

CHM 421/621

Statistical Mechanics

**Lecture 28 Statistical Mechanics of Molecules and
Solids**

Molecules and Solids

Lecture Plan

Born-Oppenheimer Approximation

Normal modes of vibration: polyatomic molecules

Normal modes of vibration in crystals: Phonons

Debye theory of specific heat of crystals

Molecules and Solids

Born-Oppenheimer Approximation

Full Molecular Schrodinger Equation

$$\hat{H}\Phi(\{r_i, R_I\}) = E\Phi(\{r_i, R_I\})$$

where

$$\hat{H} = \sum_{I=1}^N -\frac{\hbar^2}{2M_I} \nabla_I^2 + \hat{H}_{el}(\{\vec{r}_i, \vec{R}_I\})$$

$$\hat{H}_{el}(\{\vec{r}_i, \vec{R}_I\}) = \sum_{i=1}^{N_e} -\frac{\hbar^2}{2m} \nabla^2 - \sum_{I=1}^N \sum_{i=1}^{N_e} \frac{K Z_I e^2}{r_{i,I}} + \sum_{i=1}^{N_e} \sum_{j=1}^{N_e} \frac{e^2}{r_{i,j}} + \sum_{I=1}^N \sum_{J=1}^N \frac{Z_I Z_J e^2}{R_{I,J}}$$

Clamped nuclear equation or Electronic Schrodinger equation

$$\hat{H}_{el}(\{\vec{r}_i; \vec{R}_I\}) \Psi_n(\{\vec{r}_i; \vec{R}_I\}) = E_n(\{\vec{R}_I\}) \Psi_n(\{\vec{r}_i; \vec{R}_I\})$$


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Born-Oppenheimer Approximation

B-O Approximation: Nuclei much more massive than electrons => we can treat nuclei as static in the electronic problem

$$\Phi_n (\{r_i, R_I\}) \approx \chi_n (\{R_I\}) \times \Psi_n (\{\vec{r}_i\}; \{\vec{R}_I\})$$

So that effectively,

$$\hat{H} = \sum_{I=1}^N -\frac{\hbar^2}{2M_I} \nabla_I^2 + E_n (\{R_I\})$$


Potential energy surface (PES)

Nuclear motion is often treated classically unless the nuclei are light.

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Born-Oppenheimer Approximation

Potential energy surface for diatomic molecule

$$\hat{H} \approx \hat{T}_{CM} + \frac{\hat{J}^2}{2\mu R_0^2} + \left[\frac{-\hbar^2}{2\mu} \frac{d^2}{dR^2} + E_n(R) \right]$$

Translational motion

Rotational motion (Rigid rotor)

Vibrational motion (Harmonic oscillator)

R_0 is equilibrium bond length

$$E_n(R) \approx E_n(R_0) + \frac{1}{2}(R - R_0)^2 \left(\frac{\partial^2 E_n}{\partial R^2} \right)_{R=R_0} + \dots$$

Molecules and Solids

Born-Oppenheimer Approximation

Potential energy surface for polyatomic molecules

\mathbf{R}_0 is equilibrium configuration

$$E_n(\mathbf{R}) \approx E_n(\mathbf{R}_0) + \frac{1}{2} \sum_{I,J} \sum_{\alpha,\beta} (\Delta R_{I,\alpha}) (\Delta R_{J,\beta}) \left(\frac{\partial^2 E_n}{\partial R_{I,\alpha} \partial R_{J,\beta}} \right)_{\mathbf{R}=\mathbf{R}_0}$$

Can be transformed into normal mode coordinates (uncoupled harmonic oscillators).

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Born-Oppenheimer Approximation

Potential energy surface for polyatomic molecules

$$D_{I\alpha, J\beta} = \sqrt{M_I M_J} \left(\frac{\partial^2 E_n}{\partial R_{I,\alpha} \partial R_{I,\beta}} \right)_{\mathbf{R}_0} \quad \text{Dynamical Matrix}$$

We can show that

$$\Delta E_n(\mathbf{R}) = \frac{1}{2} \sum_{j=1}^{3N-d} \omega_j^2 Q_j^2$$

$d = 5$ (linear) or 6 (non-linear)

Q_j - normal mode coordinate of the j^{th} eigenvector

ω_j^2 - j^{th} eigenvalue of the dynamical matrix

Therefore,

$$\hat{H}_{vib} = \sum_{j=1}^{3N-d} \frac{1}{2} \left[-\hbar^2 \frac{\partial^2}{\partial Q_j^2} + \omega_j^2 Q_j^2 \right]$$

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Molecular vibrational partition function for polyatomic

So we can essentially treat the system as having $3N-d$ harmonic oscillators

The canonical partition function then follows as

$$Z_{vib} = \prod_{j=1}^{3N-d} \left(\frac{e^{-\beta\hbar\omega_j/2}}{1 - e^{-\beta\hbar\omega_j}} \right)$$

$$\bar{\epsilon}_{vib} = \sum_{j=1}^{3N-d} \frac{\hbar\omega_j}{2} + \sum_{j=1}^{3N-d} \frac{\hbar\omega_j}{e^{\frac{\hbar\omega_j}{k_B T}} - 1}$$

$$C_{V,vib} = k_B \sum_{j=1}^{3N-d} \left(\frac{\hbar\omega_j}{2k_B T} \right)^2 \frac{1}{\sinh^2 \left(\frac{\beta\hbar\omega_j}{2k_B T} \right)}$$
$$\approx (3N - d)k_B \quad (\hbar\omega_j \ll k_B T)$$

Molecules and Solids

Normal modes of vibrations in a crystal

In crystals N is very large. Additionally, we can expect that there may be many modes differing very slightly in frequency.

In this case, it is more appropriate to use a density of states to integrate over all allowed vibration frequencies.

$$\bar{\epsilon} = \int_0^{\infty} d\nu \, g(\nu) \frac{h\nu}{e^{\frac{h\nu}{k_B T}} - 1}$$

The density of states can be obtained by simple theories or numerical calculations.

Molecules and Solids

Normal modes of vibrations in a crystal

Debye model: In this model it is assumed that the frequencies in a crystal are continuously distributed in the range $0 < \nu < \nu_m$

The number of oscillators with frequencies between ν to $\nu + d\nu$ is taken to be

$$g(\nu)d\nu = \left(\frac{9N}{\nu_m^3}\right) \nu^2 d\nu \quad (\text{see McQuarrie})$$

assuming that they all correspond to an *acoustic* branch of lattice vibrations.

$$\begin{aligned} \bar{\epsilon} &= \left(\frac{9N}{\nu_m^3}\right) \int_0^{\nu_m} d\nu \nu^2 \frac{h\nu}{e^{\frac{h\nu}{k_B T}} - 1} \quad \Longrightarrow \quad C_V = \left(\frac{9N}{\nu_m^3}\right) \int_0^{\nu_m} d\nu \nu^2 \frac{(\beta h\nu/2)^2}{\sinh(\beta h\nu/2)^2} \\ &= 3Nk_b D \left(\frac{\Theta_D}{T}\right) \end{aligned}$$