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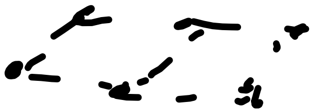
Last time:

Properties of solids.

Interacting atoms.



$\xi_{i\alpha} = x_{i\alpha} - x^0_{i\alpha}$ 3N coordinates

$$H = V_0 + \frac{1}{2} \sum_{i,\alpha} m_i \dot{\xi}_{i\alpha}^2 + \frac{1}{2} \sum_{i\alpha, j\gamma} A_{i\alpha, j\gamma} \xi_{i\alpha} \xi_{j\gamma}$$

$\Downarrow$ change of basis to q_r (generalized coordinates),

$$H = V_0 + \frac{1}{2} \sum_{r=1}^{3N} \left(\dot{q}_r^2 + \omega_r^2 q_r^2 \right)$$

We see that H is written in terms of $3N$ Hamiltonians $\mathcal{H}_r$

$$\mathcal{H}_r = \frac{1}{2}\left(\dot{q}_r^2 + \omega_r^2 q_r^2\right)$$ 1D harmonic oscillator.

We know that

$$\varepsilon_r = \left(n_r + \frac{1}{2}\right)\hbar\omega_r \qquad n_r = 0, 1, \ldots.$$

The state of the system is given by $3N$ integers n_r : $\{n_1, n_2, \ldots n_{3N}\}$

We can associate the occupation numbers n_r for each oscillator with a number of "quasiparticles" like we did with photons that are the quasiparticles associated to electromagnetic waves. The quasiparticles associated to lattice vibrations or sound waves are called phonons.

Then

$$E_{n_1, n_2, \ldots, n_{3N}} = V_0 + \sum_{r=1}^{3N} \left(n_r + \frac{1}{2}\right) \hbar \omega_r =$$

$$= -N\eta + \sum_{r=1}^{3N} n_r \hbar \omega_r$$

Where

$$-N\eta = V_0 + \frac{1}{2}\sum_r \hbar\omega_r$$

energy of the system with all $n_r = 0$.

η represents the binding energy per atom when they are at rest at $T=0$ - Notice that it is not just V_0 but it contains also the $T=0$ energy of the oscillators.

Partition function:

Phonons are bosons since there are no restrictions on the value of n_r.

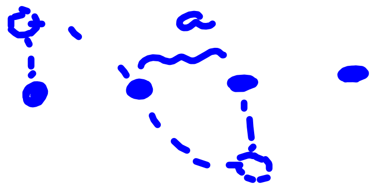
$$Z = \sum_{n_1, n_2, \dots n_{3N}} e^{-\beta(-N\mu + n_1 \hbar\omega_1 + \dots + n_{3N}\hbar\omega_{3N})} =$$

$$= e^{+\beta N\mu} \underbrace{\left(\sum_{n_1=0}^{\infty} e^{-\beta n_1 \hbar\omega_1}\right)}_{\frac{1}{1-e^{-\beta\hbar\omega_1}}} \cdots \underbrace{\left(\sum_{n_{3N}=0}^{\infty} e^{-\beta n_{3N}\hbar\omega_{3N}}\right)}_{\frac{1}{1-e^{-\beta\hbar\omega_{3N}}}}$$

$$Z = e^{\beta N \eta} \prod_{r=1}^{3N} \frac{1}{1-e^{-\beta\hbar\omega_r}}$$

$$\ln Z = \beta N \eta - \sum_{r=1}^{3N} \ln\left(1-e^{-\beta\hbar\omega_r}\right)$$

$$\omega_{max} = \frac{\pi}{a} = \frac{\pi}{R_0}$$



smallest $\lambda = \frac{2\pi}{\omega}$

$\lambda_{min} = 2a$

$\omega_{max} = \frac{\pi}{a}$

Experimental shape of density of normal frequencies

If we assume that there are many ω_r's in an interval $d\omega$ then we can write

$$\ln Z = \beta N \eta - \int_0^\infty \ln\left(1 - e^{-\beta\hbar\omega}\right) \sigma(\omega)\, d\omega$$

$$\therefore \quad \bar{E} = -\frac{\partial \ln Z}{\partial \beta} = -N\eta + \int_0^\infty \frac{\hbar\omega}{e^{\beta\hbar\omega} - 1}\, \sigma(\omega)\, d\omega$$

$$C_V = \left.\frac{\partial \bar{E}}{\partial T}\right|_V = -k\beta^2 \left.\frac{\partial \bar{E}}{\partial \beta}\right|_V = k \int_0^\infty \frac{e^{\beta\hbar\omega} (\beta\hbar\omega)^2 \sigma(\omega)\, d\omega}{\left(e^{\beta\hbar\omega} - 1\right)^2}$$

Hardest part of the problem is to find $\sigma(\omega)$.

First consider some limits:

$\frac{\hbar\omega}{kT}$ defines the temperature regime.

If $\frac{\hbar\omega}{kT} << 1 \Rightarrow \hbar\omega << kT$ and T is large.

Then $\frac{\hbar\omega_{max}}{kT} << 1$ Notice that $\sigma(\omega) = 0$ for $\omega > \omega_{max}$

and $\frac{\hbar\omega_r}{kT} << 1 \quad \forall r$

$\therefore e^{\beta\hbar\omega} \simeq 1 + \beta\hbar\omega + \ldots$

Then

$$c_V = k \int_0^\infty \frac{e^{\beta\hbar\omega}(\beta\hbar\omega)^2}{(e^{\beta\hbar\omega}-1)^2}\,\sigma(\omega)\,d\omega =$$

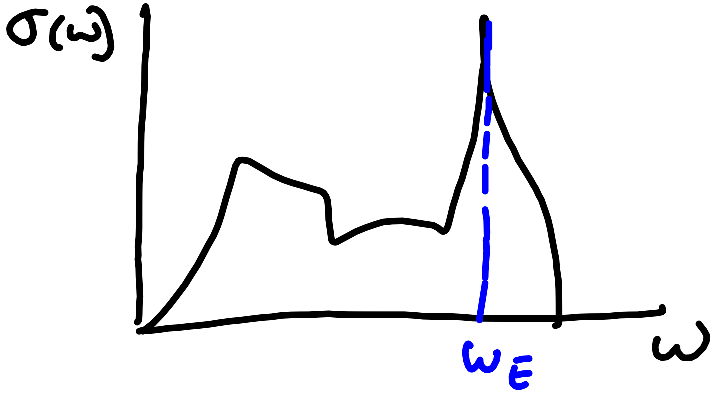
$$\cancel{e^{\beta\hbar\omega}} = 1 + \beta\hbar\omega$$

$$\cong k \int_0^\infty \sigma(\omega)\,d\omega = k3N$$

Dulong and Petit law for c_V of a solid at room temperature

For $\frac{\hbar\omega}{kT} \gg 1$ (low T) we need to make an assumption about $\sigma(\omega)$.

1) We saw time ago Einstein's assumption:



$\sigma_E(\omega) = \delta(\omega-\omega_E)$

$$c_V = k\int_0^\infty \frac{e^{\beta\hbar\omega}}{(e^{\beta\hbar\omega}-1)^2}(\beta\hbar\omega)^2\,\delta(\omega-\omega_E)\,d\omega =$$

$$= \frac{k\,e^{\beta\hbar\omega_E}}{(e^{\beta\hbar\omega_E}-1)^2}(\beta\hbar\omega_E)^2 \xrightarrow[\frac{\hbar\omega_E}{kT}\gg 1]{} k\,e^{-\beta\hbar\omega_E}(\beta\hbar\omega_E)^2$$

goes to zero like an exponential.

But experimentally it is known that

$c_V \propto T^3$

To improve the agreement we will use

2) Debye's approximation.

He viewed the solid as a continuous ellastic medium. But with the assumption that there is a minimum λ that can propagate due to the finite separation between atoms.

$\sigma_c(\omega)\,d\omega$ is calculated in the same way as for photons. We found the number of modes per unit frequency for a particle with energy $\hbar\omega$ in a box with periodic boundary conditions. For photons we multiplied that number by 2 to account for the 2 polarizations. Now for phonons we need to multiply by 3 since there are 3 possible propagation directions.

$$\sigma_c(\omega)\,d\omega = 3\,\frac{V}{2\pi^2 c_s^3}\,\omega^2\,d\omega$$

If $c_\ell \neq c_t$ then $\frac{1}{c_s^3} = \frac{1}{c_\ell^3} + \frac{2}{c_t^3}$

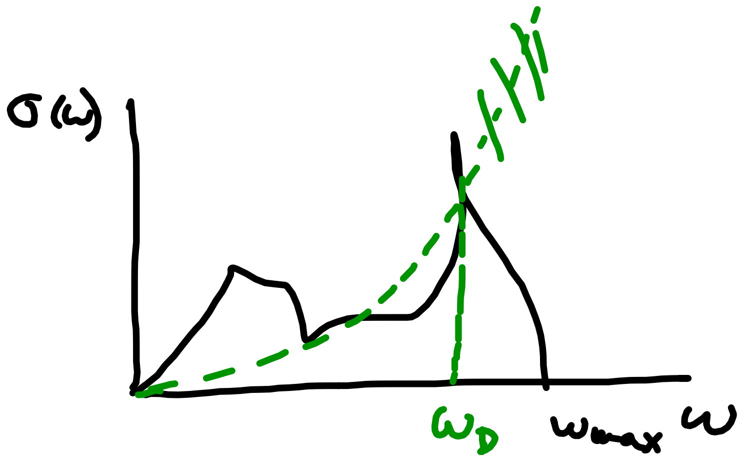
c_ℓ: longitudinal speed of sound

c_t: transversal " " ".

Debye's approximation:

$$\sigma_D(\omega) = \begin{cases} \sigma_c(\omega) & \text{for } \omega \leq \omega_D \\ 0 & \text{for } \omega > \omega_D \end{cases}$$

ω_D: Debye's Frequency



ω_D is obtained from the normalization condition:

$$3N = \int_0^\infty \sigma_D(\omega)\,d\omega = \int_0^{\omega_D} \sigma_c(\omega)\,d\omega = \frac{3V}{2\pi^2 c_s^3}\int_0^{\omega_D} \omega^2\,d\omega =$$

$$= \frac{V}{2\pi^2 c_s^3}\,\omega_D^3 \Rightarrow \boxed{\omega_D = c_s\left(6\pi^2 \frac{N}{V}\right)^{1/3}}$$

Now we can calculate c_V for $\hbar\omega >> kT$

$$C_V = k\int_0^{\omega_D} \frac{e^{\beta\hbar\omega}(\beta\hbar\omega)^2\, 3V\omega^2\, d\omega}{2\pi^2 c_s^3\,(e^{\beta\hbar\omega}-1)^2}$$

Define $x = \beta\hbar\omega$

$$C_V = \frac{3Vk}{2\pi^2(c_s\beta\hbar)^3}\int_0^{\beta\hbar\omega_D}\frac{e^x}{(e^x-1)^2}\,x^4\,dx =$$

$$y = \frac{\hbar\omega_D}{kT}$$

$$= 3Nk\,\frac{3k^3T^3}{\hbar^3\omega_D^3}\int_0^{\frac{\hbar\omega_D}{kT}}\frac{e^x}{(e^x-1)^2}\,x^4\,dx =$$

$$C_V = 3Nk\,\frac{3}{y^3}\int_0^y \frac{e^x}{(e^x-1)^2}\,x^4\,dx =$$

$$= 3Nk\,f_D\left(\frac{\hbar\omega_D}{kT}\right) = 3Nk\,f_D\left(\frac{\theta_D}{T}\right)$$

Debye's function:

$$f_D(y) = \frac{3}{y^3}\int_0^y \frac{e^x}{(e^x-1)^2}\,x^4\,dx$$

material dependent.

$$y = \frac{\hbar\omega_D}{kT} = \frac{\theta_D}{T}$$

with $\boxed{\theta_D = \frac{\hbar\omega_D}{k}}$

Debye's temperature.

Limits of $J_D(y)$:

If $y << 1 \Rightarrow (\theta_D << T)$ high T

$e^x \approx 1 + x$

$$\frac{3}{y^3} \int_0^y \frac{e^x}{(e^x - 1)^2} x^4 \, dx = \frac{3}{y^3} \int_0^y \frac{1}{(1 + x - 1)^2} x^4 \, dx =$$

$$= \frac{3}{y^3} \int_0^y x^2 \, dx = \frac{1}{y^3} x^3 \Big|_0^y = 1$$

Then for $\Theta_D << T$

$C_V = 3NK$ (Dulong and Petit)

For $y >> 1$ $(\Theta_D >> T) \Rightarrow$ low T

$$\frac{3}{y^3} \underbrace{\int_0^{\infty} \frac{e^x \; x^4}{(e^x - 1)^2} dx}_{\frac{4\pi^4}{5}} =$$

We can integrate up to ∞ because $e^{-x} << 1$ for large w due to large β.

$$\frac{4\pi^4}{5} \frac{3}{\Theta_D^3} T^3 \propto T^3$$

In agreement with the experiments.

Non - ideal classical gas :

Note : we will follow Reif but after that we will use the cluster expansion method in Kardar's book.

Assume N identical particles , m , V , T

T is high.

$\frac{N}{V} = n \sim$ small

} However, T is not as high or/and n is not so small that the ideal gas eq. of state can be used.

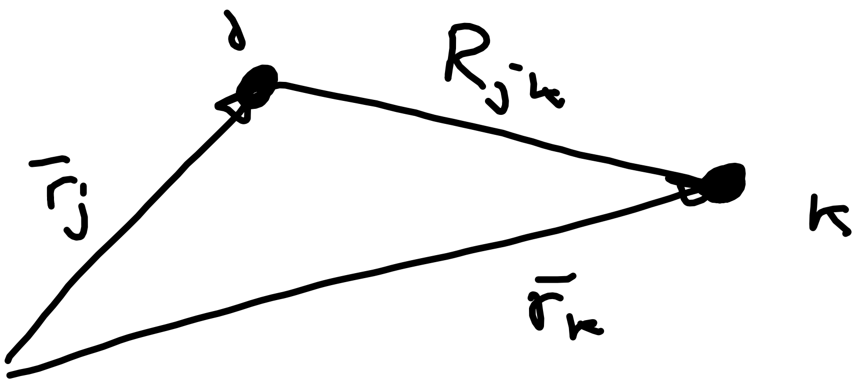
Now we will have to consider the interaction U between molecules that we neglected when we studied the ideal gas.

$$\mathcal{H} = K + U$$

$$K = \frac{1}{2m} \sum_{j=1}^{N} \vec{p}_j^{\,2}$$

classical limit of the quantum case.

We will consider that only the interactions between 2 particles are relevant.

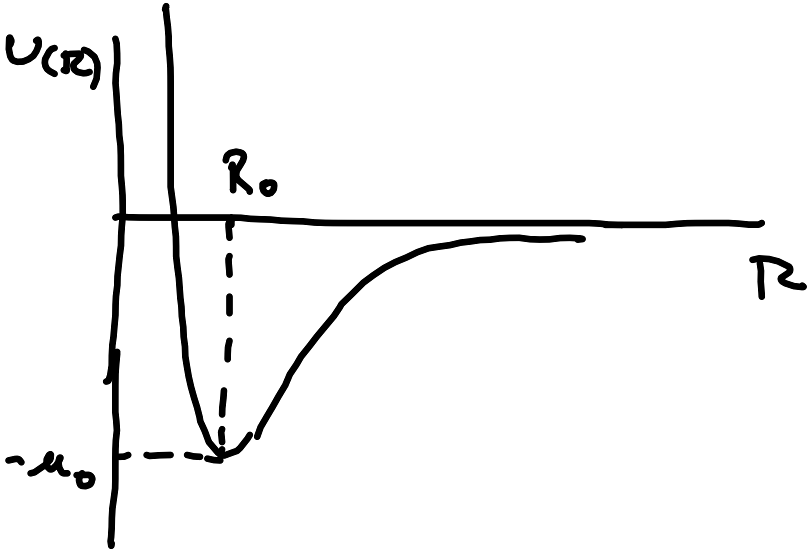


$$R_{jk} = |\bar{r}_j - \bar{r}_k|$$

$$u_{jk} = u(R_{jk})$$

$$U = u_{12} + u_{13} + \ldots + u_{1N} + u_{23} + u_{24} + \ldots =$$

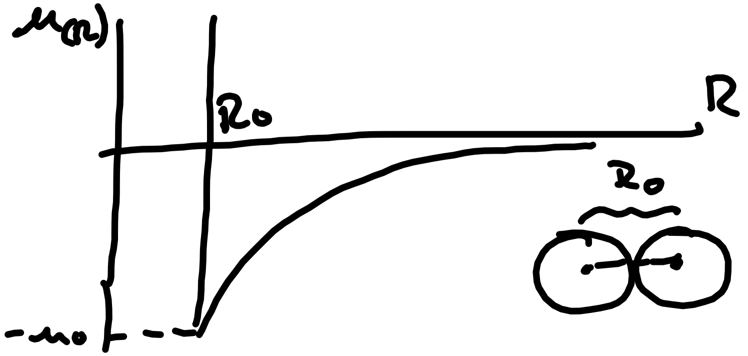
$$= \sum_{j=1}^{N} \sum_{\substack{k=2 \\ j<k}}^{N} u_{jk} = \frac{1}{2} \sum_{j=1}^{N} \sum_{\substack{k=1 \\ j \neq k}}^{N} u_{jk}$$



Lennard-Jones potential

$$u(R) = u_0 \left[\left(\frac{R_0}{R}\right)^{12} - 2\left(\frac{R_0}{R}\right)^{6} \right]$$

It can be simplified (van der Waals):



molecules in-fu finite radius

$R_0/2$.

$$u(R) = \begin{cases} \infty & \text{for } R < R_0 \\ -u_0 \left(\frac{R_0}{R}\right)^{s} & R \geq R_0 \end{cases}$$

$s > 3 \quad s = 6$