Phonon Dispersion,
Interatomic Force Constants
Thermodynamic Quantities

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OUTLINE

● Vibrations and interatomic force constants (IFC)

● Extended periodic versus confined Systems

● IFCs of extended periodic systems

● Thermodynamic properties:
  – Harmonic description
  – Weak anharmonic effects
  – Strong anharmonic effects
Introduction

- Vibrations:
  - Brillouin, Infra-Red and Raman spectroscopies
  - Thermal properties
  - Ferroelectricity, pyroelectricity (piezoelectrics)
  - Superconductivity
  - Transport properties

- Force constant matrices:
  \[ K^{\alpha\beta}_{\kappa\kappa'} = \frac{\partial F_{\kappa\alpha}}{\partial \tau_{\kappa'\beta}} \]
  → Frozen phonon calculations
  \[ K^{\alpha\beta}_{\kappa\kappa'} = \frac{\partial^2 E}{\partial \tau_{\kappa\alpha} \partial \tau_{\kappa'\beta}} \]
  → Linear response calculations

Eigenvalues of \( D^{\alpha\beta}_{\kappa\kappa'} = K^{\alpha\beta}_{\kappa\kappa'}/\sqrt{M_{\kappa}M_{\kappa'}}; \quad \omega_\mu^2 \)

- \( K \): Nature of interaction: (1) anisotropy (2) short-range (covalent) vs. long-range (ionic)
Confined vs. Extended Systems

- Confined System: Eg. molecule, cluster
  - Number of vibrations $= 3 \times N_a$
  - Force constants matrices between two atoms directly relate to their interaction potential.

- Extended periodic systems: Eg. Crystal
  - Number of vibrations $= \infty$
    $3 \times N_a$ per unit cell, $\vec{q} \in BZ$.
  - Image effects in the force constants:
    - force constant matrix between two atoms depends on the interaction between them AND their images.
Phonons in Periodic Systems

- Phonon bands (analogous to electrons)
  \[ \omega(\vec{q}, l), \vec{q} \in BZ, l \in [1, 3Na] \]
  \[ e_i(\kappa|\vec{q}, l): l\text{th band eigenvector at } \vec{q}, \]
  \[ i \text{ and } \kappa \text{ denote Cartesian and atom indices} \]
  obtained with diagonalization of dynamical matrix:
  \[ A_{ij}(\kappa\kappa'|\vec{q}): \text{DFT-LR} \]

- Interatomic force constants:

  \[ \Phi_{ij}(0\kappa; \vec{R}\kappa') = \frac{1}{\Omega_{BZ}} \int_{BZ} A_{ij}(\kappa\kappa'|\vec{q})e^{-i\vec{q} \cdot \vec{R}} d^3 \vec{q} \]

  Assuming short-ranged interactions,

  \[ \Phi_{ij}(0\kappa; \vec{R}\kappa') = \sum_{\vec{q} \in \text{Grid}(N_1N_2N_3)} A_{ij}(\kappa\kappa'|\vec{q})e^{-i\vec{q} \cdot \vec{R}} d^3 \vec{q} \]

  for \( \vec{R} + \vec{r}_\kappa - \vec{r}_{\kappa'} \in \text{Box}(N_1N_2N_3). \)

  **Interactions are not short-ranged**;

  Effects of images enter. e.g. Dipolar interactions, Fridel oscillations in metals.
IFCs in Periodic Systems

- Decompose the dynamical matrices into
  (a) long-ranged part (treated analytically).
  (b) remaining short-range part (treated with a grid Fourier transform).

- Insulators: long-ranged interactions manifest in the LO-TO splitting (nonanalyticity) in $\omega(\vec{q}, \ell)$ at $\vec{q} = \vec{0}$:

$$A_{ij}^{dd}(\kappa\kappa' | \vec{q} \to \vec{0}) = \frac{4\pi}{\Omega} \frac{(\sum_k Z_{\kappa,i}^* q_k)(\sum_k Z_{\kappa',j}^* q_k)}{\sum_{kl} q_k e_{kl} q_l}$$

- Limiting behavior of dipole-dipole interatomic forces, with $\epsilon^{-1}$ as a metric in real-space
  - $\mu_{\kappa i} = \sum_j Z_{\kappa,i}^* \epsilon_{ij}^{-1} \Delta \tau_{\kappa,j}$
  - evaluated using Ewald summation technique.

Phonons in periodic systems

1. Obtain phonons at wavevectors $\vec{q} \in (N_1, N_2, N_3)$ grid (BZ) using DFT-LR: $A(\vec{q})$

2. Use $\epsilon$ and $Z^*\kappa_{ij}$ obtained from DFT-LR at $\Gamma$ ($\vec{q} = (000)$), to model dipolar interatomic interaction: $A^{dd}(\vec{q})$

3. Obtain short-range part of the dynamical matrix $A^{SR}(\vec{q}) = A(\vec{q}) - A^{dd}(\vec{q})$

4. Fourier (discrete) transform $A^{SR}(\vec{q})$ to obtain real-space interatomic force constants: $\Phi$

5. Phonons at any $\vec{q}$ can now be obtained: $A(\vec{q}) = A^{dd}(\vec{q}) + \text{Fourier}(\Phi)$

6. Thermodynamic quantities can be obtained with access to $A$ on a fine grid of $\vec{q}$. 
Thermodynamic Properties

- Phonons: primary contributors to thermodynamic properties
electrons: metals at low temperatures.

- Many properties depend on only phonon frequencies.

\[
\sum_{\vec{q}, l} f(\omega(\vec{q}, l)) = 3N_a N \int_0^{\omega_{max}} f(\omega) g(\omega) d\omega
\]

- Normalized phonon density of states:

\[
g(\omega) = \frac{1}{3N_a N} \sum_{\vec{q}, l} \delta(\omega - \omega(\vec{q}, l))
\]

- Partition function:

\[
Z = \prod_{\vec{q}, l} (2 \sinh(\frac{\hbar \omega(\vec{q}, l)}{2k_B T}))^{-1}
\]
• Helmholtz free energy:
  (obtained as \(\ln\) of \(Z\))

\[
\Delta F = 3N_a N k_B T \int_0^{\omega_{max}} \ln(2 \sinh(\frac{\hbar \omega(q, l)}{2k_B T})) g(\omega) d\omega
\]

• Internal energy:
  obtained using (Ashcroft and Mermin)

\[
U = E_{eq} + \sum_{\vec{q}, \ell} \frac{1}{2} \frac{\hbar \omega(\vec{q} \ell)}{2} \left(1 + \frac{2}{e^{\frac{\hbar \omega(\vec{q}, l)}{k_B T}} - 1}\right)
\]

Thus,

\[
\Delta U = 3N_a N \frac{\hbar}{2} \int_0^{\omega_{max}} \omega \coth(\frac{\hbar \omega(\vec{q}, l)}{2k_B T}) g(\omega) d\omega
\]

• Specific heat (constant volume):
  (derivative of \(U\) with respect to \(T\))

\[
C_v = 3N_a N k_B \int_0^{\omega_{max}} \left(\frac{\hbar \omega}{2k_B T}\right)^2 \cosh^2(\frac{\hbar \omega(\vec{q}, l)}{2k_B T}) g(\omega) d\omega
\]
• Entropy: \( S = (U - F)/T \)

\[
C_v = 3N_aNk_B \int_{0}^{\omega_{max}} \left[ \frac{\hbar \omega}{2k_B T} \coth \left( \frac{\hbar \omega (q, l)}{2k_B T} \right) \right. \\
- \ln \left( 2 \sinh \left( \frac{\hbar \omega (q, l)}{2k_B T} \right) \right) g(\omega) d\omega
\]

• Note that phonons have been treated here within harmonic approximation. One can obtain variation in \( F, U, S \) and \( C_v \) with \( T \), but no thermal expansion!

• To determine structure, bulk modulus, \( C_p \) as a function of \( T \), one has to include anharmonic interactions among phonons.

• A simple approach - quasi-harmonic approximation:
Free energy is calculated using above formalism as a function of structural parameters and the structure is obtained by free-energy minimization (eg. Ref. Xie et al, PRB 59, 965 (99)).
Thermodynamics: thermal expansion

- $V(T)$ determined from a quasi-harmonic approximation can yield $\alpha$ (thermal expansion coefficient).

- In terms of density of states:

$$
\alpha = \frac{N_a N k_B}{B} \int d\omega \frac{\partial g(\omega)}{\partial \Omega} \left[ \ln\left( e^{\frac{\hbar \omega}{k_B T}} - 1 \right) - \frac{\hbar \omega}{k_B T} \frac{e^{\frac{\hbar \omega}{k_B T}}}{e^{\frac{\hbar \omega}{k_B T}} - 1} \right]
$$

- Atomic temperature factor (X-ray diffraction) $e^{-W(\kappa)}$

Structure factor $F_T = \sum_\kappa e^{-W(\kappa)} e^{i\vec{G}\cdot\vec{\kappa}}$

$$
e^{-W(\kappa)} = \exp\left(-\frac{1}{2} \sum_{ij} B_{ij}(\kappa) G_i G_j \right),
$$

$$
B_{ij} = \frac{1}{N} \sum_{\vec{q}\ell} \frac{\hbar}{2\omega} \coth\left( \frac{\hbar \omega}{2 k_B T} \right) e_i(\kappa|\vec{q}\ell) e_j^*(\kappa|\vec{q}\ell)
$$
Local harmonic approximation


- Classical limit ($\hbar \to 0$)

- Work with only on-site (local) harmonic interactions, neglect coupling between vibrations of different atoms.

- Given a perfect crystal at a volume (structure) and $T$, determine its Helmholtz free energy:

\[
A = \frac{1}{2} \sum_{\kappa\kappa'} u_{\kappa\kappa'}^0(r_{\kappa\kappa'}^0) + 3k_B T \sum_{\kappa} \ln \left( \frac{D_i^{1/6}}{k_B T} \right),
\]

where $D_i = (\prod_i \omega_{i\kappa})^2$.

- First-principles IFCs (local) can be directly input to this.
stress and electric field dependence of various properties can be determined by augmenting the free energy function:

$$F = F_0 - \Omega \sum_{ij} \sigma_{ij} e_{ij} - \sum_{ijk} E_i Z^*_{kij} \tau_{kj} + E_{\text{elastic}}$$

$$-\frac{\Omega}{4\pi} \sum_{ij} E_i \epsilon_{ij} E_j - \Omega \sum_{ijk} \epsilon_{ij} \gamma_{ijk} E_k + \sum_{ijkk} L_{ijkk} \epsilon_{ij} \tau_{kk}$$

See: $ABINIT/Infos/Theory/vanderbilt-anaddb-notes.pdf

Practically, modelling is a good idea: Taylor expand the free energy functional in terms of $\bar{\tau}$, $e_{ij}$ and $E_i$ and parameters in the expansion can be obtained from DFT calculations.

Ref. Hill and Waghmare.
Thermodynamics: strong anharmonicity


- Determine the full phonon dispersion and examine it along high symmetry lines.

- Identify the softest vibrational modes.

- Carry out symmetry analyses of modes at high symmetry $q$–points.

- Determine the symmetry of localized lattice Wannier function (centre and transformation property) that would span the subspace of softest modes.

- Determine the precise LWF by fitting to normal mode eigenvectors at high symmetry points.
• Write total energy as a Taylor expansion in lattice Wannier function coordinates and strain (and possibly harmonic expansion of other modes).

• Parameters in this expansion need be determined from DFT.

• Carry out large-scale Monte Carlo or Molecular Dynamics simulations to study thermodynamic properties.
Construction of Model for Transition

- High symmetry phase: reference structure
  \{ \vec{d}_{i\tau} \}: atomic displacements
  \{ e_{\alpha\beta} \}: strain
  \[ E_{lat} = E_h(\{\vec{d}_{i\tau}\}) + E_{anh}(\{\vec{d}_{i\tau}\}) + E_{elastic} \]

\[ E_{lat} = E_{h,\Lambda_0}(\xi_i) + E_{anh,\Lambda_0}(\xi_i) + E_{h,\Lambda_s}(u_i) \]

\[ Z = \int \prod_i du_i d\xi_i \exp(-E_{lat}) = Z_{\Lambda_0} \times Z_{\Lambda_s} \]

* Focus on the lowest energy subspace \( \Lambda_0 \), relevant to the phase transition.

\[ E_{model} = E_{h,\Lambda_0} + E_{anh,\Lambda_0} + E_{strain} \]

\( E_{model} \) is Projection of \( E_{lat} \) onto \( \Lambda_0 \) subspace
Resulting Model

Classical Spins

\[
PbTiO_3 \quad BaTiO_3
\]
Resulting Model: Form

**Model**

\[ H(\xi_i) \text{ Internal Distortions (atomic displacements/phonon)} \]

\[ + \ H( e_{\alpha\beta}) \text{ Homogeneous Distortions of the unit cell (strain) Elastic energy} \]

\[ + \ H(\xi_i, e_{\alpha\beta}) \text{ Coupling between strain and phonons} \]

\[ + \ H(\xi_i, \sigma_i) \text{ Compositional Order, } \sigma_i \text{ its local field effects} \]

Polarization: \( P \propto \Sigma \xi_i \)

Cubic: \( P = (0, 0, 0) \)

Tetragonal: \( P = (0, 0, 1) \) p

Orthorhombic: \( P = (1, 1, 0) \) p

Rhombohedral: \( P = (1, 1, 1) \) p
Summary

- Phonons: thermodynamic properties
- Interatomic force constants: nature of interactions
- IFCs of periodic systems: long ranged + short ranged
- → Access to full phonon dispersion
- Thermodynamics:
  - Quasi-harmonic approximation
  - Lattice Wannier functions
References


