From Atoms to Materials: Predictive Theory and Simulations

Week 4: Connecting Atomic Processes to the Macroscopic World

Lecture 4.3: Statistical Mechanics of the Harmonic Solid

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Review of important ensembles

Microcanonical (NVE)	Canonical (NVT)	Isobaric/isothermal (NPT)
Probability distributions		
$P(\{P_i\}\{R_i\}) = \frac{1}{\Omega(E,V,N)}$	$P(\{R_i\},\{P_i\}) = \frac{e^{-\frac{H(\{R_i\},\{P_i\})}{kT}}}{Z(T,V,N)}$	$P(\{R_i\},\{P_i\},V) = \frac{e^{-\frac{1}{kT}\left[H(\{R_i\},\{P_i\})-PV\right]}}{Z_P(T,P,N)}$
$\Omega(E,V,N) = \sum_{micro} \delta(E - H(\{R_i\}\{P_i\}))$	$Z(T,V,N) = \underline{\sum_{micro}} e^{-\frac{E}{kT}}$	$Z_P(T,P,N) = \sum_V \sum_{micro} e^{-\frac{E-PV}{kT}}$
Free energies (atomistic ↔ macroscopic thermodynamics)		
$S = k \log \Omega(E,V,N)$	$F(T,V,N) = -kT \log Z$	$G(T,P,N) = -kT \log Z_p$

Some useful relationships + grand canonical

From the definition of canonical partition function:

$$Z(T,V,N) = \underbrace{\sum_{microstates-i}}\ e^{-\beta E_i}$$

Average energy can be obtained from the partition function:

$$\langle E \rangle = \frac{1}{Z} \sum_{microstates-i} E_i e^{-\beta E_i} = \boxed{-\frac{\partial \log(Z(T,V,N))}{\partial \beta}}$$

Grand canonical ensemble (energy and number of particles fluctuate):

chemical pot.

$$\Xi(\mu,V,T) = \sum_{N=0}^{\infty} \sum_{\substack{microstates-i \\ with\ N\ atoms}} e^{-\beta(E_i-\mu N)} = \sum_{N=0}^{\infty} e^{\beta\mu N} Z(N,V,T)$$

$$\langle N(\mu,V,T) \rangle = \frac{1}{\Xi} \sum_{N=0}^{\infty} N e^{\beta\mu N} Z(N,V,T) = kT \frac{\partial \log(\Xi)}{\partial \mu}$$

Fluctuations

Fluctuations from equilibrium are also related to materials properties

$$\left\langle \delta A^2 \right\rangle = \frac{1}{\tau} \int_0^\tau \left[A(t) - \left\langle A \right\rangle \right]^2 dt = \left\langle A^2 \right\rangle - \left\langle A \right\rangle^2$$

Specific heat:

$$C_V = \left. \frac{\partial E}{\partial T} \right|_{NVT}$$

$$\left\langle \delta H^2 \right\rangle_{NVT} = kT^2 C_V$$

Compressibility:

$$\beta_V = \frac{1}{V} \left. \frac{\partial V}{\partial P} \right|_{NVT}$$

$$\left\langle \delta V^2 \right\rangle_{NPT} = k \left\langle V \right\rangle T \beta_T$$

Classical mechanics of the harmonic solid

Second order expansion of Hamiltonian around equilibrium (week 3 lecture 5)

$$H = \underbrace{\sum_{i=1}^{3N} \frac{P_i^2}{2M_i}} + \underbrace{V\left(\left\{R_i^\circ\right\}\right)} + \underbrace{\frac{1}{2}\sum_{i,j}^{3N} \left.\frac{\partial^2 V}{\partial R_i \partial R_j}\right|_{\left\{R_i^\circ\right\}}} \Delta R_i \Delta R_j$$

After diagonalizing the Hessian matrix H can be written as a sum of 3N de-coupled harmonic oscillators

$$H = \underbrace{V\left(\left\{R_i^0\right\}\right) + \sum_{\alpha=1}^{3N}\left(\frac{\pi_\alpha^2}{2} + \frac{1}{2}\omega_\alpha^2 \rho_\alpha^2\right)} + \sum_{i=1}^{3N} \frac{P_i^2}{2M_i}$$

Equipartition: each degree of freedom contributes 1/2kT of energy:

$$E(N,V,T) = V\left(\left\{R_0\right\}\right) + \frac{2\times 3N}{2} kT = V\left(\left\{R_0\right\}\right) + 3NkT$$

Specific heat : $$C_V(N,V,T) = \frac{\partial E}{\partial T} = \boxed{3Nk}$$

Comparing with experiments

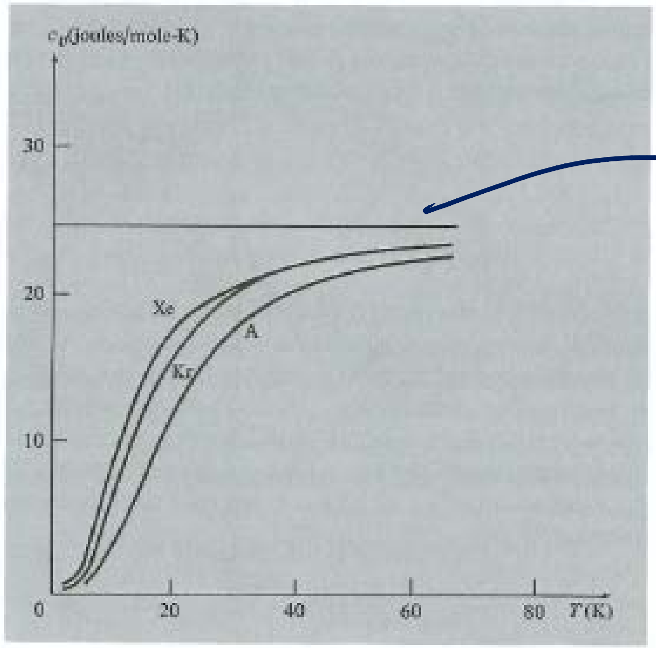


Figure 22.3
Measured specific heats of argon, xenon, and krypton. The horizontal line is the classical Dulong and Petit value. (Quoted in M. L. Klein, G. K. Horton, and J. L. Feldman, *Phys. Rev.* 184, 68 (1969).)

Solid-state Physics
Ashcroft-Mermin

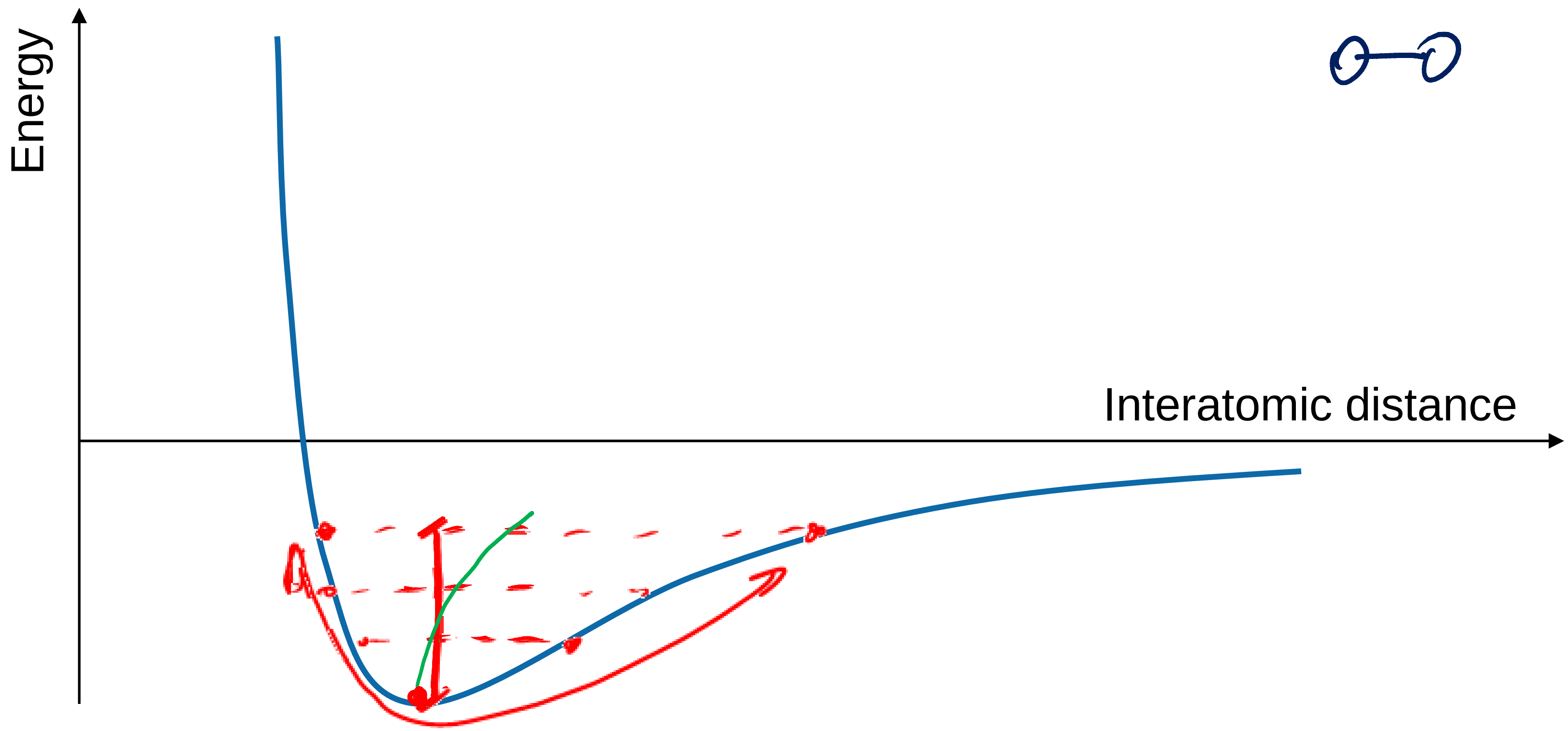
Classical harmonic result:

$$C_V(N,V,T) = \frac{\partial E}{\partial T} = \boxed{3Nk}$$

What error did we make?

Quantum effects

When does classical mechanics for atoms stop working?



Temperature at which quantum effects kick in depends on frequency

$kT >> \hbar\omega$ Classical regime

$kT \sim< \hbar\omega$ Quantum regime

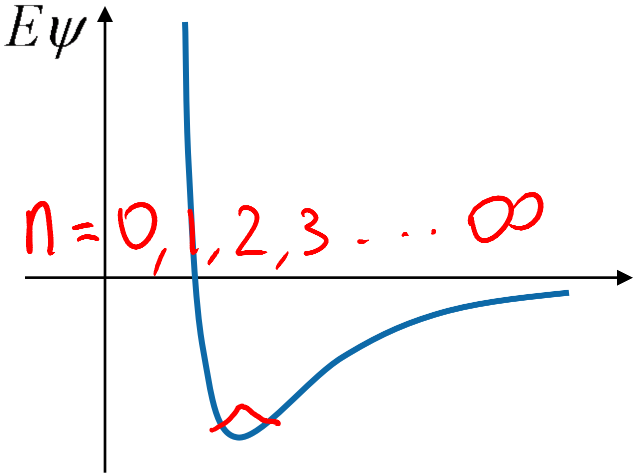
Quantum harmonic oscillator

How do we solve a harmonic oscillator using QM?

Write the Hamiltonian: $$H = \frac{P^2}{2M} + \frac{1}{2}KX^2 = -\frac{\hbar^2}{2M}\frac{\partial^2}{\partial X^2} + \frac{1}{2}KX^2$$

Solve the Schrödinger Equation: $$H\psi = E\psi$$

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



Compute the partition function:

$$Z = \sum_{\substack{microstates}} e^{-\beta E_n} = \sum_{\substack{microstates \\ n}} e^{-\beta\hbar\omega\left(\frac{1}{2}+n\right)}$$