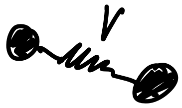
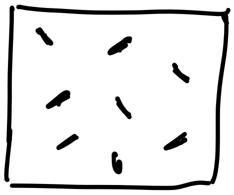
Chapter 5: Breakdown of classical statistical mechanics

See chapter 6 of Kardar for a more detailed presentation

5.1) Heat capacity of dilute diatomic gases

E.g. O_2 



dilute gas of rod-like molecules

Partition function:

$$Z(V,T,N) = \frac{z_1^N}{N!} \; ; \; z_1 = \int \frac{d^3\vec{p}_1 d^3\vec{q}_1 d^3\vec{p}_2 d^3\vec{q}_2}{h^6} e^{-\beta\left[\frac{\vec{p}_1^{\,2}}{2m} + \frac{\vec{p}_2^{\,2}}{2m} + V(\vec{q}_1 - \vec{q}_2)\right]}$$

***Change of coordinates** to center of mass $\vec{Q} = \frac{\vec{q}_1+\vec{q}_2}{2} \to$ momentum $\vec{\pi} = \vec{p}_1+\vec{p}_2$, mass $M = 2m$

& relative displacement $\vec{q} = \vec{q}_1 - \vec{q}_2 \to$ momentum $\vec{p} = \frac{1}{2}(\vec{p}_1 - \vec{p}_2)$, mass $\mu = \frac{m}{2}$

such that $d^3\vec{q}_1 d^3\vec{p}_1 d^3\vec{q}_2 d^3\vec{p}_2 = d\vec{Q}\, d\vec{\pi}\, d\vec{q}\, d\vec{p}$ & $K = \frac{\vec{p}_1^{\,2}}{2m} + \frac{\vec{p}_2^{\,2}}{2m} = \frac{\vec{\pi}^{\,2}}{2M} + \frac{\vec{p}^{\,2}}{2\mu}$

Proof:

Jacobian in 1d:

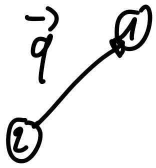
$$\begin{array}{c|cccc|} & q_1 & q_2 & p_1 & p_2 \\ \hline Q & \frac{1}{2} & \frac{1}{2} & 0 & 0 \\ q & 1 & -1 & 0 & 0 \\ \pi & 0 & 0 & 1 & 1 \\ p & 0 & 0 & 1/2 & -1/2 \end{array} = \left|\left(-\tfrac{1}{2}-\tfrac{1}{2}\right) \times \left(-\tfrac{1}{2}-\tfrac{1}{2}\right)\right| = 1$$

$$H = \frac{\vec{p}_1^{\,2}}{2m} + \frac{\vec{p}_2^{\,2}}{2m} = \frac{1}{4m}\Big[\underbrace{(\vec{p}_1-\vec{p}_2)^2}_{4p^2} + \underbrace{(\vec{p}_1+\vec{p}_2)^2}_{\pi^2}\Big] = \frac{\vec{p}^{\,2}}{m} + \frac{\vec{\pi}^{\,2}}{4m} = \frac{\vec{p}^{\,2}}{2\mu} + \frac{\vec{\pi}^{\,2}}{2M}$$

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

$$\Rightarrow z_1 = \int \frac{d^3\vec{Q}\, d^3\vec{\pi}}{h^3} e^{-\beta\frac{\vec{\pi}^{\,2}}{2M}} \cdot \int \frac{d^3\vec{q}\, d^3\vec{p}}{h^3} e^{-\beta\frac{\vec{p}^{\,2}}{2\mu} - \beta V(\vec{q})}$$

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



$\vec q \Rightarrow q, \theta, \varphi$

$\vec p \to p, \vec L$

$\frac{\vec p^{\,2}}{2m} \to \frac{p}{2m} + \frac{\vec L^2}{2I}$

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

Expand $q = q^* + \delta q$; $V(q) = V(q^*) + \underbrace{V'(q^*)}_{=0}\,\delta q + \frac{1}{2}\,\delta q^2\, \underbrace{V''(q^*)}_{\mu\omega^2}$

ω oscillation frequency

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

$$Z_1 = \frac{V}{\Lambda_M^3}\; \overbrace{\sqrt{\frac{2\pi\mu k_B T}{h^2}}\; e^{-\beta V(d^*)} \sqrt{\frac{2\pi k_B T}{\mu\omega^2}}}\; \overbrace{4\pi\,\frac{1}{\Lambda_I^2}} \qquad (*)$$

position

kinetic energy

kinetic energy

position

position

kinetic energy

μ cancels out

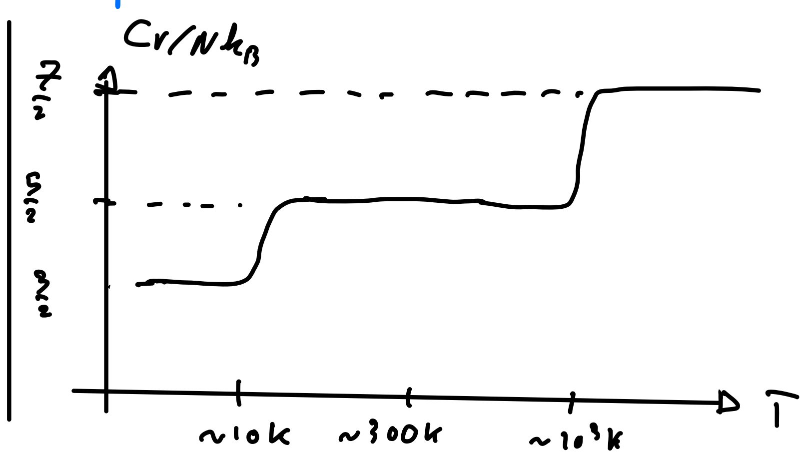
Heat capacity:

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

$$\langle E\rangle = N V(d^*) + \frac{7N}{2}k_B T$$

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

experiments



Measurement at room temperature are **not** consistent with classical statistical mechanics.

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

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

Quantization of vibration $\quad \int dE\, e^{-\beta E} \to \sum_n e^{-\beta E_n}$

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

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

Sanity check: High temperature $\quad \beta \to 0\ Z \to \frac{kT}{\hbar\omega} = \frac{2\pi kT}{h\omega}$ as in (*)

We recover classical stat mech at large T, $T > \Theta = \frac{\hbar\omega}{k_B} \simeq 10^3 K$

[FYI Low temperature $\quad T \to 0;\ \beta \to \infty\ ;\ Z \simeq e^{-\beta\frac{\hbar\omega}{2}}\left(1 + e^{-\beta\hbar\omega} + e^{-2\beta\hbar\omega} + \dots\right)$]

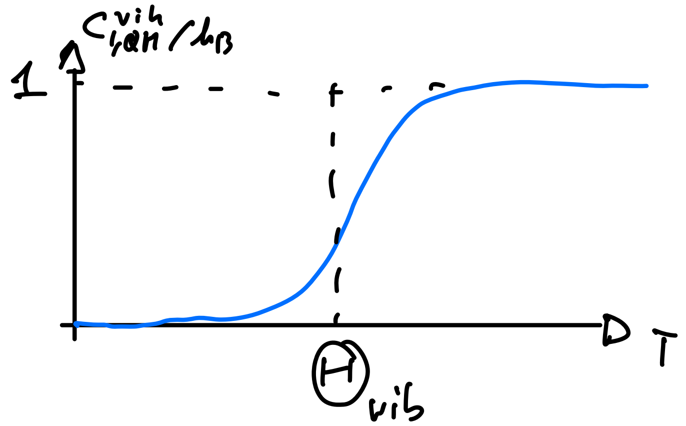
Heat capacity

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

$$C^{vib}_{1,QM} = \frac{dE^{vib}_{1,QM}}{dT} = \frac{d\beta}{dT}\frac{d}{d\beta}\frac{\hbar\omega\, e^{-\beta\hbar\omega}}{1 - e^{-\beta\hbar\omega}}$$

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

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



Interesting! explains that $C_V \simeq \frac{5}{2} N k T$ at $T \simeq 300°K$

But not what happens at low T :-

Quantization of rotation

$$\mathcal{H}^{rot}_{classical} = \frac{L^2}{2I} \rightarrow E^{rot}_{QM} = \frac{\hbar^2}{2I} \ell(\ell+1) \; ; \; \ell = 0, 1, \ldots$$

each level has a degeneracy $g = 2\ell + 1$

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

High temperature limit

$$T < \frac{\hbar^2}{2I k_B} \sim 1 - 10 \text{ K}$$

$$Z^{rot}_{QM} \stackrel{!}{=} \frac{1}{\varepsilon} \sum_{\ell=0}^{\infty} \underbrace{(2\ell+1)\varepsilon}_{dx(\ell)} e^{-\underbrace{\ell(\ell+1)\varepsilon}_{x(\ell)}}$$

when $\varepsilon = \frac{\hbar^2}{2IkT}$ is small

handwaving: $x(\ell) = (\ell^2 + \ell)\varepsilon \; ; \; dx \simeq (2\ell+1)\varepsilon \underbrace{d\ell}_{=1}$

$$Z_{QM} = \frac{1}{\varepsilon} \sum_{\ell=0}^{\infty} dx_\ell \, e^{-x_\ell} \simeq \frac{1}{\varepsilon} \int_0^\infty dx \, e^{-x} = \frac{1}{\varepsilon} = \frac{2IkT}{\hbar^2} \; ; \text{ Agrees with } (*)$$

:-)

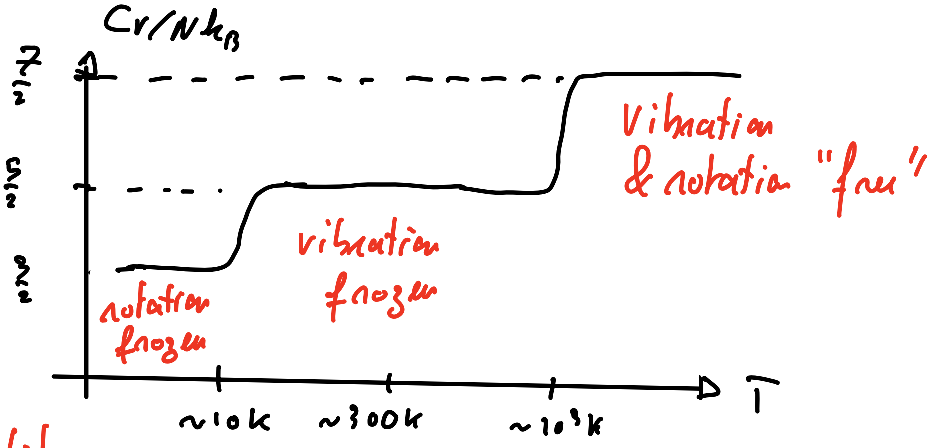
Abel - Plana gives a formal proof; see PSet 8.

Low temperature

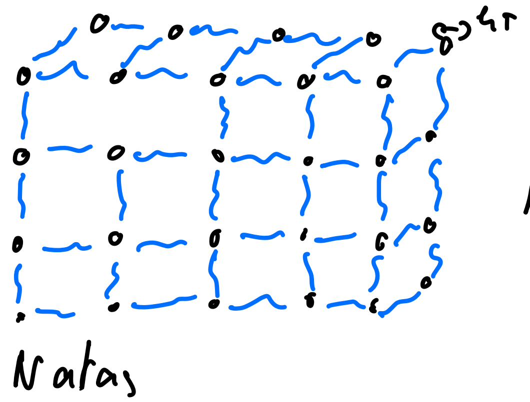
$$Z \simeq 1 + 3 e^{-\frac{\beta \hbar^2}{I}} \Rightarrow \langle E \rangle \simeq -\partial_\beta \ln Z \simeq \frac{3\hbar^2}{I} e^{-\beta \frac{\hbar^2}{I}}$$

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

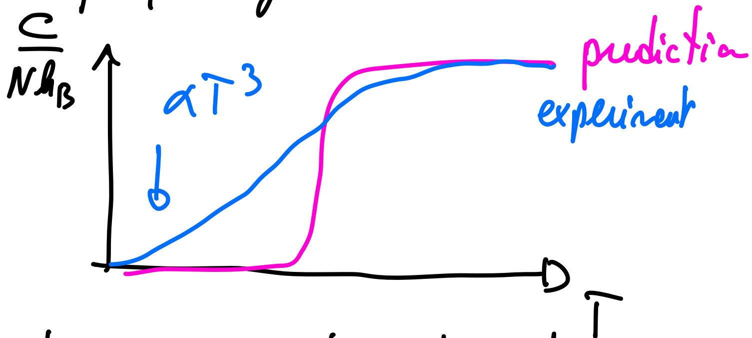
Summary



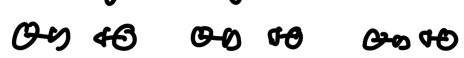
5.2 Heat capacity of solids

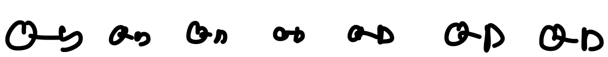


First guess $\approx 3N$ harmonic oscillators at frequency ω



Wrong image: the vibrations are not independent

 costly in energy (large compression/extension of oscillators)

 less costly (small ______)

The larger the wavelength λ, the lower the energy cost.

wave vector $|\vec{q}| = \frac{2\pi}{\lambda}$ $\Rightarrow$ frequency of corresponding harmonic oscillator

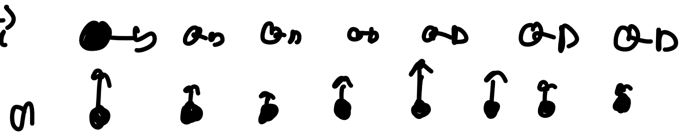
$$\omega(\vec{q}) \xrightarrow[|\vec{q}|\to 0]{} 0$$

Classically $E(\vec{q}) = E(-\vec{q}) \Rightarrow E \underset{q\to 0}{\propto} q^2 u_n^2$ with u_n the mode amplitude

$$\Rightarrow \omega(q) \propto |\vec{q}| \Rightarrow \omega(\vec{q}) = v|\vec{q}|$$

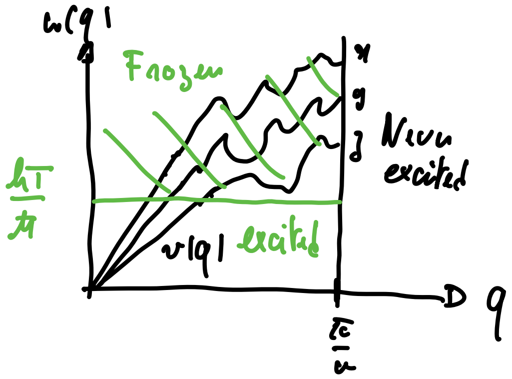
$v \Rightarrow$ speed of sound

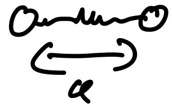
Comment: displacements along $\hat{x}, \hat{y}, \hat{z}$

$\vec{q} = \alpha\vec{x}$ 

displacement along x, y, z can be periodic along x, y, z

"polarization" α



* 

$q_{max} = \frac{2\pi}{a}$

* All the $T \to 0$ physics is controlled by $\omega(q) = v|\vec{q}|$

$\omega(\vec{q}) = v_\alpha |q| = v|q|$ for simplicity

$$E = \sum_{\substack{|q|<q_{max} \\ \text{polarization } \alpha}} \left(\frac{\hbar\omega(q)}{2} + \frac{\hbar\omega(q) e^{-\beta\hbar\omega(q)}}{1 - e^{-\beta\hbar\omega(q)}} \right)$$