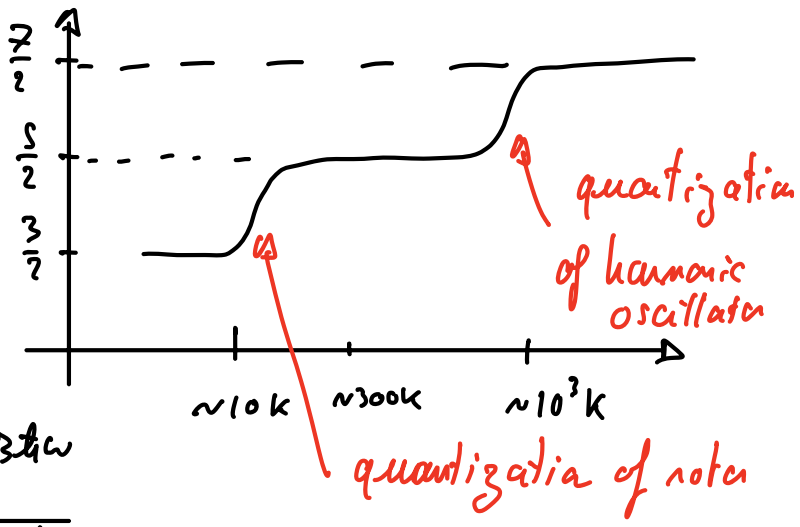
Heat capacity of diatomic gas

Experiments



Harmonic oscillator

$$E_n = \hbar\omega\left(n+\frac{1}{2}\right)$$

$$Z = \sum_n e^{-\beta E_n} = \frac{e^{-\beta\frac{\hbar\omega}{2}}}{1-e^{-\beta\hbar\omega}}$$

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

Low temperature $\langle E\rangle = \frac{\hbar\omega}{2} + \hbar\omega\sum_{n=1}^{\infty} e^{-\frac{n\hbar\omega}{k_BT}}$

$\simeq 1$ if $k_BT \gg n\hbar\omega$

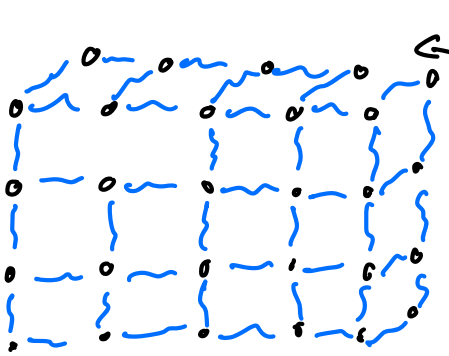
$\simeq 0$ if $k_BT \ll n\hbar\omega$

Quantum states populated up to $E_n \sim k_BT$

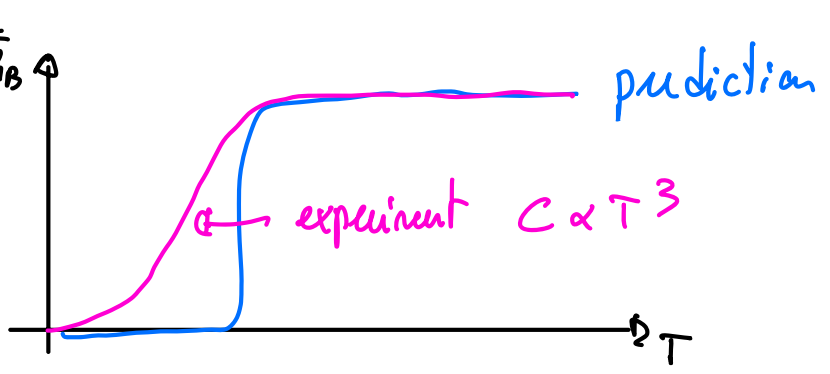
$$C_V \underset{T\to 0}{\sim} \frac{\hbar^2\omega^2}{k_BT^2} e^{-\beta\hbar\omega}$$

$\Rightarrow$ δT gives very little energy at $T=0$ since $E_1 = \hbar\omega\frac{3}{2}$ is very far & unlikely to be populated.

5.2) Heat capacity of solids



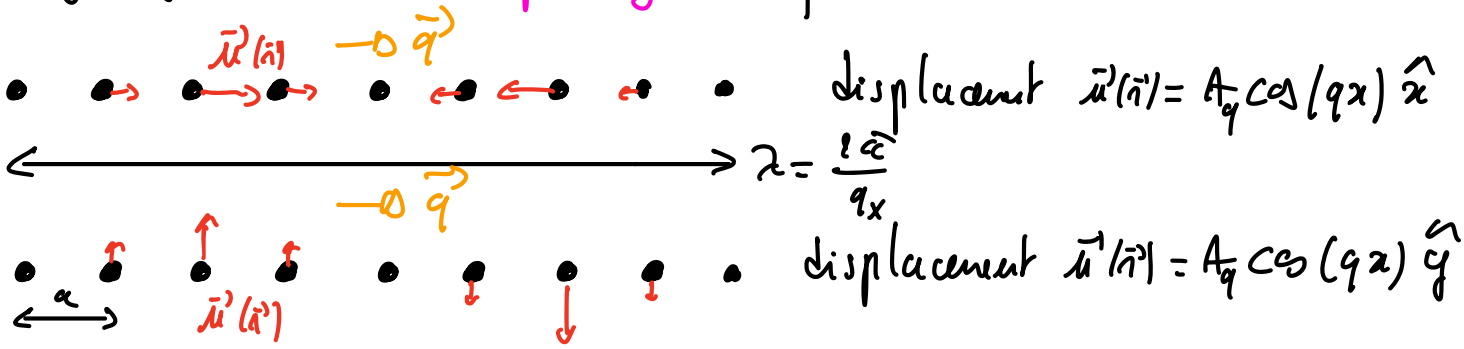
N atoms



Vibrations in solids: the longer the wavelength λ of the deformation, the cheaper the energy cost.

(1) For small deformations, the Hamiltonian of the deformations can be considered as (2) a superposition of independent harmonic oscillators of frequency $\omega(\vec{q})$, where $\vec{q}$ is the wavevector, such that $\omega(\vec{q}) \xrightarrow[|\vec{q}|\to\infty]{} 0$.

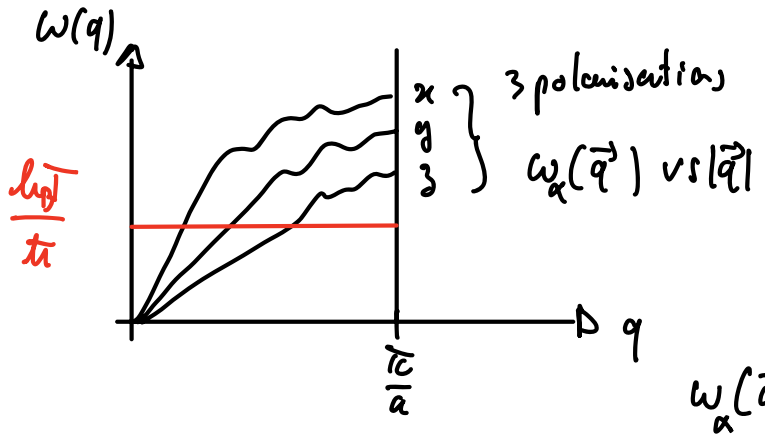
(11) A periodic modulation along $\vec{q}$ can correspond to displacements $\vec{u}(\vec{n})$ along $\hat{x}, \hat{y}, \hat{z}$ $\Rightarrow$ three polarizations for the wave



(111) Symmetry $\Rightarrow E(\vec{q}) = E(-\vec{q}) \Rightarrow E \underset{q\to 0}{\propto} \vec{q}^2 A_{\vec{q}}^2$, with $A_{\vec{q}}$ 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.



Only modes with $\hbar\omega < k_B T$ are excited

$T \to 0$ physics controlled by $\omega_\alpha(\vec{q}) \sim v_\alpha |\vec{q}| = v|\vec{q}|$ for simplicity.

$$\Rightarrow E = \sum_{\substack{|q|<q_{MAX} \\ \alpha}} E(\vec{q},\alpha) = \sum_{\substack{|q|<q_{MAX} \\ \alpha}} \left[\frac{\hbar\omega(q)}{2} + \frac{\hbar\omega(q)\, e^{-\beta\hbar\omega(q)}}{1 - e^{-\beta\hbar\omega(q)}} \right]$$

$$E \simeq E_0 + 3 \sum_{\vec{q}} \frac{\hbar v |q|}{e^{\beta \hbar v |q|} - 1} \quad \rightarrow \underline{Q^o}: \text{ how to compute this sum? } (3)$$

From sum to integral

$$\sum_{q_x, q_y, q_z} f(q_x, q_y, q_z) = \frac{V}{(2\pi)^3} \sum_{q_x} \frac{2\pi}{L} \sum_{q_y} \frac{2\pi}{L} \sum_{q_z} \frac{2\pi}{L} f \qquad (dq_x, dq_y, dq_z)$$

$$\underset{L \to \infty}{\simeq} \frac{V}{(2\pi)^3} \int d^3\vec{q}\, f(q_x, q_y, q_z)$$

$$E(T) = E_0 + 3 \frac{V}{(2\pi)^3} \int^{q_{max}} 4\pi q^2 dq \; k_B T \frac{\beta \hbar v q}{e^{\beta \hbar v q} - 1}$$

Let's turn this integral into a dimensionless quantity

$$x = \beta \hbar v q \iff q = \frac{x k_B T}{v \hbar} \quad \& \quad dq = dx \frac{k_B T}{v \hbar}$$

$$\Rightarrow E(T) = E_0 + \frac{3V}{2\pi^2} k_B T \left(\frac{k_B T}{v \hbar}\right)^3 \int_0^{x_{max}} dx \frac{x^3}{e^x - 1} \quad ; \; x_{max} \propto \frac{q_{max}}{T} \underset{T \to 0}{\to} \infty$$

Using that $\int_0^\infty dx \frac{x^3}{e^x - 1} = \frac{\pi^4}{15}$, one finds

$$E(T) \underset{T \to 0}{\simeq} E_0 + \frac{V \pi^2}{10} k_B T \left(\frac{k_B T}{v \hbar}\right)^3 \quad ; \; V = N a^3$$

$$C_V \sim \frac{2\pi^2}{5} N k_B \left(\frac{k_B T a}{\hbar v}\right)^3 \Rightarrow \boxed{\frac{C_V}{N k_B} \simeq \frac{2\pi^2}{5} \left(\frac{T}{\Theta_D}\right)^3}$$

where $\boxed{\Theta_D = \frac{\hbar v}{a k_B} \simeq 10^2 K}$ is the Debye temperature (1912)

As $L \to \infty$, $\hbar\omega \Rightarrow 0$ & the spectrum becomes gapless. The exponential decay of C_r is replaced by a power law.

Chapter 6: Quantum statistical mechanics

6.1) Density matrix

Quantum microstates:

$(\vec{q}, \vec{p}) \Rightarrow |\psi\rangle$ unit vector in a Hilbert space $\mathcal{H}$ with scalar product $\langle \psi_1 | \psi_2 \rangle$

Basis $|n\rangle$ such that $\langle n|\psi\rangle$ is the component of $|\psi\rangle$ along $|n\rangle$

$$|\psi\rangle = \sum_n \langle n|\psi\rangle |n\rangle = \sum_n \underbrace{|n\rangle\langle n|}_{\text{projector along } |n\rangle} \psi\rangle$$

E.g. basis $|x\rangle$; $\langle x|\psi\rangle = \psi(x)$ is the wave function

Observables, fluctuations & average

*Classical observable $O(q,p)$ ⟶ Quantum operator $\hat{O}$

Ex: $\hat{p}$ is such that $\langle x|\hat{p} = -i\hbar\vec{\nabla}\langle x|$

Eigenvectors $|\psi_{\vec{p}}\rangle$ such that $\langle x|\psi_{\vec{p}}\rangle = e^{i\frac{\vec{p}\cdot\vec{x}}{\hbar}}$

Indeed, $\langle x|\hat{p}|\psi_{\vec{p}}\rangle = -i\hbar\vec{\nabla} e^{i\frac{\vec{p}\cdot\vec{x}}{\hbar}} = \vec{p}\, e^{i\frac{\vec{p}\cdot\vec{x}}{\hbar}} = \langle x|\psi\rangle$

$\Rightarrow \hat{P}|\psi_{\vec{p}}\rangle = \vec{p}\,|\psi_{\vec{p}}\rangle$

* If a system is in a state $|\psi\rangle$, the measurement of an observable does not necessarily give deterministic outcome

$\Rightarrow$ quantum fluctuations

The average over these fluctuations is $\boxed{\langle \hat{O}\rangle_{QM} = \langle\psi|O|\psi\rangle}$

* Typically, we do not know in which quantum state a system is.

- If the system has a probability p_α to be in $|\psi_\alpha\rangle$, then, in $|\psi_\alpha\rangle$, we have $\langle \hat{O}\rangle_{QM} = \langle\psi_\alpha|O|\psi_\alpha\rangle$

- In addition, the statistical uncertainty due to p_α lead to

$$\langle \hat{O}\rangle = \sum_\alpha p_\alpha \langle\psi_\alpha|\hat{O}|\psi_\alpha\rangle$$

p_α: prob to be in $|\psi_\alpha\rangle$; $\langle\psi_\alpha|\hat{O}|\psi_\alpha\rangle$: average of O given the system is in $|\psi_\alpha\rangle$

Density matrix $\boxed{\hat{\rho} = \sum_\alpha p_\alpha |\psi_\alpha\rangle\langle\psi_\alpha|}$

Take any basis $|m\rangle$

$$\langle \hat{O}\rangle = \sum_\alpha p_\alpha \sum_{m,l} \langle\psi_\alpha|m\rangle\langle m|\hat{O}|l\rangle\langle l|\psi_\alpha\rangle$$

$$= \sum_{m,l} \langle m|\hat{O}|l\rangle \langle l| \sum_\alpha p_\alpha |\psi_\alpha\rangle\langle\psi_\alpha| m\rangle$$

$\sum_l |l\rangle\langle l| = \mathbb{1}$; $\sum_\alpha p_\alpha |\psi_\alpha\rangle\langle\psi_\alpha| = \hat{\rho}$

$$= \sum_m \langle m | \hat{O} \hat{\rho} | m \rangle$$

$$\boxed{\langle \hat{O} \rangle = \mathrm{Tr}(\hat{O}\hat{\rho}) = \mathrm{Tr}(\hat{\rho}\hat{O})}$$

Properties:

positivity $\langle \phi | \hat{\rho} | \phi \rangle = \sum_\alpha p_\alpha \underbrace{\langle \phi | \psi_\alpha \rangle \langle \psi_\alpha | \phi \rangle}_{|\langle \phi | \psi_\alpha \rangle|^2} \geq 0$

hermiticity $\hat{\rho} = \hat{\rho}^\dagger$

Proof: $\langle m | \hat{\rho}^\dagger | n \rangle = \left(\langle n | \hat{\rho} | m \rangle \right)^* = \sum_\alpha p_\alpha \langle n | \psi_\alpha \rangle^* \langle \psi_\alpha | m \rangle^*$

$$= \sum_\alpha p_\alpha \langle m | \psi_\alpha \rangle \langle \psi_\alpha | n \rangle = \langle m | \hat{\rho} | n \rangle$$

Normalization $\mathrm{Tr}(\hat{\rho}) = 1$

Proof: $\langle \mathbb{1} \rangle = 1$:-)

$$\mathrm{Tr}(\hat{\rho}) = \sum_{m\alpha} p_\alpha \langle m | \psi_\alpha \rangle \langle \psi_\alpha | m \rangle = \sum_\alpha p_\alpha \langle \psi_\alpha | \underbrace{\sum_m |m\rangle\langle m|}_{\mathbb{1}} | \psi_\alpha \rangle$$

$$= \sum_\alpha p_\alpha \langle \psi_\alpha | \psi_\alpha \rangle^2 = \sum_\alpha p_\alpha = 1$$

Quantum vs thermal mixture

The system is in a single quantum state (pure state) $|\psi\rangle$ iff $\hat{\rho}^2 = \hat{\rho}$.

$\Leftrightarrow \mathrm{Tr}(\hat{\rho}^2) = 1$

Proof: If $\hat{\rho} = |\psi\rangle\langle\psi|$, then $\hat{\rho}^2 = |\psi\rangle \underbrace{\langle\psi|\psi\rangle}_{=1} \langle\psi| = \hat{\rho}$

Conversely, $\hat{\rho}$ Hermitian $\Rightarrow \hat{\rho} = \sum_n \lambda_n |\psi_n\rangle\langle\psi_n|$ with $|\psi_n\rangle$

an orthonormal basis. Thus

$$\rho^2 = \sum_{k,k'} \lambda_k \lambda_{k'} |\psi_k\rangle\langle\psi_k|\psi_{k'}\rangle\langle\psi_{k'}| = \sum_k \lambda_k^2 |\psi_k\rangle\langle\psi_k| \quad (\langle\psi_k|\psi_{k'}\rangle = \delta_{k,k'})$$

$\rho^2 = \rho \Rightarrow \lambda_k^2 = \lambda_k \Rightarrow \lambda_k \in \{0,1\}$. Since $\mathrm{Tr}(\rho) = \sum_k \lambda_k = 1$, only one λ_k can be equal to 1.

Coherence

* $\langle m|\rho|m\rangle = \sum_\alpha p_\alpha \langle m|\psi_\alpha\rangle^2$ = proba that the system is measured in $|m\rangle$.

$\Rightarrow$ In a given basis $|i\rangle$, ρ_{ii} is the proba the system is measured in $|i\rangle$.

* $\langle m|\rho|k\rangle = \sum_\alpha p_\alpha \langle m|\psi_\alpha\rangle\langle\psi_\alpha|k\rangle \neq 0$ iff there exist one $|\psi_\alpha\rangle$ which is a quantum superposition of $|m\rangle$ & $|k\rangle$.

ρ_{ij}, with $j \neq i$, measures the (average) coherence between $|i\rangle$ & $|j\rangle$.

* This is a basis-dependent property

Evolution

Schrödinger's eq°: $i\hbar \partial_t |\psi_\alpha\rangle = \hat{H}|\psi_\alpha\rangle \Leftrightarrow -i\hbar \partial_t \langle\psi_\alpha| = \langle\psi_\alpha|\hat{H}^+ = \langle\psi_\alpha|\hat{H}$

$$i\hbar \frac{\partial \hat{\rho}}{\partial t} = \sum_\alpha p_\alpha \partial_t |\psi_\alpha\rangle\langle\psi_\alpha|$$
$$= \sum_\alpha p_\alpha \left(\hat{H}|\psi_\alpha\rangle\langle\psi_\alpha| - |\psi_\alpha\rangle\langle\psi_\alpha|\hat{H}\right) = \hat{H}\hat{\rho} - \hat{\rho}\hat{H}$$

$$\boxed{i\hbar \frac{\partial \hat{\rho}}{\partial t} = [\hat{H}, \hat{\rho}]} \qquad \Rightarrow \partial_t \langle\hat{O}\rangle = \langle[H, \hat{O}]\rangle$$

Steady state : $\partial_t \hat{\rho} = 0 \iff [\hat{H}, \hat{\rho}] = 0$

As in classical statistical mechanics, $\hat{\rho} = f(\hat{H})$ does the job.

$\Rightarrow \rho_{eq}(H)$ replaced by $\hat{\rho}_{eq}(\hat{H})$

$|m\rangle$ eigenbasis of $\hat{H}$: $\hat{\rho} = \hat{\rho} \sum_m |m\rangle\langle m| = \sum_m f(\hat{H}) |m\rangle\langle m| = \sum_m f(E_m) |m\rangle\langle m|$

$\Rightarrow p_m = f(E_m)$, as in classical stat mech !

Microcanonical :

$p_m = 1/\Omega(E)$ if $E_m = E$; $\Omega(E) = \sum_m \delta_{E_m, E}$

$= 0$ otherwise

Entropy $S = k_B \ln \Omega(E)$

Canonical : $p_m = \frac{1}{Z} e^{-\beta E_m} \iff \hat{\rho} = \frac{1}{Z} e^{-\beta \hat{H}}$

$\mathrm{Tr}(\hat{\rho}) = 1 \Rightarrow Z = \mathrm{Tr}(e^{-\beta \hat{H}}) = \sum_m e^{-\beta E_m}$, which validates the approach of chapter 5

Grand canonical : $\hat{\rho} = \frac{1}{\mathcal{Q}} e^{-\beta \hat{H} + \beta\mu \hat{N}}$: $\mathcal{Q}(\beta, \mu) = \mathrm{Tr}\left(e^{-\beta \hat{H} + \beta\mu \hat{N}}\right)$

Comment: Steady state requires $[\hat{\rho}, \hat{H}] = 0$

In the grand canonical, we have either $[\hat{N}, \hat{H}] = 0$ or $\mu = 0$

Since $i\hbar \partial_t \langle \hat{N} \rangle = \langle [\hat{N}, \hat{H}] \rangle$, we need $\mu = 0$ if the number of particles is not conserved (e.g. for photons, due to stimulated emission & absorption).

Maximum entropy & quantum ensembles

Defining Gibbs-Shannon entropy $S = -k_B \mathrm{Tr}(\hat{\rho} \ln \hat{\rho})$

Jaynes approach can also be used to build quantum ensembles. [Jaynes, Phys Rev 108, 171, (1957)]

6.2) A particle in a box

$$H = \frac{\hat{p}^2}{2m} \quad ; \quad \langle x|\hat{p}|\psi\rangle = -i\hbar \vec{\nabla} \langle x|\psi(x)\rangle$$

$$H|\psi\rangle = \lambda|\psi\rangle \Rightarrow -\frac{\hbar^2}{2m}\Delta\langle x|\psi\rangle = \lambda\langle x|\psi\rangle \text{ & } \langle x|\psi\rangle = \psi(x) \text{ periodic}$$

$$\Rightarrow |\psi\rangle = |\vec{k}\rangle \text{, with } \vec{k} = \frac{2\pi}{L}(n_x, n_y, n_z) \text{ & } \langle x|k\rangle = \frac{1}{\sqrt{V}} e^{i\vec{k}\cdot\vec{x}}$$

Then $H|\vec{k}\rangle = \varepsilon(\vec{k})|\vec{k}\rangle$ with $\varepsilon(\vec{k}) = \frac{\hbar^2\vec{k}^2}{2m} = \frac{\vec{p}^2}{2m}$ with $\vec{p} = \hbar\vec{k}$

Partition function

$$Z = \mathrm{Tr}(e^{-\beta\hat{H}}) = \sum_{\vec{k}} e^{-\beta\frac{\hbar^2k^2}{2m}} = \frac{V}{(2\pi)^3}\int d^3\vec{k}\, e^{-\beta\frac{\hbar^2k^2}{2m}} = \frac{V}{(2\pi)^3}\sqrt{\frac{2\pi m k_B T}{\hbar^2}} = \frac{V}{\lambda^3}$$

We recover the classical stat mech result!

Density matrix

$$\langle x'|\hat{\rho}_c|x\rangle = \sum_{\vec{k}} \frac{e^{-\beta\varepsilon(\vec{k})}}{Z}\langle x'|k\rangle\langle k|x\rangle = \frac{\lambda^3}{V}\frac{V}{(2\pi)^3}\int d^3\vec{k}\, e^{-\beta\frac{\hbar^2\vec{k}^2}{2m}}\frac{e^{-i\vec{k}\cdot(\vec{x}-\vec{x}')}}{V}$$

$$= \frac{1}{V}\exp\left[-\frac{\pi}{2}\frac{(\vec{x}-\vec{x}')^2}{\lambda^2}\right] \text{ where we used } \beta\frac{\hbar^2}{m} = \frac{1}{2\pi}\frac{h^2}{2\pi m k_B T} = \frac{\lambda^2}{2\pi}$$

(i) $\langle x | \hat{g}_c | x \rangle = \frac{1}{V}$, as expected

(ii) The statistical mixture is coherent over a scale $|\vec{x} - \vec{x}'| \sim \Lambda$

$\Rightarrow$ the thermal de Broglie wavelength measures the coherence length of the thermal mixture.

$\Rightarrow$ At temperature T, the particle is a wave packet spread over Λ

6.3) Quantum gases