{1}{2} \cosh \gamma/2}{\sinh \gamma/2} \right] = \\
 &= g \mu_0 J \frac{1}{J} \left[(J+\frac{1}{2}) \coth (J+\frac{1}{2}) \gamma - \frac{1}{2} \coth \gamma/2 \right] \\
 \ln Z_a &= \ln \sinh (J+\frac{1}{2}) \gamma - \ln \sinh \gamma/2
 \end{aligned}$$

$$\langle \mu_z \rangle = g \mu_0 J B_J(\gamma)$$

$B_J(\gamma)$: Brillouin function.

Let's plot B_J vs η :

$$\eta = \frac{g \mu_B H}{k_B T}$$



For η large \Rightarrow low T

$$B_J \rightarrow 1$$

For η small \Rightarrow large T

$$B_J \approx \frac{(J+1)}{3} \eta$$

For N_0 atoms: $Z = Z_a^{N_0}$ and

$$\langle M_z \rangle = N_0 \langle \mu_z \rangle = N_0 \mu_B g J B_J(\eta)$$

$$\langle M_z \rangle = N_0 \mu_0 g J B_J(\eta)$$

Behavior of $\langle M_z \rangle$ with T :

For $\eta \ll 1$ (large T)

magnetic susceptibility.

$$\langle M_z \rangle \propto \eta \propto \frac{H}{T} \quad \text{then} \quad \langle M_z \rangle = \chi H$$

Replacing $\langle M_z \rangle = \frac{N_0 g^2 \mu_0^2 J(J+1) H}{3 k T}$

$$\chi = \frac{N_0 g^2 \mu_0^2 J(J+1)}{3 k T} \quad \text{then} \quad \chi \propto T^{-1}$$

Curie's law.

For low T $y \gg 1$ $\langle M_z \rangle \approx N_0 g \mu_B J$

$\langle M_z \rangle \rightarrow N_0 g \mu_B J$ (total magnetization).

We see that as a function of temperature at fix H , the system goes from totally disordered with $\langle M_z \rangle = 0$ to totally magnetized as $T \rightarrow 0$. This means that all the spins are aligned with \vec{H} .

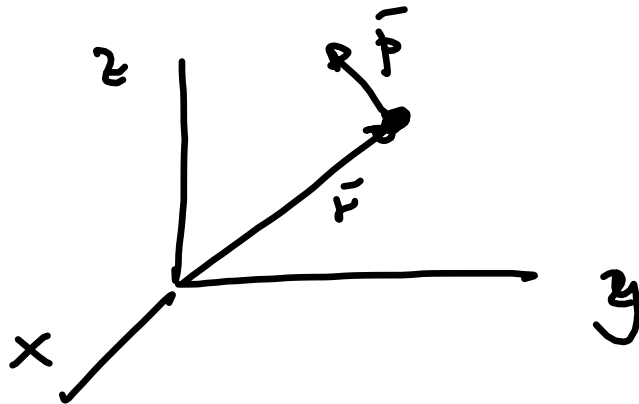
Kinetic Theory of Dilute Gases in Equilibrium.

- Ideal gas
 - Microstates defined by $\{\bar{p}_i\} \{\bar{q}_i\}$ $6N$ coordinates.
 - Macrostates defined by $\{P, E, T, N\}$
- there are many more microstates than
macrostates \therefore many microstates fit into
one macrostate.

$$\mathcal{E} = \frac{\bar{p}^2}{2m} + \mathcal{E}_{\text{internal}}$$

\int
 classical
 kinetic energy
 at high T
 and low density

\int internal degrees of
 freedom (quantum
 mechanical)
 but $\mathcal{E} \neq \mathcal{E}(\bar{p})$



one particle
in the gas.

$P_s(\bar{r}, \bar{p}) d^3\bar{r} d^3\bar{p}$: probability that one molecule is in state s and has momentum between \bar{p} and $\bar{p} + d\bar{p}$ and is located between \bar{r} and $\bar{r} + d\bar{r}$.

$$P_s(\bar{r}, \bar{p}) d^3\bar{r} d^3\bar{p} \propto e^{-\beta \left[\frac{p^2}{2m} + \epsilon_s \right]} d^3\bar{r} d^3\bar{p} \quad \text{canon-ical}$$

$$\propto e^{-\beta \frac{p^2}{2m}} e^{-\beta \epsilon_s} d^3\bar{r} d^3\bar{p}$$

If we do not care about the state s of the particle:

$$P(\bar{r}, \bar{p}) d^3\bar{r} d^3\bar{p} \propto e^{-\beta \frac{p^2}{2m}} d^3\bar{r} d^3\bar{p} \underbrace{\sum_s e^{-\beta \epsilon_s}}_C \quad \text{(constant)}$$

Then we can say that there are

$$N P(\bar{r}, \bar{p}) d^3 \bar{r} d^3 \bar{p} \quad (\text{average volume}).$$

molecules within $\bar{p} - \bar{p} + d\bar{p}$ and $\bar{r} - \bar{r} + d\bar{r}$