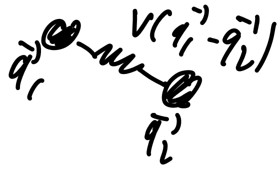
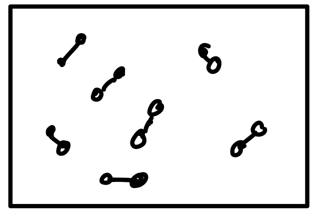
Chapter 5: Breakdown of classical statistical mechanics

Following closely Chapter 6 of Kardar

5.1) Heat capacity of dilute diatomic gases

E.g. O_2 $\leftrightarrow$ 



Partition function

$$Z(V,T,N)=\frac{Z_1^N}{N!}\quad;\quad Z_1=\int\frac{d^3\vec{p}_1\,d^3\vec{p}_2\,d^3\vec{q}_1\,d^3\vec{q}_2}{h^6}\,e^{-\beta\left[\frac{\vec{p}_1^{\,2}}{2m}+\frac{\vec{p}_2^{\,2}}{2m}+V(\vec{q}_1-\vec{q}_2)\right]}$$

Change of coordinates:

centre of mass $\vec{Q}=\frac{\vec{q}_1+\vec{q}_2}{2}$; $\vec{\pi}=\vec{p}_1+\vec{p}_2$; $M=2m$

& relative displacement $\vec{q}=\vec{q}_1-\vec{q}_2$; $\vec{p}=\frac{\vec{p}_1-\vec{p}_2}{2}$; $\mu=\frac{m}{2}$

such that $d\vec{q}_1\,d\vec{q}_2\,d\vec{p}_1\,d\vec{p}_2=d\vec{Q}\,d\vec{\pi}\,d\vec{q}\,d\vec{p}$ & $\frac{\vec{p}_1^{\,2}}{2m}+\frac{\vec{p}_2^{\,2}}{2m}=\frac{\vec{\pi}^{\,2}}{2M}+\frac{\vec{p}^{\,2}}{2\mu}$

Proof: Jacobian in 1d

$$\begin{array}{c|cccc|}
 & q_1 & q_2 & p_1 & p_2 \\
Q & 1/2 & 1/2 & 0 & 0 \\
q & 1 & -1 & 0 & 0 \\
\pi & 0 & 0 & 1 & 1 \\
p & 0 & 0 & 1/2 & -1/2
\end{array}=\left|-\tfrac{1}{2}-\tfrac{1}{2}\right|\times\left|-\tfrac{1}{2}-\tfrac{1}{2}\right|=1$$

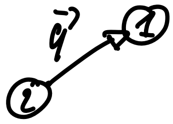
$$H=\frac{\vec{p}_1^{\,2}+\vec{p}_2^{\,2}}{2m}=\frac{(\vec{p}_1-\vec{p}_2)^2+(\vec{p}_1+\vec{p}_2)^2}{4m}=\frac{\vec{p}^{\,2}}{m}+\frac{\vec{\pi}^2}{4m}=\frac{\vec{p}^{\,2}}{2\mu}+\frac{\vec{\pi}^2}{2M}$$

Sanity check: $\dot{\vec{Q}}=\frac{\partial H}{\partial\vec{\pi}}=\frac{\vec{\pi}}{M}=\frac{\vec{p}_1+\vec{p}_2}{2m}=\frac{1}{2}(\dot{\vec{q}}_1+\dot{\vec{q}}_2)$; $\dot{\vec{q}}=\frac{\partial H}{\partial\vec{p}}=\frac{\vec{p}}{\mu}=\frac{\vec{p}_1-\vec{p}_2}{m}=\dot{\vec{q}}_1-\dot{\vec{q}}_2$

$$\Rightarrow Z_1=\int\frac{d^3\vec{Q}\,d^3\vec{\pi}}{h^3}\,e^{-\beta\frac{\vec{\pi}^2}{2M}}\int\frac{d^3\vec{q}\,d^3p}{h^3}\,e^{-\beta\left[\frac{\vec{p}^{\,2}}{2\mu}+V(\vec{q})\right]}$$

②

Spherical coordinates: $V(\vec q) = V(|\vec q|)$



$\vec q \to q, \theta, \varphi$ & $\vec p \to p, \vec L$ $\qquad \frac{\vec p^{\,2}}{2\mu} \to \frac{p^2}{2\mu} + \frac{\vec L^2}{2I}$

Rigid binding potential: $|\vec q| = q^* = \arg\min_q V(q)$

Small oscillations around q^*: $q = q^* + \tilde q$; $V(q) = V(q^*) + \underbrace{V'(q^*)}_{=0}\tilde q + \frac{1}{2}\underbrace{V''(q^*)}_{\equiv \mu\omega^2}\tilde q^2$

ω is the frequency of oscillations

$$Z_1 = \frac{V e^{-\beta V(q^*)}}{\Lambda_M^3} \underbrace{\int \frac{d\tilde q\, dp}{h} e^{-\beta\left[\frac{p^2}{2\mu} + \frac{1}{2}\mu\omega^2 \tilde q^2\right]}}_{\text{vibration of molecules}} \underbrace{\int \frac{d\Omega\, d^2\vec L}{h^2} e^{-\beta\frac{\vec L^2}{2I}}}_{\text{rotations}} \; ; \; \Lambda_M = \sqrt{\frac{h^2}{2\pi M k_B T}}$$

rigid molecule: $I = \mu q^{*2}$ constant & $\int_{-q^*}^{\infty} d\tilde q\, e^{-\beta\frac{\mu}{2}\omega^2\tilde q^2} \sim \int_{-\infty}^{+\infty} d\tilde q\, e^{-\beta\frac{\mu}{2}\omega^2\tilde q^2}$

$$\Rightarrow Z_1 = \underbrace{\frac{\overset{\text{position}}{V}}{\underset{\text{kinetic NRG of translation}}{\Lambda_M^3}}}_{\text{translation}} \underbrace{\underbrace{\sqrt{\frac{2\pi\mu k_B T}{h^2}}}_{\text{kinetic NRG of vibrations}} \; e^{-\beta V(q^*)} \underbrace{\sqrt{\frac{2\pi k_B T}{\mu\omega^2}}}_{\text{potential NRG of vibrations}}}_{\text{vibration}} \underbrace{\underbrace{4\pi}_{\text{position}} \underbrace{\frac{1}{\Lambda_I^2}}_{\text{kinetic NRG}}}_{\text{rotations}} \; (*) ; \; \Lambda_I = \sqrt{\frac{h^2}{2\pi I k_B T}}$$

Comment: μ cancels out from the vibrational partition function. Only ω matters.

Heat capacity:

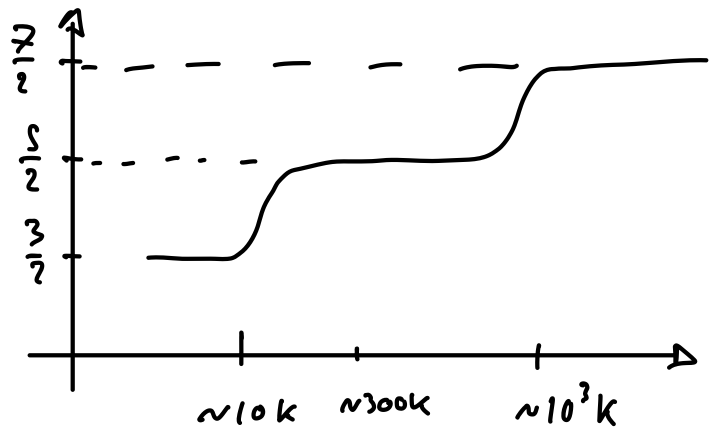
$$\langle E_1 \rangle = -\partial_\beta \ln Z_1 = V(q^*) + \underbrace{\frac{3}{2} k_B T}_{\text{center of mass}} + \underbrace{\frac{k_B T}{2} + \frac{k_B T}{2}}_{\text{vibration}} + \underbrace{k_B T}_{\text{rotation}} = V(q^*) + \frac{7}{2} k_B T$$

$$\langle E_{tot} \rangle = N\, V(q^*) + \frac{7}{2} N k_B T$$

$$C_V = \frac{\partial \langle E_{tot} \rangle}{\partial T} = \frac{7}{2} N k_B$$

At room temperature, we measure $C_V \simeq \frac{5}{2} N k_B$

Experiments



$\Rightarrow$ Not consistent with classical stat mech

1900: Planck "let's quantize the energy of light"

1905: Einstein "let's do the same for matter!"

Quantization of vibration

$$\int dE\, e^{-\beta E} \rightarrow \sum_n e^{-\beta E_n}$$

$$H^{vib}_{classical} = \frac{p^2}{2\mu} + \frac{1}{2} \mu \omega \tilde{q}^2 \Rightarrow E^{vib}_{QM} \in \{ \hbar\omega (n + \tfrac{1}{2}),\, n \in \mathbb{Z}^+ \}$$

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

Sanity check: high temperature

$$Z^{vib}_{QM} \underset{\beta \to 0}{\sim} \frac{k_B T}{\hbar \omega} = \frac{2\pi k_B T}{\omega} \text{ as in } (*)$$

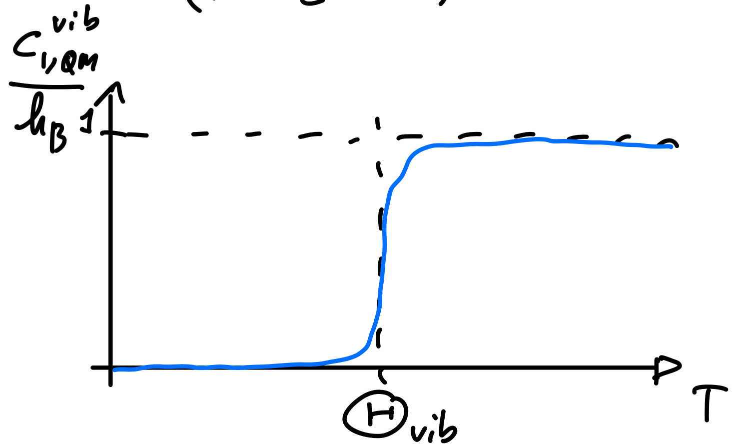
$\Rightarrow$ We recover classical stat mech when $T \gg \Theta_{vib} = \frac{\hbar \omega}{k_B} \simeq 10^3\, K$

Heat capacity:

$$E^{vib}_{1,QM} = -\partial_\beta \ln z = \frac{\hbar\omega}{2} + \frac{\hbar\omega\, e^{-\beta\hbar\omega}}{1-e^{-\beta\hbar\omega}}$$

$$C^{vib}_{1,QM} = \frac{dE^{vib}_{1,QM}}{dT} = \frac{d\beta}{dT}\frac{\partial E^{vib}_{1,QM}}{\partial\beta} = -\frac{\hbar\omega}{k_B T^2}\,\frac{-\hbar\omega e^{-\beta\hbar\omega}(1-e^{-\beta\hbar\omega}) - e^{-\beta\hbar\omega}\hbar\omega e^{-\beta\hbar\omega}}{(1-e^{-\beta\hbar\omega})^2}$$

$$\boxed{C^{vib}_{1,QM} = \frac{\hbar^2\omega^2}{k_B T^2}\,\frac{e^{-\beta\hbar\omega}}{(1-e^{-\beta\hbar\omega})^2}}$$



This explains what happens at $T \simeq 300°K$ ($C_V = \frac{5}{2} N k_B$) but not at low T.

Quantization of rotation

$$H^{rot}_{class} = \frac{L^2}{2I} \longrightarrow E^{rot}_{QM} = \frac{\hbar^2}{2I}\ell(\ell+1) \quad \text{with } \ell = 0, 1, \dots$$

with degeneracy $g = 2\ell+1$

$$Z^{rot}_{QM} = \sum_{\ell=0}^{\infty} g(\ell)\, e^{-\beta E_\ell} = \sum_{\ell=0}^{\infty} (2\ell+1)\, e^{-\beta\frac{\hbar^2}{2I}\ell(\ell+1)}$$

High temperature: $T << \frac{\hbar^2}{2Ik_B} \sim 1\text{-}10\,K$; $\varepsilon = \frac{\hbar^2}{2Ik_BT} << 1$

$$Z^R_{QM} = \frac{1}{\varepsilon}\sum_{\ell=0}^{\infty} \underbrace{(2\ell+1)\varepsilon}_{dx_\ell}\, e^{-x(\ell)} \quad , \; x(\ell) = \ell(\ell+1)\varepsilon \text{ so that } dx \simeq (2\ell+1)\varepsilon \underbrace{d\ell}_{1}$$

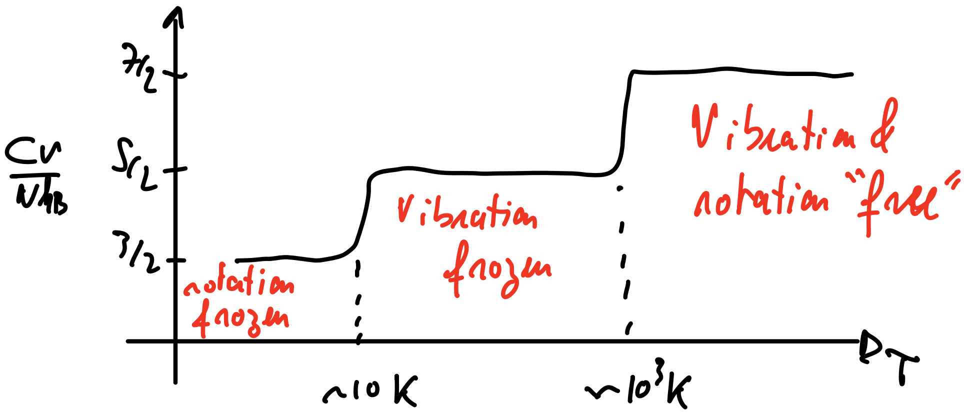
$$\sim \frac{1}{\varepsilon}\int_0^\infty dx\, e^{-x} = \frac{1}{\varepsilon} = \frac{2Ik_BT}{\hbar^2} \quad \text{as in } (*)$$

Comment: To do rigorously, one should use Abel–Plana formula.
See Pset 8, exercise 1.

Low temperature $Z^{n}_{QM} \simeq 1 + 3\, e^{-\beta \frac{\hbar^2}{I}} \Rightarrow \langle E \rangle = -\partial_\beta \ln Z \simeq \frac{3\hbar^2}{I} e^{-\beta \frac{\hbar^2}{I}}$

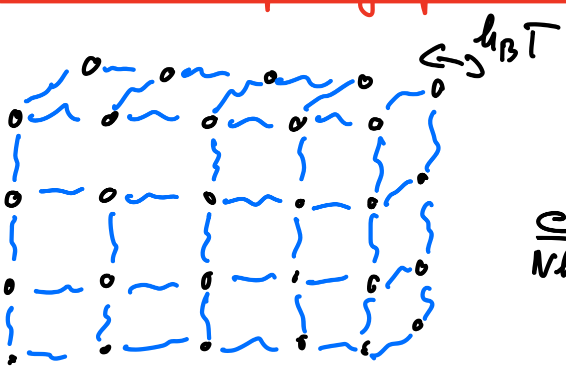
$$C_V = \frac{d\langle E\rangle}{dT} = \frac{3\hbar^4}{k_B T^2 I^2} e^{-\beta \frac{\hbar^2}{I^2}} \Rightarrow \text{exponentially suppressed}$$

Summary



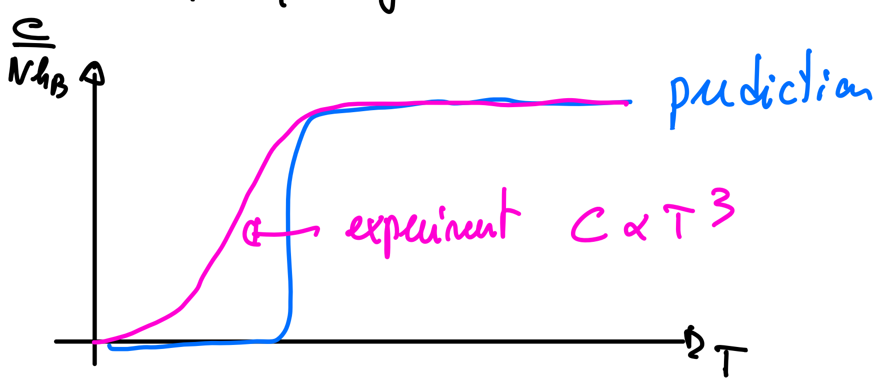
At this stage, it's quite natural to expect that quantization of energy will always suppress C_V exponentially at small T.

5.2) Heat capacity of solids



N atoms

Naively, we expect $3N$ harmonic oscillators at frequency ω.



Wrong image: the oscillators are not independent!

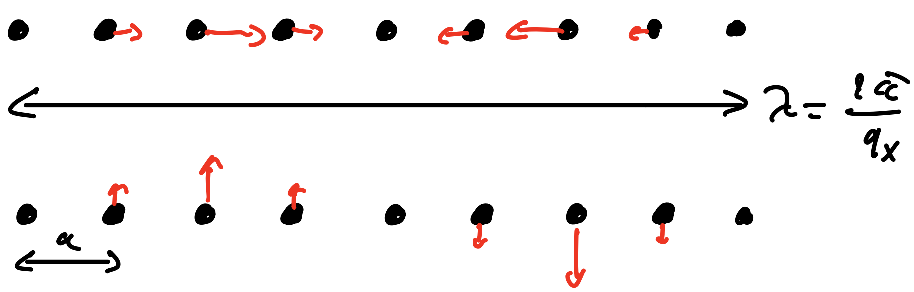
costly in energy due to large compression & extension

less costly due to small compression & extension

The larger the wavelength λ of the deformation, the cheaper in energy.

(I) For small deformations, the deformations can be considered as superposition of independent harmonic oscillators of frequency $\omega(\vec{q})$, where $\vec{q}$ is the wavevector, such that $\omega(\vec{q}) \xrightarrow[|\vec{q}| \to 0]{} 0$.

(II) A wave along $\vec{q} = q_x \hat{x}$ can modulate displacements along $\hat{x}, \hat{y}, \hat{z}$ $\Rightarrow$ three polarizations for the wave



(III) Symmetry $\Rightarrow$ $E(\vec{q}) = E(-\vec{q}) \Rightarrow E \underset{q \to 0}{\propto} \vec{q}^{\,2} u_{\vec{q}}^2$, with $u_{\vec{q}}$ the amplitude of the mode $\vec{q}$

Since $E \propto \omega^2$ for a harmonic oscillator, $\omega(\vec{q}) \underset{q \to 0}{\propto} |\vec{q}| \Rightarrow \omega(\vec{q}) = v|\vec{q}|$

where v is the speed of sound in the solid.