

# Introduction to the Theory of Lattice Vibrations and their Ab Initio Calculation

## Lecture 3: Quantum theory of lattice vibrations

Ion Errea

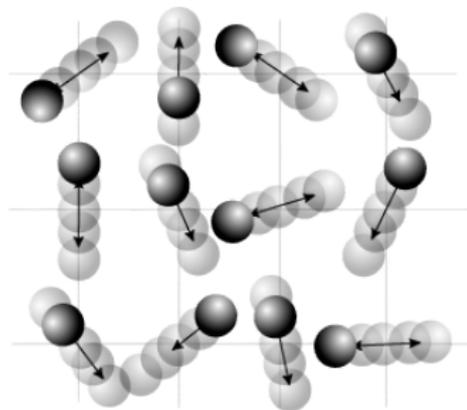
Dept. Applied Physics, University of the Basque Country (UPV/EHU),  
San Sebastian, Spain

Centro de Física de Materiales (CSIC-UPV/EHU), San Sebastian, Spain

Donostia International Physics Center,  
San Sebastian, Spain

*University of Science and Technology Beijing*

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Universidad del País Vasco  
Euskal Herriko Unibertsitatea

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Materialen Fisika Zentroa

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- 1 The harmonic Hamiltonian
  - Solving the quantum Hamiltonian in the harmonic approximation
- 2 Thermodynamics in the harmonic approximation
  - Free energy, the density matrix, and the partition function
  - The Bose-Einstein occupation factor
  - Classical and quantum contributions to the energy of phonons
  - The probability distribution function
  - Quantum statistical averages
  - The mean square displacement
  - The constant volume specific heat, Einstein and Debye approximations
- 3 The phonon density of states
- 4 The harmonic phonon Green function and the displacement correlation function
- 5 Exercises

# The quantum Hamiltonian

- Instead of solving the classical equations of motion, we need to solve the Schrödinger equation

$$H_i|\Psi_\beta^i\rangle = [\hat{T}_i + V(\hat{R})]|\Psi_\beta^i\rangle = E_\beta|\Psi_\beta^i\rangle$$

- The operator symbol has been included for the kinetic energy and the position operator
- The Taylor expansion of the potential is valid so that

$$\begin{aligned} V(\hat{R}) &= V(\mathbf{R}_0) + V_2(\hat{R}) + V_3(\hat{R}) + V_4(\hat{R}) + \dots, \\ V_n(\hat{R}) &= \frac{1}{n!} \sum_{a_1 \dots a_n} \phi_{a_1 \dots a_n}^{(n)} (\hat{R}_{a_1} - R_{a_1 0}) \dots (\hat{R}_{a_n} - R_{a_n 0}) \end{aligned}$$

# The quantum Hamiltonian in the harmonic approximation

- In the harmonic approximation the potential is truncated at second order:

$$H_i = \hat{T}_i + \frac{1}{2} \sum_{ab} \phi_{ab}^{(2)} (\hat{R}_a - R_{a0})(\hat{R}_b - R_{b0}) = \sum_a \frac{\hat{p}_a^2}{2M_a} + \frac{1}{2} \sum_{ab} \phi_{ab}^{(2)} \hat{u}_a \hat{u}_b$$

where  $\hat{\mathbf{p}}$  is the momentum operator

- We have defined the displacement operator simply as

$$\hat{u}_a = \hat{R}_a - R_{a0}$$

which measures the displacement from the reference position

# The quantum Hamiltonian in the normal mode basis

- We perform the transformation to the normal mode basis with this transformation of the position and momentum operators

$$\hat{u}_a = \sum_{\mu} \frac{e_{\mu}^a}{\sqrt{M_a}} \hat{Q}_{\mu}$$
$$\hat{p}_a = \sum_{\mu} \sqrt{M_a} e_{\mu}^a \hat{P}_{\mu}$$

where

$$\sum_b \frac{\overset{(2)}{\phi}_{ab}}{\sqrt{M_a M_b}} e_{\mu}^b = \omega_{\mu}^2 e_{\mu}^a$$

and  $\hat{Q}_{\mu}$  and  $\hat{P}_{\mu}$  are the normal displacement and momentum operators in the normal mode basis

- The Hamiltonian becomes a sum of  $3N_{at}$  independent harmonic oscillators

$$H_i = \sum_{\mu} \frac{1}{2} \left( \hat{P}_{\mu}^2 + \omega_{\mu}^2 \hat{Q}_{\mu}^2 \right)$$

# The quantum Hamiltonian in the normal mode basis in reciprocal space

- In reciprocal space we can also do the same:

$$\hat{u}_a(\mathbf{T}_a) = \frac{1}{\sqrt{N}} \sum_{\mathbf{q}\mu} \frac{e_\mu^a(\mathbf{q})}{\sqrt{M_a}} \hat{Q}_\mu(\mathbf{q}) e^{-i\mathbf{q}\cdot\mathbf{T}_a}$$
$$\hat{p}_a(\mathbf{T}_a) = \frac{1}{\sqrt{N}} \sum_{\mathbf{q}\mu} \sqrt{M_a} e_\mu^a(\mathbf{q}) \hat{P}_\mu(\mathbf{q}) e^{-i\mathbf{q}\cdot\mathbf{T}_a}$$

- The Hamiltonian becomes a sum of  $3N_{at}$  independent complex harmonic oscillators

$$\hat{H}_i = \frac{1}{2} \sum_{\mu\mathbf{q}} \left( |\hat{P}_\mu(\mathbf{q})|^2 + \omega_\mu^2 |\hat{Q}_\mu(\mathbf{q})|^2 \right)$$

- Both in real space and reciprocal space the problem is simply to solve the harmonic oscillator problem
- The harmonic problem is a separable Hamiltonian in single-particle Hamiltonians, in this case harmonic oscillators

# The solution of the harmonic Hamiltonian in quantum mechanics

$$\hat{H} = \frac{1}{2} (\hat{P}^2 + \omega^2 \hat{Q}^2)$$

- We transform the normal mode displacement and momentum operator to ladder operators:

$$\hat{Q} = \sqrt{\frac{\hbar}{2\omega}} (\hat{b} + \hat{b}^\dagger)$$

$$\hat{P} = -i\sqrt{\frac{\hbar\omega}{2}} (\hat{b} - \hat{b}^\dagger)$$

which satisfy the bosonic commutation relations  $[\hat{b}, \hat{b}^\dagger] = 1$

- The Hamiltonian is thus written as

$$\hat{H} = \hbar\omega \left( \hat{b}^\dagger \hat{b} + \frac{1}{2} \right)$$

# The solution of the harmonic Hamiltonian in quantum mechanics

- The eigenvectors of the Hamiltonian are the Fock states  $|n\rangle$  with  $n \geq 0$

$$\hat{H}|n\rangle = E_n|n\rangle$$

- The ladder operators act on the Fock states as

$$\begin{aligned}\hat{b}|n\rangle &= \sqrt{n}|n-1\rangle \\ \hat{b}^\dagger|n\rangle &= \sqrt{n+1}|n+1\rangle\end{aligned}$$

- The number operator is  $\hat{n} = \hat{b}^\dagger \hat{b}$  and  $|n\rangle$  is an eigenvector of it

$$\hat{n}|n\rangle = \hat{b}^\dagger \hat{b}|n\rangle = n|n\rangle$$

- Thus, the eigenvalues of the quantum harmonic Hamiltonian are

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

# The solution of the harmonic Hamiltonian in normal mode coordinates

- The Schrödinger equation to be solved for  $\langle Q|n\rangle = \Psi_n(Q)$

$$-\frac{\hbar^2}{2} \frac{d^2 \Psi_n(Q)}{dQ^2} + \frac{1}{2} \omega^2 Q^2 \Psi_n(Q) = \hbar \omega \left( n + \frac{1}{2} \right) \Psi_n(Q)$$

- The solution of this differential equation gives

$$\Psi_n(Q) = \frac{1}{\sqrt{2^n n!}} \left( \frac{\omega}{\pi \hbar} \right)^{1/4} e^{-\frac{\omega Q^2}{2\hbar}} H_n(\sqrt{\omega/\hbar} Q)$$

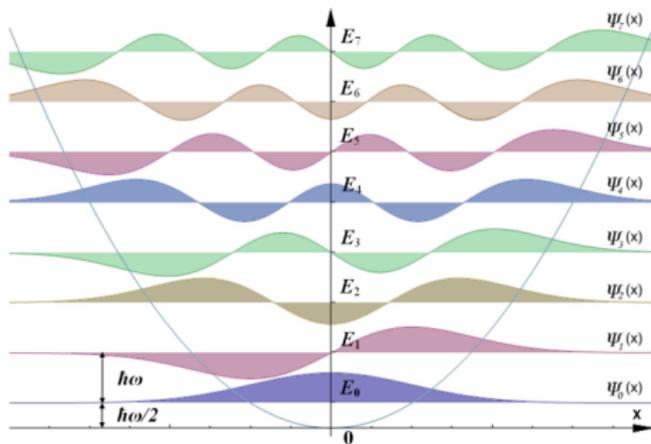
where  $H_n(x)$  are hermite polynomials:

$$\begin{aligned} H_0(x) &= 1 \\ H_1(x) &= 2x \\ &\dots \end{aligned}$$

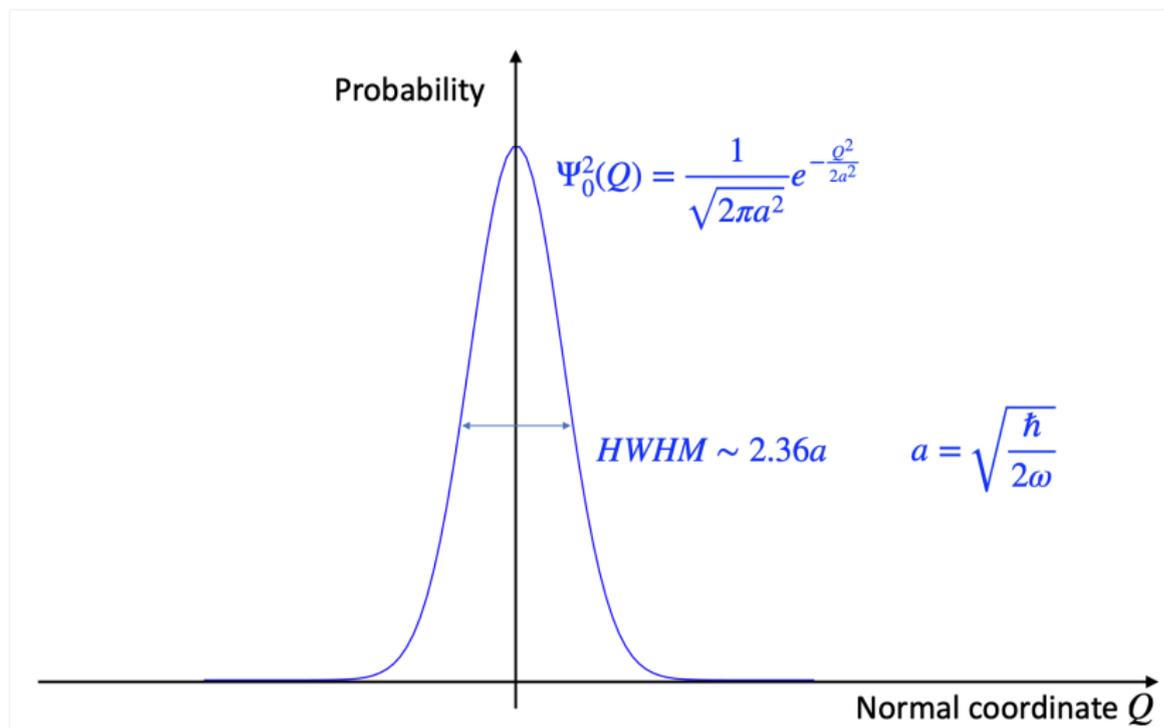
# The solution of the harmonic Hamiltonian in normal mode coordinates

- If  $n$  is even,  $\Psi_n(Q)$  is even
- If  $n$  is odd,  $\Psi_n(Q)$  is odd
- The probability defined by each state is  $\Psi_n^2(Q)$
- The ground state probability is a normalized Gaussian

$$\Psi_0^2(Q) = \sqrt{\frac{\omega}{\pi\hbar}} e^{-\frac{\omega Q^2}{\hbar}}$$



# The solution of the harmonic Hamiltonian in normal mode coordinates



# Solution of the quantum harmonic Hamiltonian for a full crystal

- As the Hamiltonian becomes is sum of  $3N_{at}$  independent harmonic oscillators

$$\hat{H}_i = \sum_{\mu} \frac{1}{2} \left( \hat{P}_{\mu}^2 + \omega_{\mu}^2 \hat{Q}_{\mu}^2 \right)$$

and phonons are bosons, we can write

$$\begin{aligned} \hat{H}_i |n_1 \cdots n_{3N_{at}}\rangle &= E_{n_1 \cdots n_{3N_{at}}} |n_1 \cdots n_{3N_{at}}\rangle \\ \Psi_{n_1 \cdots n_{3N_{at}}}(\mathbf{Q}) = \langle \mathbf{Q} | n_1 \cdots n_{3N_{at}} \rangle &= \prod_{\mu} \Psi_{n_{\mu}}(Q_{\mu}) \\ E_{n_1 \cdots n_{3N_{at}}} &= \sum_{\mu} \hbar \omega_{\mu} \left( n_{\mu} + \frac{1}{2} \right) \end{aligned}$$

- $n_{\mu}$  is the called the occupation of each phonon mode and  $\omega_{\mu}$  is the phonon frequency
- Phonons are the quasiparticles that diagonalize the harmonic Hamiltonian
- In this normal mode basis, the ground state probability distribution is a product of Gaussians

$$\Psi_{0 \cdots 0}^2(\mathbf{Q}) = \prod_{\mu} \Psi_0^2(Q_{\mu})$$

Do quantum harmonic ions fluctuate from the  $R_0$  positions at 0K?

# The contribution of ionic vibrations to the free energy

- The free energy is

$$F = E - TS$$

where  $E$  is the total energy and  $S$  the entropy

- If the ionic system is described by a Hamiltonian  $H$  the density matrix is

$$\rho_H = e^{-\beta H} / Z_H$$

where the partition function is

$$Z_H = \text{tr}(e^{-\beta H})$$

and  $\beta = k_B T$

- Then

$$E = \langle H \rangle_{\rho_H} = \text{tr}(H\rho_H)$$

$$S = -k_B \langle \ln \rho_H \rangle_{\rho_H} = -k_B \text{tr}(\rho_H \ln \rho_H)$$

$$F = \text{tr}(H\rho_H) + \frac{1}{\beta} \text{tr}(\rho_H \ln \rho_H) = -\frac{1}{\beta} \ln Z_H$$

# The contribution of ionic vibrations to the free energy in the harmonic approximation

- In the harmonic approximation the partition function can be calculated

$$\begin{aligned} Z_H &= \text{tr}(e^{-\beta H}) = \sum_{n_1 \cdots n_{3N_{at}}} \langle n_1 \cdots n_{3N_{at}} | e^{-\beta H} | n_1 \cdots n_{3N_{at}} \rangle \\ &= \sum_{n_1 \cdots n_{3N_{at}}} \langle n_1 | \cdots \langle n_{3N_{at}} | e^{-\beta H_1} \cdots e^{-\beta H_{3N_{at}}} | n_1 \rangle \cdots | n_{3N_{at}} \rangle \end{aligned}$$

where  $H_i$  is a single harmonic oscillator Hamiltonian

- Then,

$$Z_H = \prod_{\mu} \sum_{n_{\mu}} e^{-\beta \hbar \omega_{\mu} (n_{\mu} + \frac{1}{2})} = \prod_{\mu} e^{-\beta \hbar \omega_{\mu} / 2} \sum_{n_{\mu}} \left( e^{-\beta \hbar \omega_{\mu}} \right)^{n_{\mu}} = \prod_{\mu} \frac{e^{-\beta \hbar \omega_{\mu} / 2}}{1 - e^{-\beta \hbar \omega_{\mu}}}$$

- The free energy in the harmonic approximation is thus

$$F = -\frac{1}{\beta} \ln Z_H = \sum_{\mu} \left[ \frac{1}{2} \hbar \omega_{\mu} - \frac{1}{\beta} \ln(1 + n_B(\omega_{\mu})) \right]$$

with  $n_B(\omega) = 1/(e^{\beta \hbar \omega} - 1)$  the Bose-Einstein occupation factor of bosons

# The contribution of ionic vibrations to the free energy in the harmonic approximation

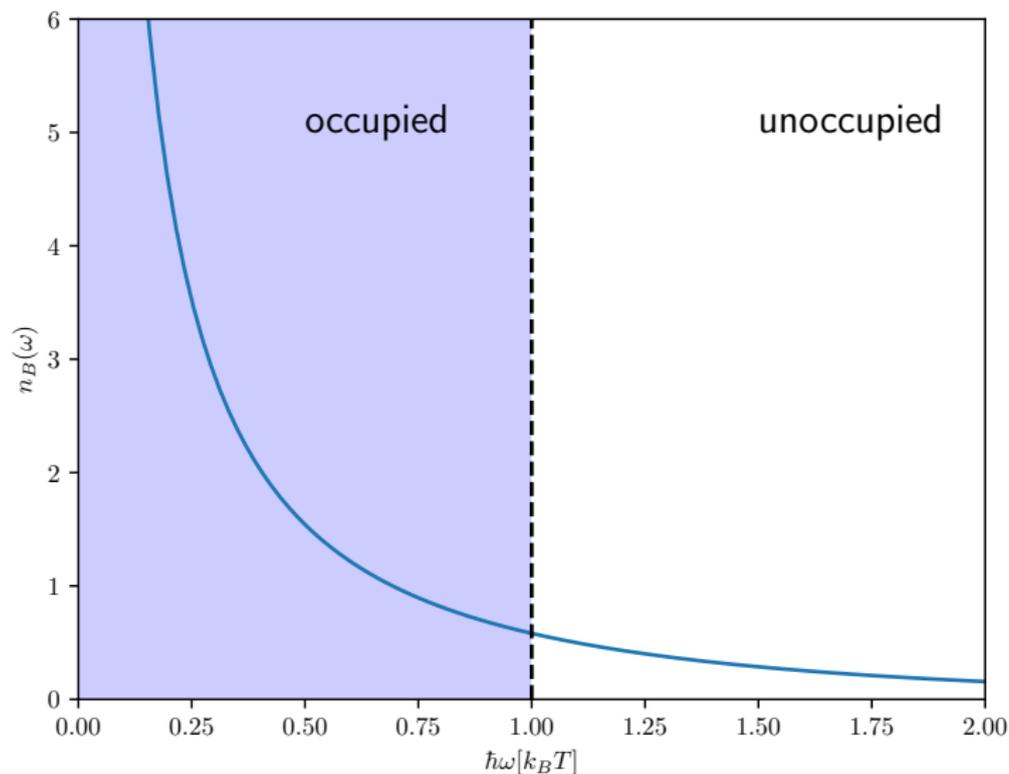
- It is easy to show that

$$E = \sum_{\mu} \hbar\omega_{\mu} \left( \frac{1}{2} + n_B(\omega_{\mu}) \right)$$
$$S = \sum_{\mu} \left[ \frac{\hbar\omega_{\mu}}{T} n_B(\omega_{\mu}) + k_B \ln(1 + n_B(\omega_{\mu})) \right]$$

- Comparing the equation for the energy with the eigenenergy of the Hamiltonian,  $\sum_{\mu} \hbar\omega_{\mu} [n_{\mu} + \frac{1}{2}]$ , we observe that at thermal equilibrium the occupation of each normal mode is given by  $n_B(\omega_{\mu})$

# The Bose-Einstein occupation factor

- Only phonon modes with  $\hbar\omega_\mu < k_B T$  are occupied



# The Bose-Einstein occupation factor and the quantum or classical contribution to the energy

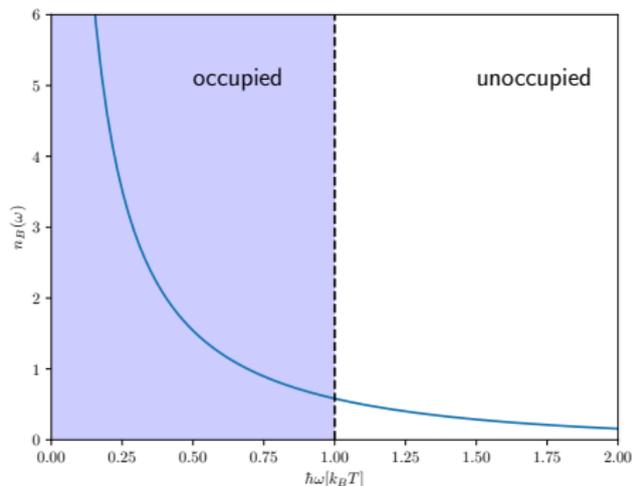
- The contribution of each mode to the energy is

$$E_\mu = \hbar\omega_\mu \left( \frac{1}{2} + n_B(\omega_\mu) \right)$$

- If the mode is largely occupied,  $k_B T \gg \hbar\omega_\mu$

$$E_\mu \sim \frac{1}{2} \hbar\omega_\mu + k_B T$$

- $\hbar\omega_\mu/2$  is the quantum contribution
- Despite been unoccupied, all modes have always a quantum contribution
- $k_B T$  the classical contribution of one oscillator in statistical mechanics



- If temperature is sufficiently large the system will behave classically and

$$E_\mu \sim k_B T$$

What is the main problem of molecular dynamics simulations?

# The probability distribution function defined by the harmonic density matrix

- The probability to find the ionic system in a general position  $\mathbf{R}$  can be calculated from the density matrix as

$$\rho_H(\mathbf{R}, \beta) = \langle \mathbf{R} | \rho_H | \mathbf{R} \rangle$$

- As in the harmonic approximation  $H = \sum_i H_i$  is separable in the normal mode basis, the probability in the normal mode basis  $\mathbf{Q}$  will be a product of the probability associated to a single oscillator

$$\rho_H(\mathbf{Q}, \beta) = \langle \mathbf{Q} | \rho_{H_i} | \mathbf{Q} \rangle$$

- This probability distribution function can be calculated from the differential equation

$$-\frac{\partial \rho_H(\mathbf{Q}, \beta)}{\partial \beta} = H(\mathbf{Q}) \rho_H(\mathbf{Q}, \beta)$$

# The probability distribution function defined by the harmonic density matrix

- The solution is a Gaussian function (dropping the  $\beta$  dependence)

$$\rho_H(\mathbf{Q}) = \frac{1}{\sqrt{2\pi a^2}} e^{-\frac{Q^2}{2a^2}}$$

where

$$a^2 = \frac{\hbar}{2\omega} [1 + 2n_B(\omega)]$$

- At  $T = 0$   $n_B(\omega) = 0$  and  $\rho_H(\mathbf{Q}) = \Psi_0^2(\mathbf{Q})$
- The probability distribution function for the full crystal in normal modes

$$\rho_H(\mathbf{Q}) = \prod_{\mu} \frac{1}{\sqrt{2\pi a_{\mu}^2}} e^{-\frac{Q_{\mu}^2}{2a_{\mu}^2}}$$

- Transforming to the position basis

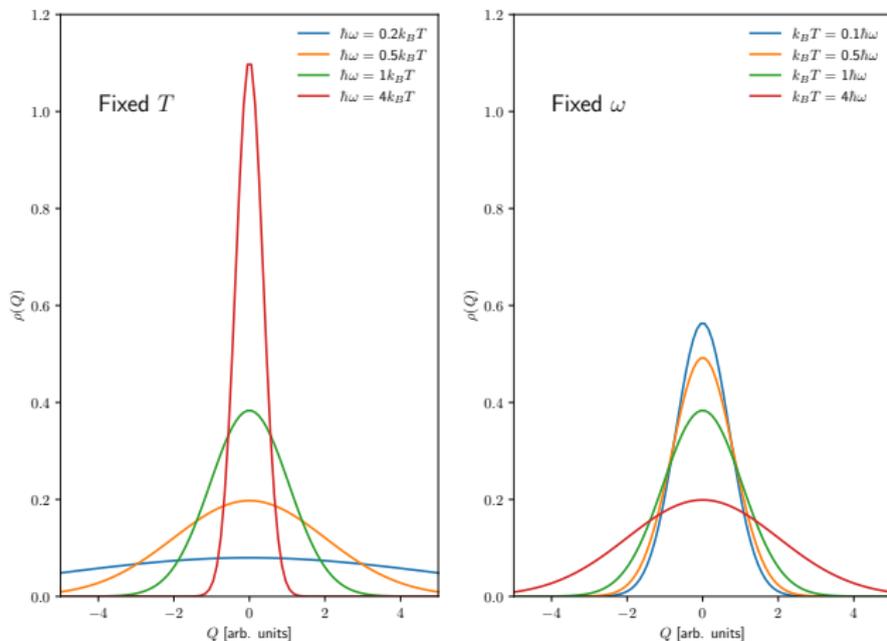
$$\rho_H(\mathbf{R}) = \sqrt{\det[\Psi^{-1}/(2\pi)]} e^{-\frac{1}{2} \sum_{ab} (R_a - R_{a0}) \Psi_{ab}^{-1} (R_b - R_{b0})}$$

where the matrix  $\Psi^{-1}$  is

$$\Psi_{ab}^{-1} = \sqrt{M_a M_b} \sum_{\mu} \frac{e_{\mu}^a e_{\mu}^b}{a_{\mu}^2}$$

# The probability distribution function defined by the harmonic density matrix

- The width of the Gaussian probability is proportional to  $a_{\mu}^2$
- The higher the frequency the more peaked the distribution, the higher the temperature the wider



# Quantum statistical averages

- Given the density matrix, the quantum statistical average of any operator that just depends on the ionic positions  $O(\mathbf{R})$  can be calculated as

$$\langle O \rangle_{\rho_H} = \text{tr}(O\rho_H) = \int d\mathbf{R} O(\mathbf{R}) \rho_H(\mathbf{R})$$

- An example:

The mean square displacement of an ion

$$\begin{aligned} \langle u_a^2 \rangle_{\rho_H} &= \int d\mathbf{R} u_a^2(\mathbf{R}) \rho_H(\mathbf{R}) = \sum_{\mu\nu} \frac{e_\mu^a e_\nu^a}{M_a} \int d\mathbf{Q} Q_\mu Q_\nu \rho_H(\mathbf{Q}) \\ &= \sum_{\mu\nu} \frac{e_\mu^a e_\nu^a}{M_a} \int d\mathbf{Q} Q_\mu Q_\nu \prod_{\mu'} \frac{1}{\sqrt{2\pi a_{\mu'}^2}} e^{-\frac{Q_{\mu'}^2}{2a_{\mu'}^2}} \\ &= \sum_{\mu\nu} \frac{e_\mu^a e_\nu^a}{M_a} \int dQ_\mu dQ_\nu Q_\mu Q_\nu \frac{1}{\sqrt{(2\pi)^2 a_\mu^2 a_\nu^2}} e^{-\frac{Q_\mu^2}{2a_\mu^2}} e^{-\frac{Q_\nu^2}{2a_\nu^2}} = \sum_{\mu\nu} \frac{e_\mu^a e_\nu^a}{M_a} \delta_{\mu\nu} a_\mu^2 \\ &= \sum_{\mu} \frac{e_\mu^a e_\mu^a}{M_a} \frac{\hbar}{2\omega_\mu} [1 + 2n_B(\omega_\mu)] \end{aligned}$$

# The mean square displacement in the quantum and classical limit

$$\langle u_a^2 \rangle_{\rho_H} = \sum_{\mu} \frac{e_{\mu}^a e_{\mu}^a}{M_a} \frac{\hbar}{2\omega_{\mu}} [1 + 2n_B(\omega_{\mu})]$$

- Even at zero temperature ( $n_B(\omega_{\mu}) = 0$ ) there is displacement

$$\langle u_a^2 \rangle_{\rho_H} = \sum_{\mu} \frac{e_{\mu}^a e_{\mu}^a}{M_a} \frac{\hbar}{2\omega_{\mu}},$$

the zero point motion

- In the classical limit ( $k_B T \gg \hbar\omega$ )

$$\langle u_a^2 \rangle_{\rho_H} \sim \sum_{\mu} \frac{e_{\mu}^a e_{\mu}^a}{M_a} \frac{\hbar}{2\omega_{\mu}} \left( 1 + \frac{2k_B T}{\hbar\omega_{\mu}} \right)$$

or even neglecting the quantum contribution

$$\langle u_a^2 \rangle_{\rho_H} \sim \sum_{\mu} \frac{e_{\mu}^a e_{\mu}^a}{M_a} \frac{k_B T}{\omega_{\mu}^2},$$

no displacement at zero temperature

# Thermodynamic quantities in the harmonic approximation

- Once the energy, entropy, and free energy are known, thermodynamic variables can be calculated
  - The constant volume specific heat

$$C_V = \left( \frac{\partial E}{\partial T} \right)_V = - \left( \frac{\partial^2 F}{\partial T^2} \right)_V$$

- The constant pressure specific heat

$$C_P = \left( \frac{\partial H}{\partial T} \right)_P$$

where the enthalpy is  $H = E + PV$  and the pressure  $P = -\frac{\partial E}{\partial V}$

# The constant volume specific heat

- The constant volume specific heat

$$C_V = \left( \frac{\partial E}{\partial T} \right)_V = \sum_{\mu} \hbar \omega_{\mu} \frac{\partial n_B(\omega_{\mu})}{\partial T}$$

- In the classical high-temperature limit  $n_B(\omega_{\mu}) \rightarrow k_B T / (\hbar \omega_{\mu})$  and

$$C_V = 3N_{\text{at}} k_B,$$

each mode contributes to the specific heat  $k_B$  (Dulong and Petit law)

- In the low-temperature limit only very low energy modes will contribute to the specific heat: acoustic modes

$$\begin{aligned} C_V &= \sum_{\mu \mathbf{q}} \hbar \omega_{\mu}(\mathbf{q}) \frac{\partial n_B(\omega_{\mu}(\mathbf{q}))}{\partial T} \sim \frac{\Omega}{(2\pi)^3} \sum_{\mu} \int d\mathbf{q} \hbar c_{\mu}(\hat{\mathbf{q}}) q \frac{\partial n_B(c_{\mu}(\hat{\mathbf{q}}) q)}{\partial T} \\ &= \frac{\Omega}{(2\pi)^3} \sum_{\mu} \int dq d\Omega_{\hat{\mathbf{q}}} \hbar c_{\mu}(\hat{\mathbf{q}}) q^3 \frac{\partial n_B(c_{\mu}(\hat{\mathbf{q}}) q)}{\partial T} \end{aligned}$$

where  $\Omega_{\hat{\mathbf{q}}}$  is the solid angle in reciprocal space

# The constant volume specific heat

- Making the  $x = \beta \hbar c_\mu(\hat{\mathbf{q}})q$  change of variables and defining the average inverse third power of the acoustic velocities as

$$\frac{1}{c^3} = \frac{1}{3} \sum_{\mu} \int \frac{d\Omega_{\hat{\mathbf{q}}}}{4\pi} \frac{1}{c_{\mu}^3(\hat{\mathbf{q}})}$$

we obtain

$$C_V \sim \Omega \frac{\partial}{\partial T} \frac{(k_B T)^4}{(\hbar c)^3} \frac{3}{2\pi^2} \int_0^{\infty} dx \frac{x^3}{e^x - 1} = \frac{2\pi^2}{5} k_B \left( \frac{k_B T}{\hbar c} \right)^3$$

- The low-temperature specific heat is not constant, it goes as  $T^3$  thanks to quantum effects

# The constant volume specific heat at intermediate temperatures

- The Debye approximation substitutes all phonons branches by three linear modes with the same  $\omega = ck$  dispersion and performs the integral in a sphere with radius  $q_D$  that contains a total number of  $N$   $\mathbf{q}$  points

$$N/\Omega = q_D^3/(6\pi^2)$$

- Then, making the  $\beta\hbar cq = x$  transformation

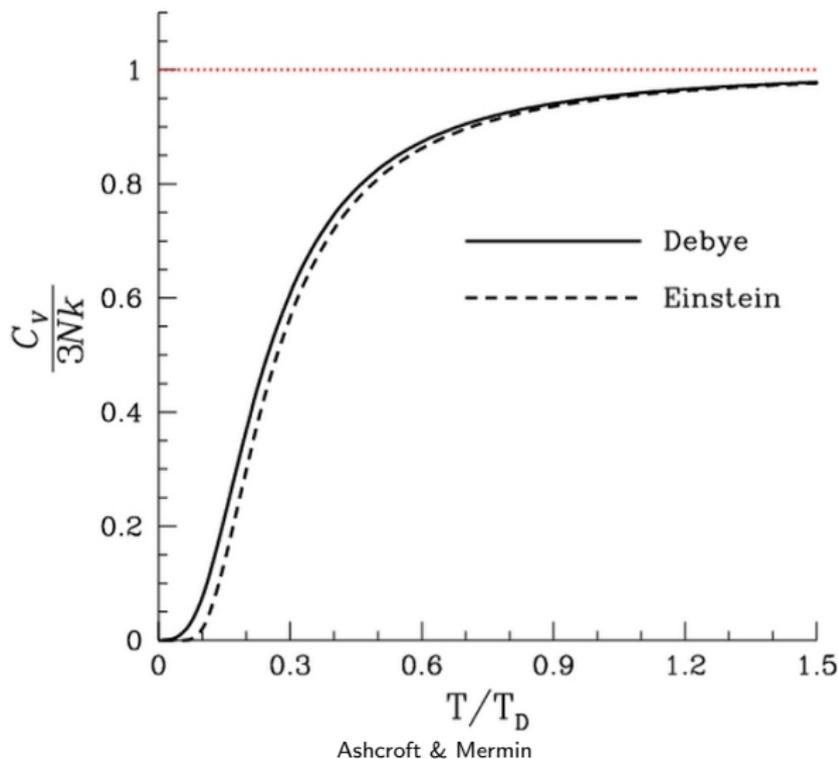
$$C_V = 9Nk_B \left( \frac{T}{\Theta_D} \right)^3 \int_0^{\Theta_D/T} dx \frac{x^4 e^x}{(e^x - 1)^2}$$

where the Debye temperature  $\Theta_D$  is defined as  $k_B\Theta_D = \hbar cq_D$

- In the Einstein approximation the acoustic modes are approximated as in the Debye model, but the optical modes are treated without dispersion and frequency  $\omega_E$
- The contribution of each mode to the specific heat is

$$Nk_B \frac{(\beta\hbar\omega_E)^2 e^{\beta\hbar\omega_E}}{(e^{\beta\hbar\omega_E} - 1)^2}$$

# The constant volume specific heat in the Debye and Einstein models



# The phonon density of states (PDOS)

- The PDOS tells as how many phonon modes are with a particular frequency
- It is usually given per unit cell

$$g(\omega) = \frac{1}{N} \sum_{\mu \mathbf{q}} \delta(\omega - \omega_{\mu}(\mathbf{q}))$$

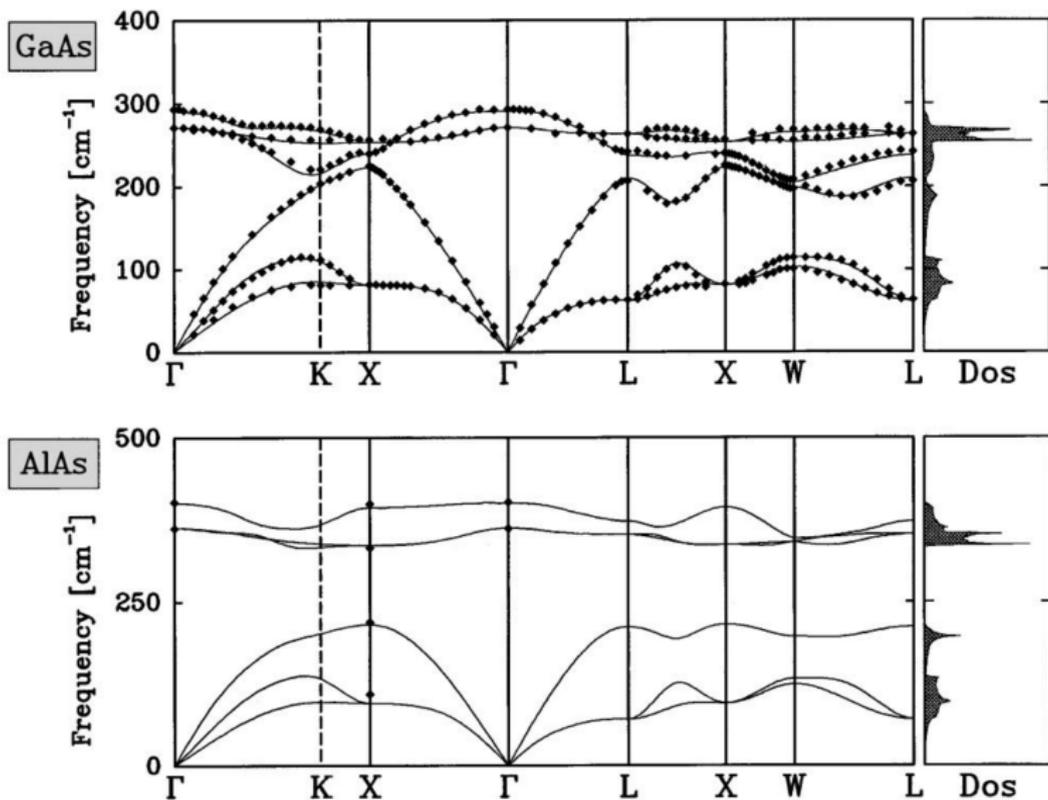
- It can be written as an integral (Ashcroft & Mermin)

$$g(\omega) = \frac{\Omega}{N} \frac{1}{(2\pi)^3} \sum_{\mu} \int d\mathbf{q} \delta(\omega - \omega_{\mu}(\mathbf{q})) = \frac{\Omega}{N} \frac{1}{(2\pi)^3} \sum_{\mu} \int dS \frac{1}{|\nabla \omega_{\mu}(\mathbf{q})|}$$

The surface integral is performed on a surface of the first BZ for which  $\omega_{\mu}(\mathbf{q}) = \omega$

- Regions of the first BZ with non-dispersive phonons will give peaks of the PDOS

# The phonon density of states (PDOS)



Baroni et al., RMP 73, 515 (2001)

# The phonon density of states (PDOS)

- The PDOS can be used to calculate many sums over the first BZ that involve phonon frequencies
- The energy per unit cell can be calculated as

$$\begin{aligned} E &= \frac{1}{N} \sum_{\mu \mathbf{q}} \hbar \omega_{\mu}(\mathbf{q}) \left( \frac{1}{2} + n_B(\omega_{\mu}(\mathbf{q})) \right) \\ &= \frac{1}{N} \sum_{\mu \mathbf{q}} \int_0^{\infty} d\omega \delta(\omega - \omega_{\mu}(\mathbf{q})) \hbar \omega \left( \frac{1}{2} + n_B(\omega) \right) \\ &= \int_0^{\infty} d\omega \hbar \omega \left( \frac{1}{2} + n_B(\omega) \right) g(\omega) \end{aligned}$$

- From the knowledge of the PDOS many thermodynamic variables can be calculated by numerical integration

# Matsubara Green's functions

- When we want to study correlation functions of different operators at finite temperature, we need the Matsubara Green's function formalism
- This is crucial to understand experimental results
- Time is complex in Matsubara's formalism:  $z$
- A bosonic correlation function is defined as

$$A(z) = -\langle T_z A(z) A(0) \rangle_{\rho_H}$$

where  $T_z$  is the time order operator and  $A(z) = e^{zH/\hbar} A e^{-zH/\hbar}$

- Then the Fourier transformed is given by

$$A(i\omega_n) = \int_0^{\hbar\beta} dz e^{i\omega_n z} A(z)$$

with  $\omega_n = \frac{2\pi n}{\beta}$  the Matsubara phononic frequencies

# The displacement correlation function in the harmonic approximation

- In order to study phononic properties the interesting Green function is the displacement correlation function

$$G_{ab}(z) = -\sqrt{M_a M_b} \langle T_z u_a(z) u_b(0) \rangle_{\rho_H}$$

- In the harmonic approximation, using bosonic ladder operators

$$G_{ab}(z) = -\sum_{\mu\mu'} e_{\mu}^a e_{\mu'}^b \frac{\hbar}{2\sqrt{\omega_{\mu}\omega'_{\mu}}} \langle e^{zH/\hbar} (b_{\mu} + b_{\mu}^{\dagger}) e^{-zH/\hbar} (b_{\mu'} + b_{\mu'}^{\dagger}) \rangle_{\rho_H}$$

- Making the use of the properties (see Mahan book)

$$e^{zH/\hbar} b_{\mu} e^{-zH/\hbar} = b_{\mu} e^{-z\omega_{\mu}} \quad \text{and} \quad e^{zH/\hbar} b_{\mu}^{\dagger} e^{-zH/\hbar} = b_{\mu}^{\dagger} e^{z\omega_{\mu}}$$

and  $\langle b_{\mu}^{\dagger} b_{\mu} \rangle_{\rho_H} = n_B(\omega_{\mu})$ , we obtain

$$G_{ab}(z) = -\sum_{\mu} e_{\mu}^a e_{\mu}^b \frac{\hbar}{2\omega_{\mu}} [(n_B(\omega_{\mu}) + 1)e^{-z\omega_{\mu}} + n_B(\omega_{\mu})e^{z\omega_{\mu}}]$$

- Performing the Fourier transform to the frequency domain

$$G_{ab}(i\omega_n) = \sum_{\mu} \frac{e_{\mu}^a e_{\mu}^b}{(i\omega_n)^2 - \omega_{\mu}^2}$$

# The displacement correlation function in the harmonic approximation

- It is interesting to note that

$$G_{ab}^{-1}(i\omega_n) = (i\omega_n)^2 \delta_{ab} - \frac{\overset{(2)}{\phi}_{ab}}{\sqrt{M_a M_b}}$$

- The 0 frequency limit, integral on time, over the inverse of the correlation function gives minus the dynamical matrix

$$G_{ab}^{-1}(i\omega_n = 0) = -\frac{\overset{(2)}{\phi}_{ab}}{\sqrt{M_a M_b}}$$

This is the result expected for thermodynamics, as this corresponds to the static limit

- The same time correlation function ( $z = 0$ ) is

$$G_{ab}(z = 0) = -\sqrt{M_a M_b} \langle u_a u_b \rangle_{\rho_H} = -\sum_{\mu} e_{\mu}^a e_{\mu}^b a_{\mu}^2 = \sqrt{M_a M_b} \Psi_{ab}$$

where the  $\Psi$  matrix was already introduced when analyzing the harmonic probability distribution function

- 1 Show that in the normal mode basis in reciprocal space the ionic Hamiltonian can be written as

$$H_i = \frac{1}{2N} \sum_{\mu q} \left( |\hat{P}_\mu|^2 + \omega_\mu^2 |\hat{Q}_\mu|^2 \right)$$

- 2 Show that in the harmonic approximation

$$E = \sum_{\mu} \hbar \omega_{\mu} \left( \frac{1}{2} + n_B(\omega_{\mu}) \right)$$

$$S = \sum_{\mu} \left[ \frac{\hbar \omega_{\mu}}{T} n_B(\omega_{\mu}) + k_B \ln(1 + n_B(\omega_{\mu})) \right]$$

- 3 Show that in the high-temperature limit the contribution to the energy of a phonon mode is  $\frac{1}{2} \hbar \omega_{\mu} + k_B T$
- 4 Show that  $N/\Omega = q_D^3/(6\pi^2)$  in the Debye approximation
- 5 Show that the contribution of each optical mode to the specific heat in the Einstein model is  $Nk_B \frac{(\beta \hbar \omega_E)^2 e^{\beta \hbar \omega_E}}{(e^{\beta \hbar \omega_E} - 1)^2}$

- 6 Show that in the harmonic approximation the displacement correlation function is given in the time and frequency domains by

$$G_{ab}(z) = - \sum_{\mu} e_{\mu}^a e_{\mu}^b \frac{\hbar}{2\omega_{\mu}} [(n_B(\omega_{\mu}) + 1)e^{-z\omega_{\mu}} + n_B(\omega_{\mu})e^{z\omega_{\mu}}]$$

$$G_{ab}(i\omega_n) = \sum_{\mu} \frac{e_{\mu}^a e_{\mu}^b}{(i\omega_n)^2 - \omega_{\mu}^2}$$