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:

$$K^{\alpha\beta}_{\kappa\kappa'} = \frac{\partial F_{\kappa\alpha}}{\partial \tau_{\kappa'\beta}}$$

  $\rightarrow$ Frozen phonon calculations

$$K^{\alpha\beta}_{\kappa\kappa'} = \frac{\partial^2 E}{\partial \tau_{\kappa\alpha} \partial \tau_{\kappa'\beta}}$$

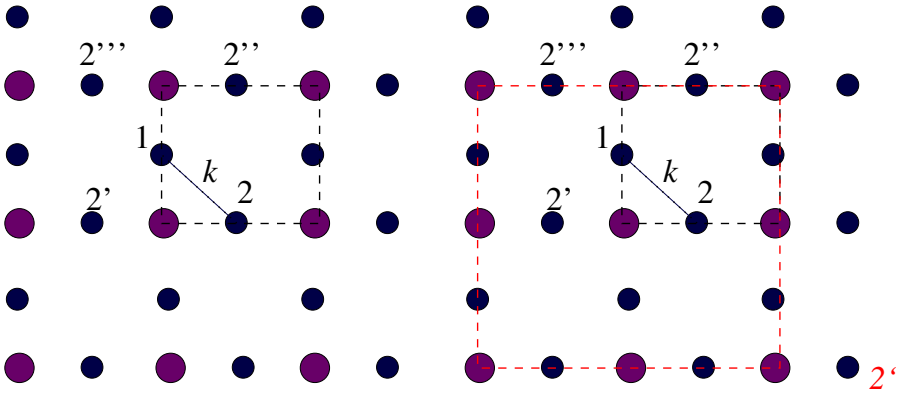
  $\rightarrow$ Linear response calculations
  Eigenvalues of $D^{\alpha\beta}_{\kappa\kappa'} = K^{\alpha\beta}_{\kappa\kappa'}/\sqrt{M_\kappa M_{\kappa'}}$: ω^2_μ

- 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 $= 3 * N_a$
  - Force constants matrices between two atoms directly relate to their interaction potential.

- Extended periodic systems: Eg. Crystal
  - Number of vibrations $= \infty$
    $3 * N_a$ 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)
  $\omega(\vec{q}, l)$, $\vec{q} \in BZ$, $l \in [1, 3N_a]$
  $e_i(\kappa|\vec{q}, l)$: lth band eigenvector at $\vec{q}$,
  i and κ denote Cartesian and atom indices obtained with diagonalization of dynamical matrix:
  $A_{ij}(\kappa\kappa'|\vec{q})$: 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,

  $$\Phi_{ij}(0\kappa; \vec{R}\kappa') = \sum_{\vec{q} \in Grid(N_1 N_2 N_3)} A_{ij}(\kappa\kappa'|\vec{q}) e^{-i\vec{q}\cdot\vec{R}} d^3\vec{q}$$

  for $\vec{R} + \vec{\tau}_\kappa - \vec{\tau}_{\kappa'} \in Box(N_1 N_2 N_3)$.
  Interactions are not short-ranged;
  Effects of images enter. eg. 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 $\omega(\vec{q}, l)$ at $\vec{q} = \vec{0}$:

$$A_{ij}^{dd}(\kappa\kappa'|\vec{q} \to \vec{0}) = \frac{4\pi}{\Omega} \frac{(\sum_k Z^*_{\kappa,ik} q_k)(\sum_k Z^*_{\kappa',jk} q_k)}{\sum_{kl} q_k \epsilon_{kl} q_l}$$

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

  Ref. X.Gonze et al, PRB 50, 13035 (1994).

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 ϵ and $Z^*\kappa ij$ obtained from DFT-LR at Γ ($\vec{q} = (000)$), 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: Φ

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

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.

$$\sum_{\vec{q},l} f(\omega(\vec{q},l)) = 3N_aN \int_0^{\omega_{max}} f(\omega)g(\omega)d\omega$$

- Normalized phonon density of states:
  $g(\omega) = \frac{1}{3N_aN} \sum_{\vec{q},l} \delta(\omega - \omega(\vec{q},l))$

- Partition function:

$$Z = \prod_{\vec{q},l} (2sinh(\frac{\hbar\omega(\vec{q},l)}{2k_BT}))^{-1}$$

- Helmholtz free energy:
  (obtained as ln of Z)

$$\Delta F = 3N_aNk_BT\int_0^{\omega_{max}} ln(2sinh(\frac{\hbar\omega(\vec{q},l)}{2k_BT}))g(\omega)d\omega$$

- Internal energy:
  obtained using (Ashcroft and Mermin)

$$U = E_{eq} + \sum_{\vec{q},l}\frac{1}{2}\hbar\omega(\vec{q}l)(1 + \frac{2}{e^{\frac{\hbar\omega(\vec{q},l)}{k_BT}} - 1})$$

  Thus,

$$\Delta U = 3N_aN\frac{\hbar}{2}\int_0^{\omega_{max}} \omega coth(\frac{\hbar\omega(\vec{q},l)}{2k_BT})g(\omega)d\omega$$

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

$$C_v = 3N_aNk_B\int_0^{\omega_{max}}(\frac{\hbar\omega}{2k_BT})^2$$

$$csch^2(\frac{\hbar\omega(\vec{q},l)}{2k_BT})g(\omega)d\omega$$

- Entropy: $S = (U - F)/T$

$$C_v = 3N_aNk_B \int_0^{\omega_{max}} [\frac{\hbar\omega}{2k_BT} coth(\frac{\hbar\omega(\vec{q},l)}{2k_BT})$$

$$-ln(2sinh(\frac{\hbar\omega(\vec{q},l)}{2k_BT}))]g(\omega)d\omega$$

- *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 α (thermal expansion coefficient).

- In terms of density of states:

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

- Atomic temperature factor (X-ray diffraction) $e^{-W(\kappa)}$
  Structure factor $F_T = \sum_\kappa e^{-W(\kappa)} e^{i\vec{G}\cdot\vec{\tau}_\kappa}$

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

$$B_{ij} = \frac{1}{N} \sum_{\vec{q}l} \frac{\hbar}{2\omega} coth(\frac{\hbar\omega}{2k_B T}) e_i(\kappa|\vec{q}l) e_j^*(\kappa|\vec{q}l)$$

Local harmonic approximation

Ref. Lesar et al, PRL 63, 624 (1989).

- 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:

$$A = \frac{1}{2}\sum_{\kappa\kappa'}^{1} u_{\kappa\kappa'}(r^0_{\kappa\kappa'}) + 3k_BT\sum_{\kappa} Ln(\frac{D_i^{1/6}}{k_BT}),$$

  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:

$$F = F_0 - \Omega \sum_{ij} \sigma_{ij} e_{ij} - \sum_{ij\kappa} E_i Z^*_{\kappa ij} \tau_{\kappa j} + E_{elastic}$$

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

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

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

Ref. Hill and Waghmare.

Thermodynamics: strong anharmonicity

Ref. Rabe and Waghmare, PRB 55, 13237 (1995).

- 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.

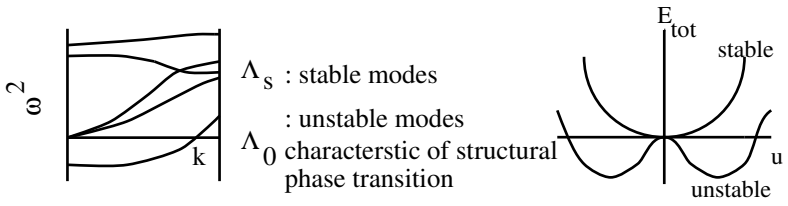
- Write total energy as a Taylor expansion in lattice Wannier function coordinates and strain (and possibly harmonic expansion of other modes).

- 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
  $E_{lat} = E_h(\{\vec{d}_{i\tau}\}) + E_{anh}(\{\vec{d}_{i\tau}\}) + E_{elastic}$



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

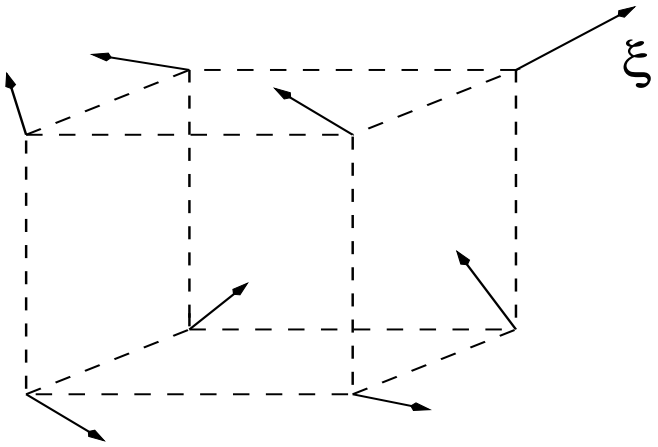
$$Z = \int \Pi_i du_i d\xi_i exp(-E_{lat}) = Z_{\Lambda_0} \times Z_{\Lambda_s}$$

⋆ Focus on the lowest energy subspace Λ_0, relevant to the phase transition.

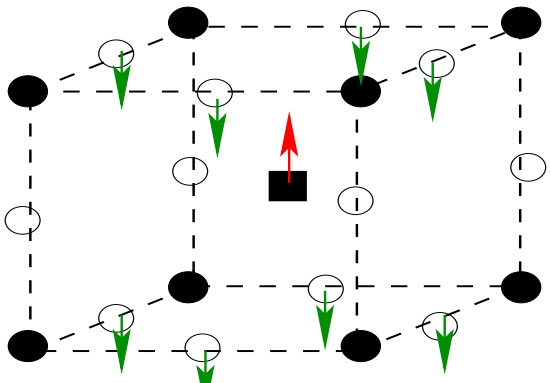
$$E_{model} = E_{h,\Lambda_0} + E_{anh,\Lambda_0} + E_{strain}$$

E_{model} is Projection of E_{lat} onto Λ_0 subspace

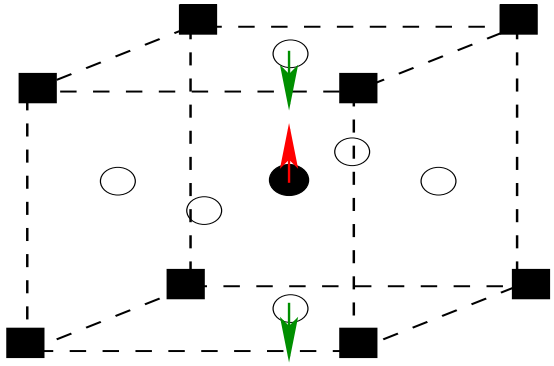
Resulting Model



Classical Spins



$PbTiO_3$



$BaTiO_3$

Resulting Model: Form

Model

$H(\xi_i)$ Internal Distortions (atomic displacements/phonon)

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

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

\+ $H(\xi_i, \sigma_\iota)$ Compositional Order, σ_i, its local field effects

Polarization: $P \alpha \Sigma \xi_i$

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
- $\rightarrow$ Access to full phonon dispersion
- Thermodynamics:
  - Quasi-harmonic approximation
  - Lattice Wannier functions

References

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