SSCHA School 2026

Lecture 1: Theory of lattice vibrations, anharmonicity, and the SSCHA

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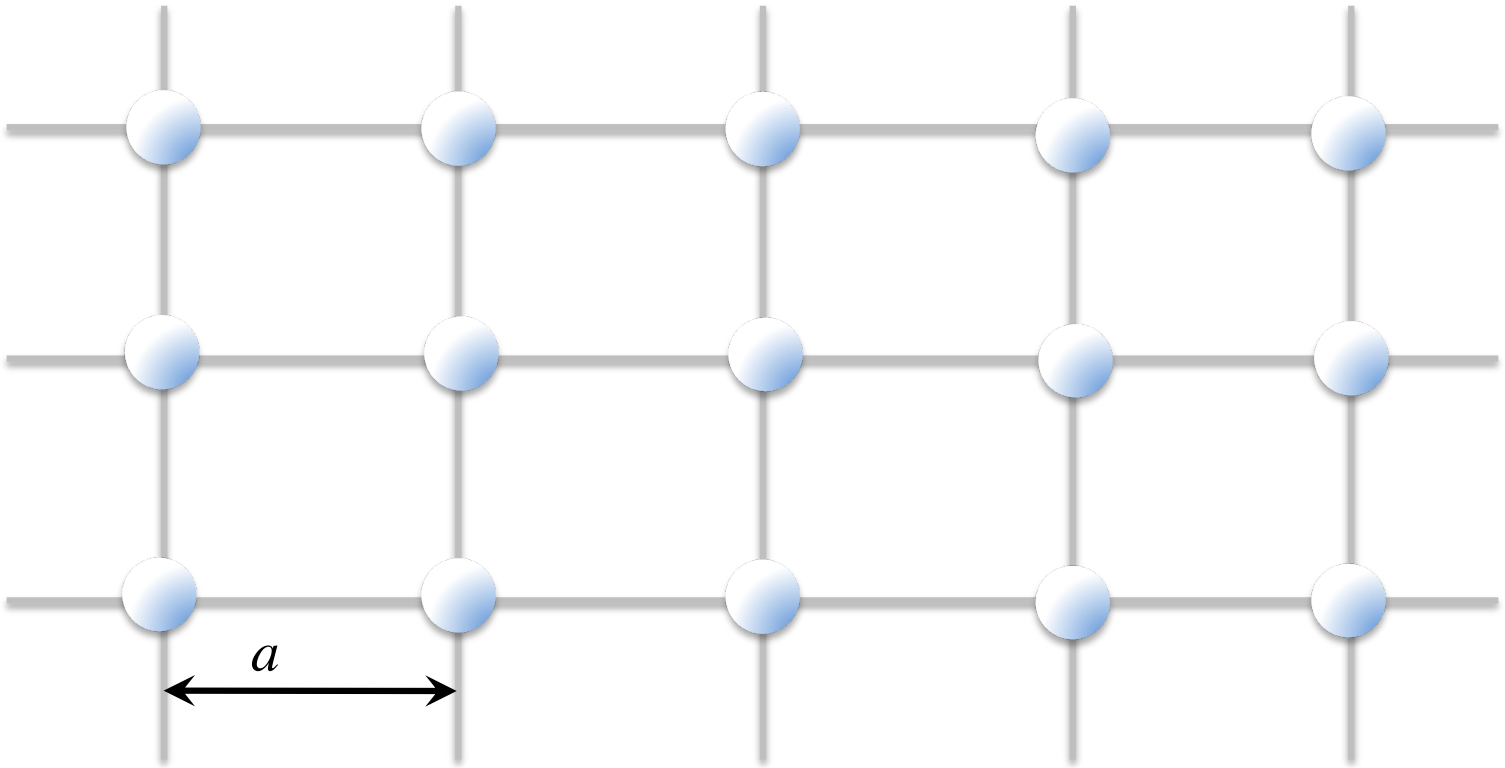
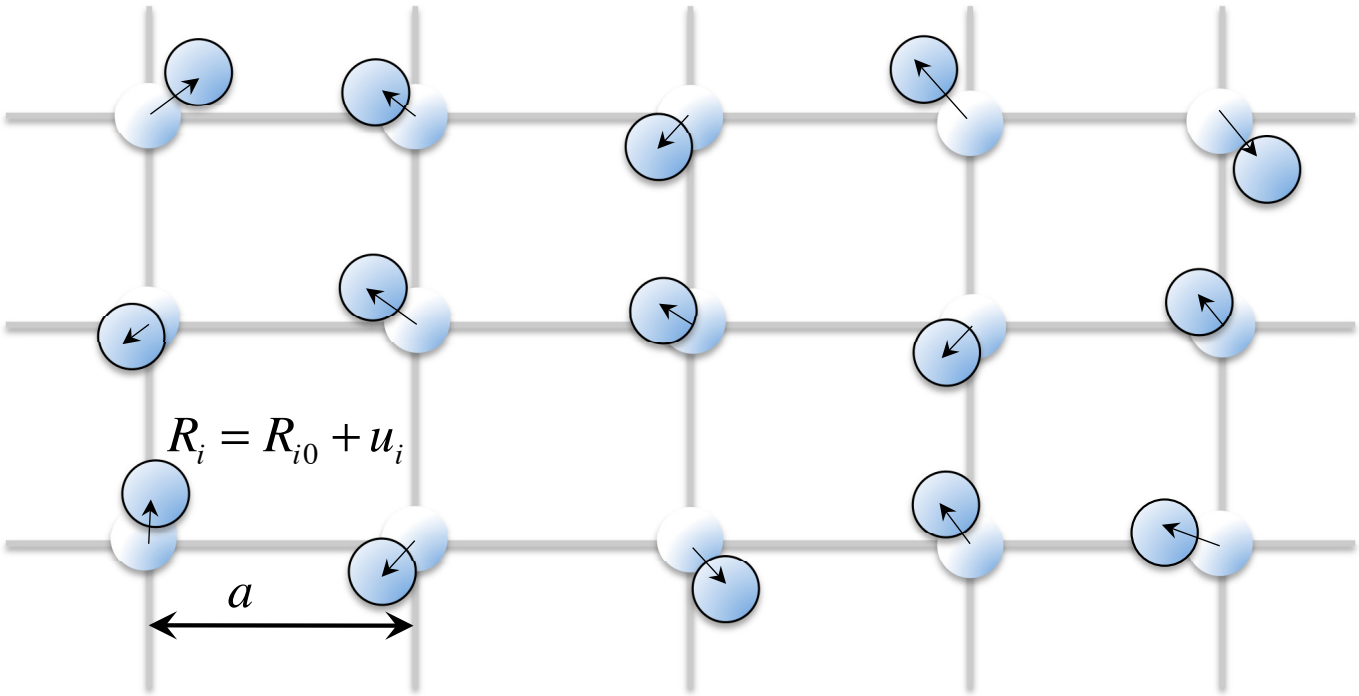
Outline

Atoms in a solid

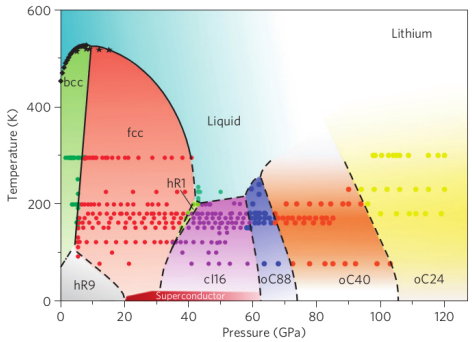


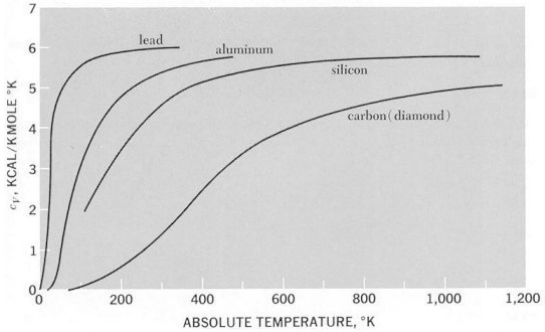
Atoms in a solid vibrate around the lattice sites

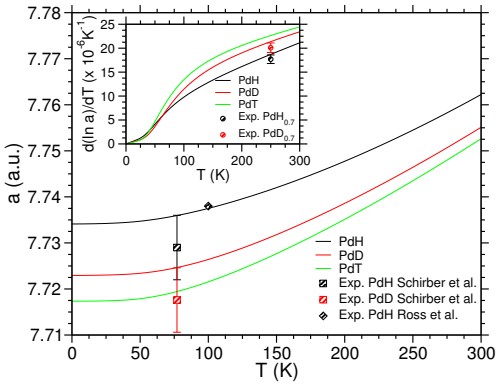


Atomic vibrations determine many physical properties

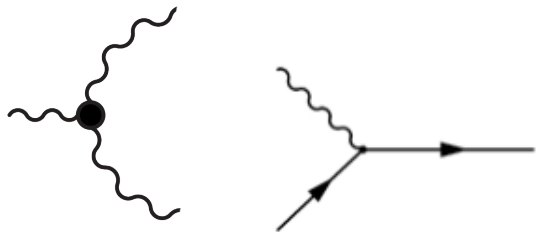
- Thermodynamic properties:
  - The temperature dependence of the Helmholtz free energy $F(V, T)$:
    $\hbar\omega_{vib} \sim 10meV \rightarrow T_{vib} = \frac{\hbar\omega_{vib}}{k_B} \sim 100K$
    $\hbar\omega_{ele} \sim 1eV \rightarrow T_{ele} = \frac{\hbar\omega_{vib}}{k_B} \sim 10000K$
  - Phase diagrams, specific heats, thermal expansion ...







- Transport properties:
  - Superconductivity (e-ph interaction)
  - Electrical conductivity (e-ph interaction)
  - Thermal conductivity (e-ph and ph-ph interactions)



The theory of everything in a solid

- A solid is formed by a set of electrons and ions interacting via Coulomb interaction
- The properties of a solid can be fully determined by solving the Schrödinger equation:

$$\begin{aligned} H|\Psi_A\rangle &= E_A|\Psi_A\rangle \\ H &= T_e + T_{ion} + V_{e-e} + V_{e-ion} + V_{ion-ion} \end{aligned}$$

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An unsolvable problem

The Born-Oppenheimer (BO) approximation

- Electrons are lighter (faster) than ions
- The BO approximation assumes that for any ionic configuration $\mathbf{R}$ electrons are at the ground state
- The BO procedure:
  - Solve the electronic part of the Hamiltonian at fixed $\mathbf{R}$:

$$H_e(\mathbf{R})|\Psi^e_\alpha(\mathbf{R})\rangle = E^e_\alpha(\mathbf{R})|\Psi^e_\alpha(\mathbf{R})\rangle,$$

    where

$$H_e(\mathbf{R}) = T_e + V_{e-e} + V_{e-ion}(\mathbf{R}) + V_{ion-ion}(\mathbf{R})$$

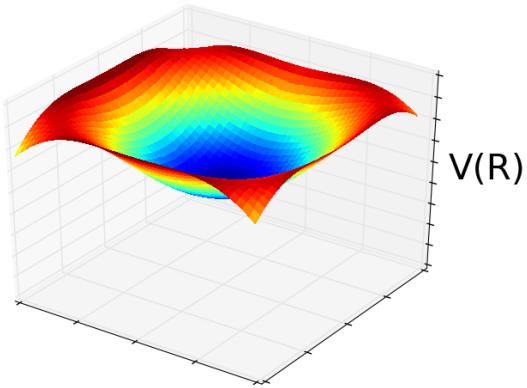
  - Usually solved with DFT
  - The ground state defines the BO energy surface (BOES): $V(\mathbf{R}) = E^e_0(\mathbf{R})$
- The $V(\mathbf{R})$ potential defines the ionic problem:

$$H_{ion}(\mathbf{R})|\Psi^{ion}_\beta\rangle = [T_{ion} + V(\mathbf{R})]\,|\Psi^{ion}_\beta\rangle = E_\beta|\Psi^{ion}_\beta\rangle$$

- The free energy can be calculated as

$$F = -k_B T \ln\left(\sum_\beta e^{-\frac{E_\beta}{k_B T}}\right)$$

BOES



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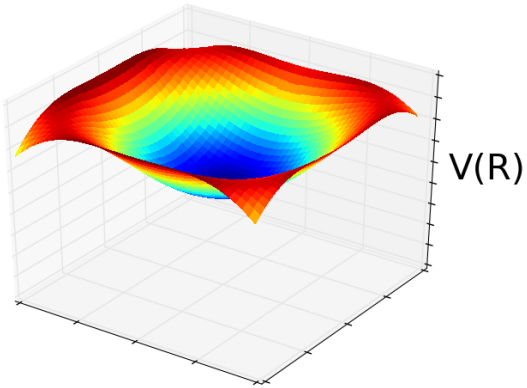


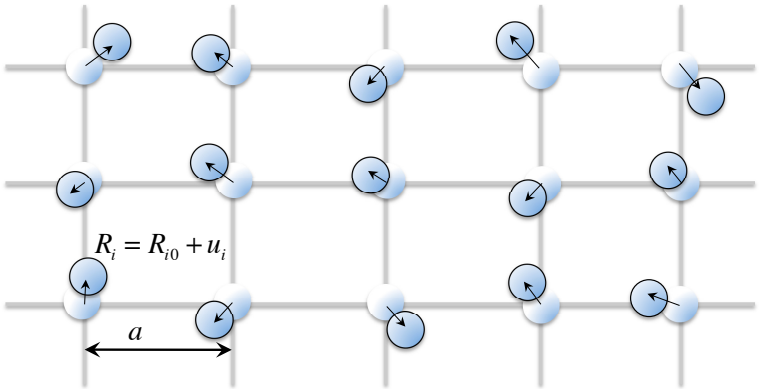
An unsolvable problem

Outline

Taylor expansion of the $V(\mathbf{R})$ potential

- Atomic displacements from the lattice equilibrium sites are small compared to the interatomic distance: $|u| << a$
- The lattice equilibrium $\mathbf{R}_0$ sites correspond to the minimum of $V(\mathbf{R})$ so that the forces vanish:

$$f_a = -\left[\frac{\partial V(\mathbf{R})}{\partial R_a}\right]_{\mathbf{R}=\mathbf{R}_0} = 0.$$



- $V(\mathbf{R})$ can be Taylor-expanded around $\mathbf{R}_0$

$$\begin{aligned} V(\mathbf{R}) &= V(\mathbf{R}_0) + V_2(\mathbf{R}) + V_3(\mathbf{R}) + V_4(\mathbf{R}) + \cdots, \\ V_n(\mathbf{R}) &= \frac{1}{n!} \sum_{a_1 \cdots a_n} \Phi_{a_1 \cdots a_n} (R - R_0)_{a_1} \cdots (R - R_0)_{a_n} \end{aligned}$$

- The n-th order force-constants are given by $\Phi_{a_1 \cdots a_n} = \left[\frac{\partial^n V(\mathbf{R})}{\partial R_{a_1} \cdots \partial R_{a_n}}\right]_{\mathbf{R}=\mathbf{R}_0}$

The harmonic approximation

- The problem becomes **solvable** assuming the harmonic approximation
- The potential is truncated at second order

$$V(\mathbf{R}) = V(\mathbf{R}_0) + V_2(\mathbf{R}) + V_3(\mathbf{R}) + V_4(\mathbf{R}) + \dots$$

- Transforming the positions and momenta to normal coordinates as

$$\left.\begin{aligned} u_a &= R_a - R_{a0} = \textstyle\sum_\mu \frac{1}{\sqrt{M_a}} \epsilon_{a\mu} q_\mu \\ P_a &= \textstyle\sum_\mu \sqrt{M_a} \epsilon_{a\mu} p_\mu \end{aligned}\right\} H_{ion} = \sum_\mu \frac{1}{2}\left(p_\mu^2 + \omega_\mu^2 q_\mu^2\right)$$

  the ionic Hamiltonian is a set of $3N_{at}$ harmonic oscillators (N_{at} number of atoms)
- This is true if the polarization vectors $\boldsymbol{\epsilon}_\mu$ diagonalize the harmonic force-constants

$$\sum_b \frac{\Phi_{ab}}{\sqrt{M_a M_b}} \epsilon_{b\mu} = \omega_\mu^2 \epsilon_{a\mu}$$

- The energy is (n_μ occupation number of each oscillator)

$$E_{n_1,\cdots,n_{3N}} = V(\mathbf{R}_0) + \sum_\mu \hbar\omega_\mu \left(\frac{1}{2} + n_\mu\right)$$

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

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

and $\beta = k_B T$

- Then

$$\begin{aligned} E &= \langle H \rangle_{\rho_H} = \mathrm{tr}(H\rho_H) \\ S &= -k_B \langle \ln \rho_H \rangle_{\rho_H} = -k_B \mathrm{tr}(\rho_H \ln \rho_H) \\ F &= \mathrm{tr}(H\rho_H) + \frac{1}{\beta}\mathrm{tr}(\rho_H \ln \rho_H) = -\frac{1}{\beta} \ln Z_H \end{aligned}$$

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

- In the harmonic approximation the partition function can be calculated

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

  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

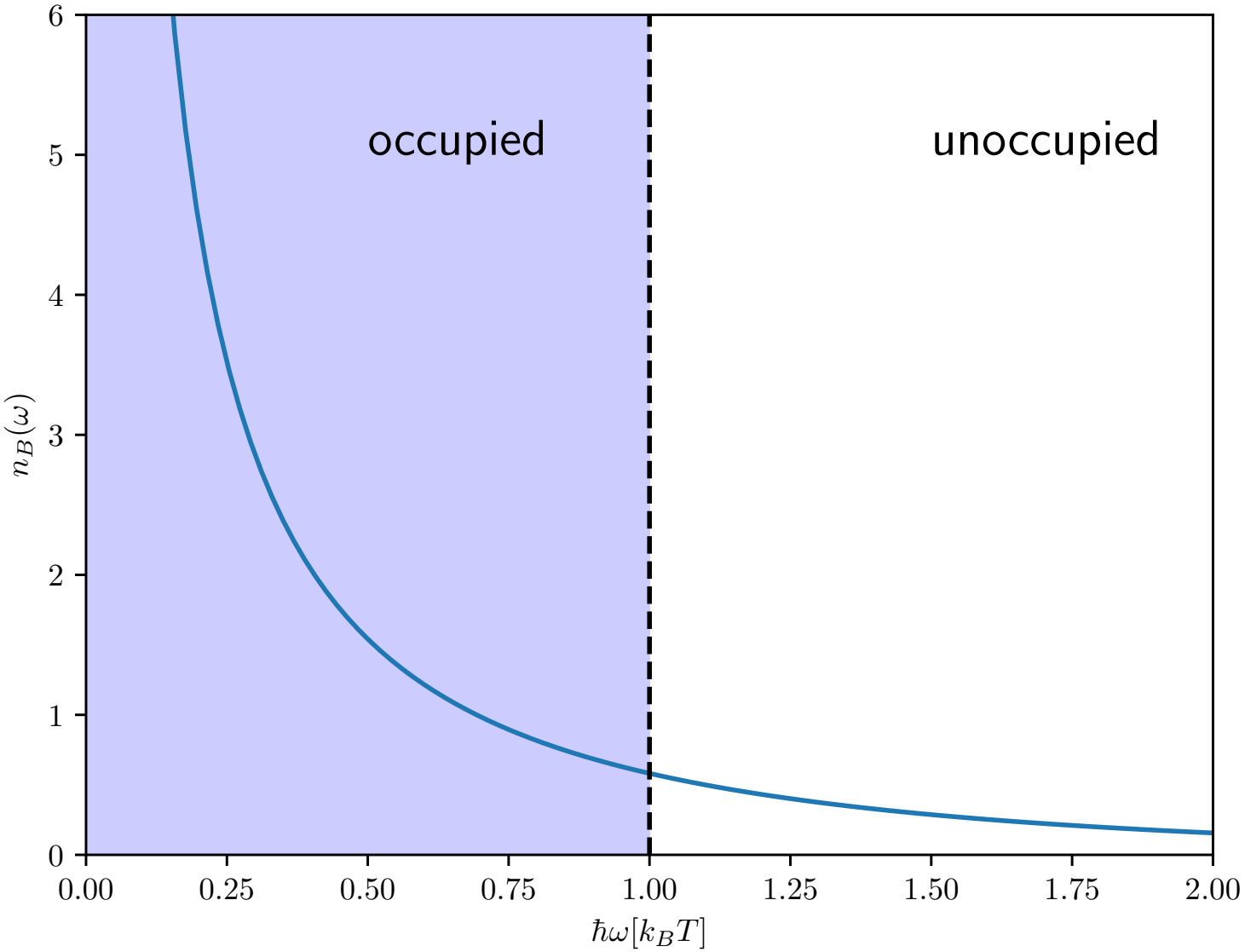
- It is easy to show that

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

- 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

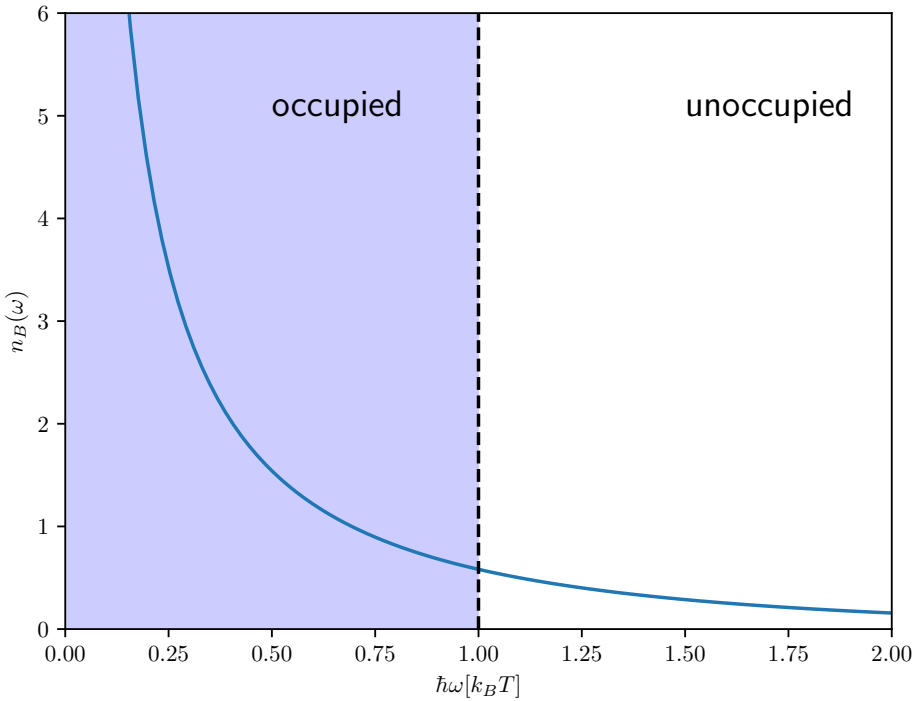
- The contribution of each mode to the energy is

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

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

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

- $\hbar\omega_\mu/2$ 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

$$E_\mu \sim k_B T$$

The probability distribution function defined by the harmonic density matrix

- The probability distribution function defined by the harmonic density matrix is given by

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

where

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

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

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

- Transforming to the position basis

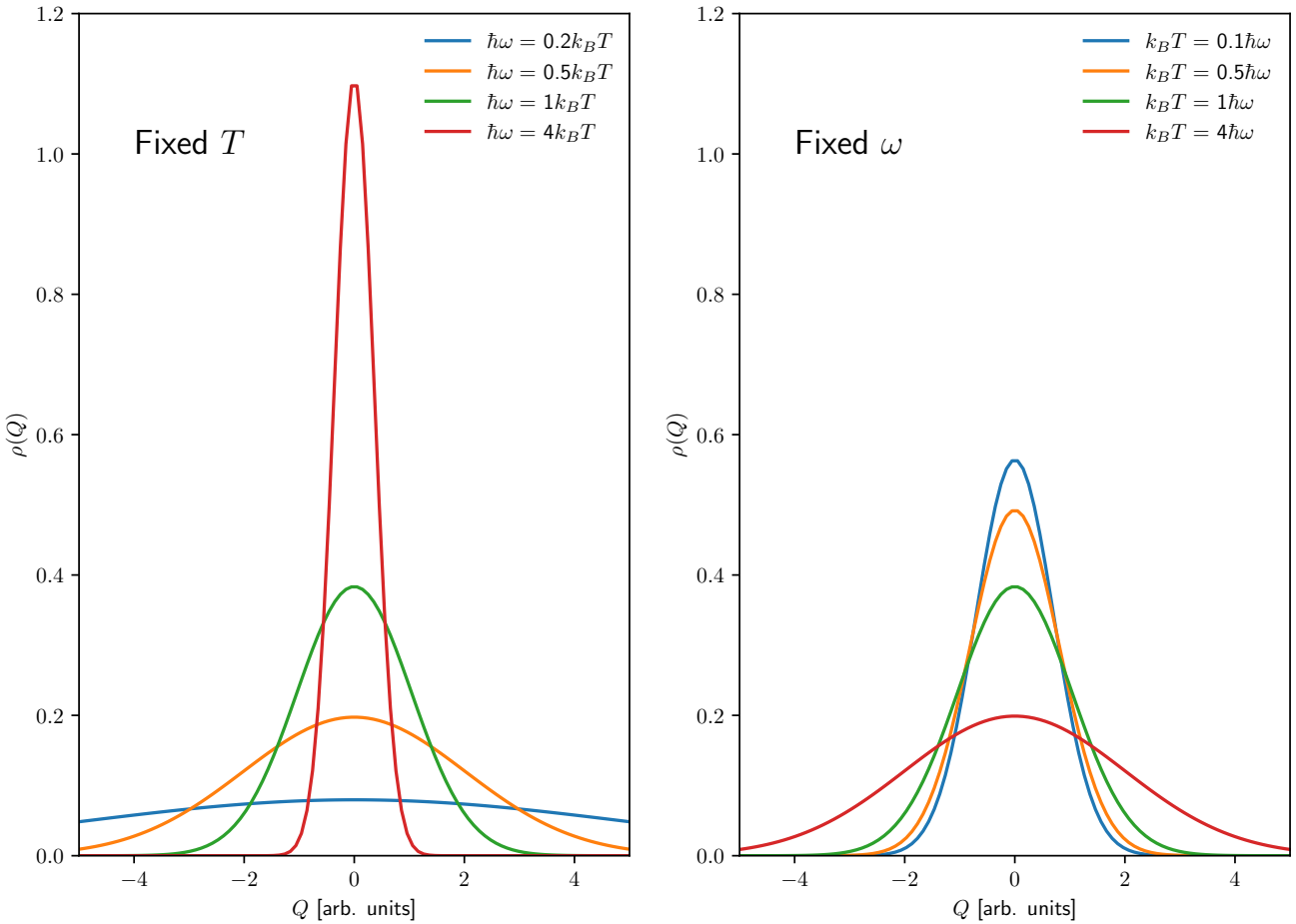
$$\rho_H(\boldsymbol{R}) = \sqrt{\det[\boldsymbol{\Psi}^{-1}/(2\pi)]}\, e^{-\frac{1}{2}\sum_{ab}(R_a - R_{a0})\Psi_{ab}^{-1}(R_b - R_{b0})}$$

where the matrix $\boldsymbol{\Psi}^{-1}$ 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_μ^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 $O(\boldsymbol{R})$ can be calculated as

$$\langle O \rangle_{\rho_H} = \mathrm{tr}(O\rho_H) = \int d\boldsymbol{R} O(\boldsymbol{R}) \rho_H(\boldsymbol{R})$$

- An example:
  The mean square displacement of an ion

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

The mean square displacement in the quantum and classical limit

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

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

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

  the zero point motion

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

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

  or even neglecting the quantum contribution

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

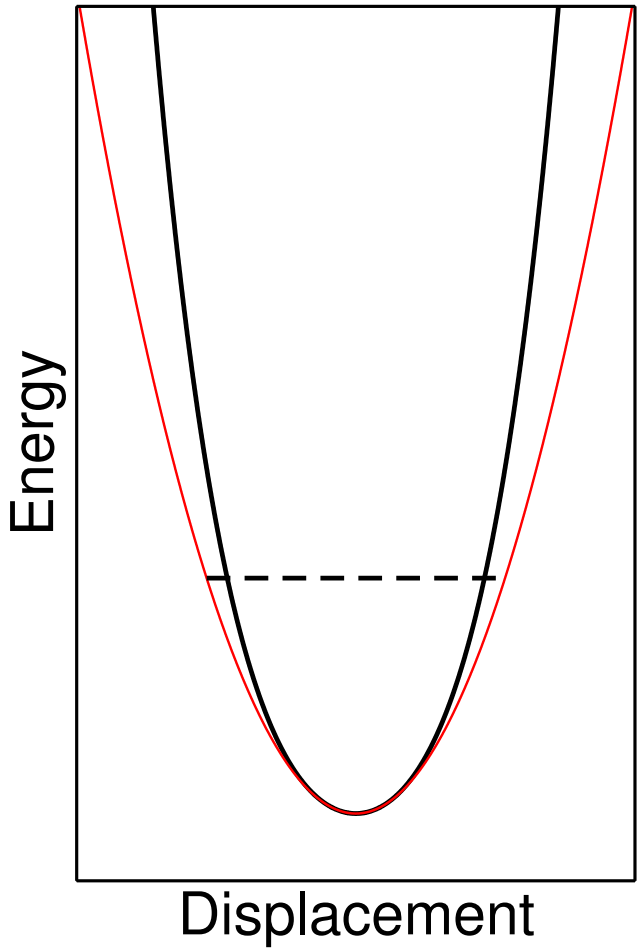
  no displacement at zero temperature

Outline

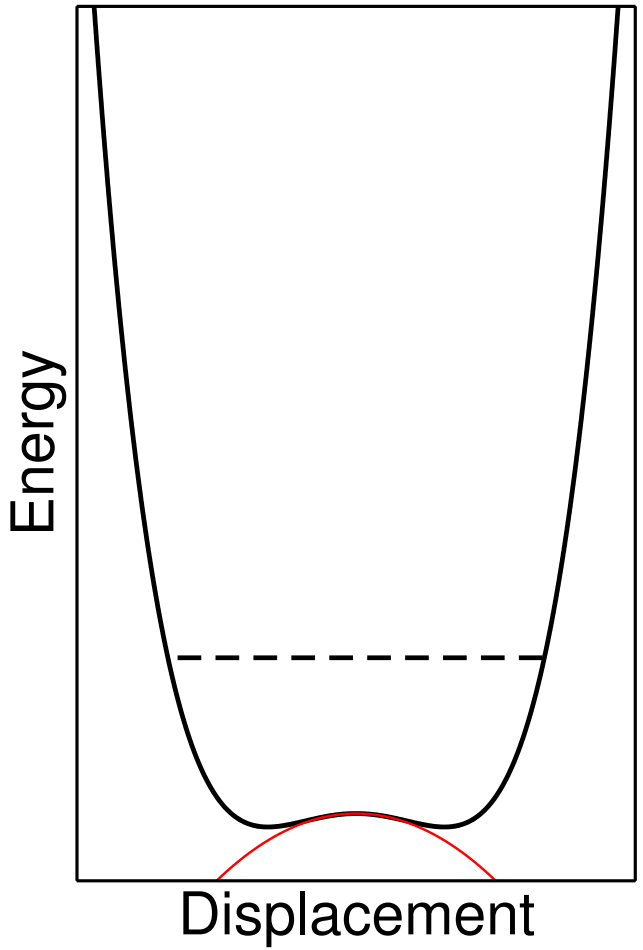
Two different regimes for anharmonicity

$$V(\mathbf{R}) = V_0 + V_2(\mathbf{R}) + V_3(\mathbf{R}) + V_4(\mathbf{R}) + \dots$$

- Perturbative regime:
  $V_3(\mathbf{R}) + V_4(\mathbf{R}) + \cdots \ll V_2(\mathbf{R})$



- Non-perturbative regime:
  $V_3(\mathbf{R}) + V_4(\mathbf{R}) + \cdots \sim V_2(\mathbf{R})$



Self-energy and the Dyson equation

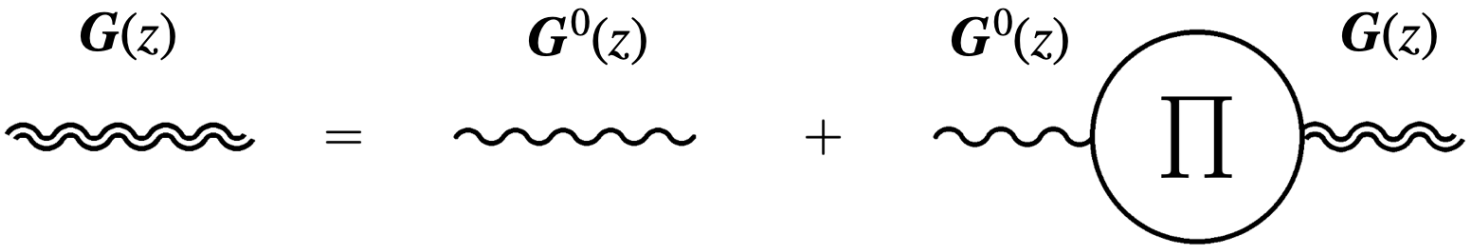
- The effect of anharmonicity (and any other interaction) can be included within many-body perturbation theory in the displacement correlation function or Green's function

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

  where now H includes anharmonic interactions
- All the interactions affecting the phonons define the phonon self energy $\mathbf{\Pi}$
- The interacting Green function can be calculated through Dyson's equation

$$\boldsymbol{G}(z) = \boldsymbol{G}^0(z) + \boldsymbol{G}^0(z)\mathbf{\Pi}(z)\boldsymbol{G}(z)$$

- The non-interacting Green's function is calculated with the harmonic H_0



The displacement correlation function in the harmonic approximation

- In the harmonic approximation, using bosonic ladder operators

$$G^0_{ab}(z) = -\sum_{\mu\mu'} e^a_\mu e^b_{\mu'} \frac{\hbar}{2\sqrt{\omega_\mu \omega'_\mu}} \left\langle e^{zH/\hbar}(b_\mu + b^\dagger_\mu) e^{-zH/\hbar}(b_{\mu'} + b^\dagger_{\mu'}) \right\rangle_{\rho_H}$$

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

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

and $\left\langle b^\dagger_\mu b_\mu \right\rangle_{\rho_H} = n_B(\omega_\mu)$, we obtain

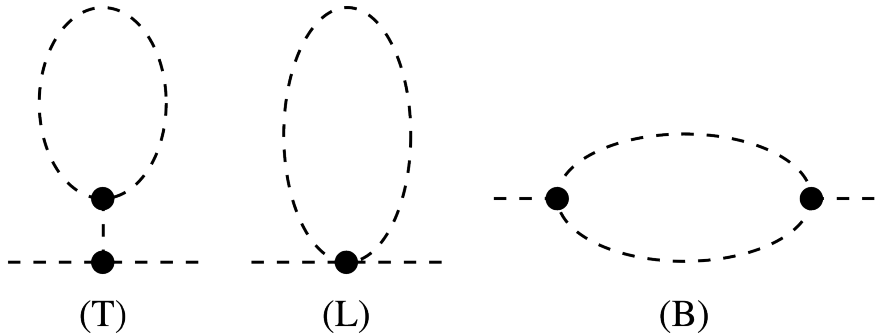
$$G_{ab}(z) = -\sum_{\mu} e^a_\mu e^b_\mu \frac{\hbar}{2\omega_\mu} \left[(n_B(\omega_\mu) + 1) e^{-z\omega_\mu} + n_B(\omega_\mu) e^{z\omega_\mu} \right]$$

- Performing the Fourier transform to the frequency domain

$$G^0_{ab}(i\omega_n) = \sum_{\mu} \frac{e^a_\mu e^b_\mu}{(i\omega_n)^2 - \omega^2_\mu}$$

The anharmonic self-energy in the perturbative limit

- At the perturbative lowest order there are 3 diagrams that contribute to the phonon self-energy: tadpole (T), loop (L), and bubble (B)
- The self-energy diagrams need to be constructed with Feyman diagram rules and have to be calculated with Matsubara summation techniques (see Mahan book)
  - These are the self-energy terms



$$\overset{(T)}{\Pi}_{\mu}(\boldsymbol{q}) = \frac{-2\omega_{\mu}(\boldsymbol{q})}{N} \sum_{\nu\nu'\boldsymbol{q}'} \overset{(3)}{\phi}_{\nu\nu\nu'}(-\boldsymbol{q}', \boldsymbol{q}, 0) \overset{(3)}{\phi}_{\nu'\mu\mu}(0, \boldsymbol{q}, -\boldsymbol{q}) \frac{2n_B(\omega_{\nu}(\boldsymbol{q}')) + 1}{\omega_{\nu'}(0)}$$

$$\overset{(L)}{\Pi}_{\mu}(\boldsymbol{q}) = \frac{\omega_{\mu}(\boldsymbol{q})}{N} \sum_{\nu\boldsymbol{q}'} \overset{(4)}{\phi}_{\mu\mu\nu\nu}(\boldsymbol{q}, -\boldsymbol{q}, \boldsymbol{q}', -\boldsymbol{q}')(2n_B(\omega_{\nu}(\boldsymbol{q}')) + 1)$$

$$\overset{(B)}{\Pi}_{\mu}(\boldsymbol{q}, \omega + i\eta) = \frac{-\omega_{\mu}(\boldsymbol{q})}{N} \sum_{\nu\nu'\boldsymbol{q}'} |\overset{(3)}{\phi}_{\mu\nu\nu'}(\boldsymbol{q}, \boldsymbol{q}', -\boldsymbol{q} - \boldsymbol{q}')|^2 F(\omega + i\eta, \omega_{\nu}(\boldsymbol{q}'), \omega_{\nu'}(-\boldsymbol{q} - \boldsymbol{q}'))$$

The anharmonic self-energy in the perturbative limit

- In the equation above

$$\overset{(n)}{\phi}_{\mu_1\cdots\mu_n}(\boldsymbol{q}_1,\cdots,\boldsymbol{q}_n) = \sum_{a_1\cdots a_n} \frac{\overset{(n)}{\phi}_{a_1\cdots a_n}(\boldsymbol{q},\cdots,\boldsymbol{q}_n)}{\sqrt{M_{a_1}\cdots M_{a_n}}} \frac{e^{a_1}_{\mu_1}(-\boldsymbol{q}_1)\cdots e^{a_n}_{\mu_n}(-\boldsymbol{q}_n)}{\sqrt{2^n\omega_{\mu_1}(\boldsymbol{q}_1)\cdots\omega_{\mu_n}(\boldsymbol{q}_n)}}$$

$$F(\omega+i\eta,\omega_1,\omega_2) = \frac{2(\omega_1+\omega_2)(1+n_B(\omega_1)+n_B(\omega_2))}{(\omega_1+\omega_2)^2-(\omega+i\eta)^2} + \frac{2(\omega_1-\omega_2)(n_B(\omega_2)-n_B(\omega_1))}{(\omega_1-\omega_2)^2-(\omega+i\eta)^2}$$

  and the phonon frequencies and polarization vectors are the eigenvalues and eigenvectors of the harmonic dynamical matrix:

$$\sum_b \frac{\overset{(2)}{\phi}_{ab}(\boldsymbol{q})}{\sqrt{M_a M_b}} e^b_\mu(\boldsymbol{q}) = \omega^2_\mu(q) e^q_\mu(\boldsymbol{q})$$

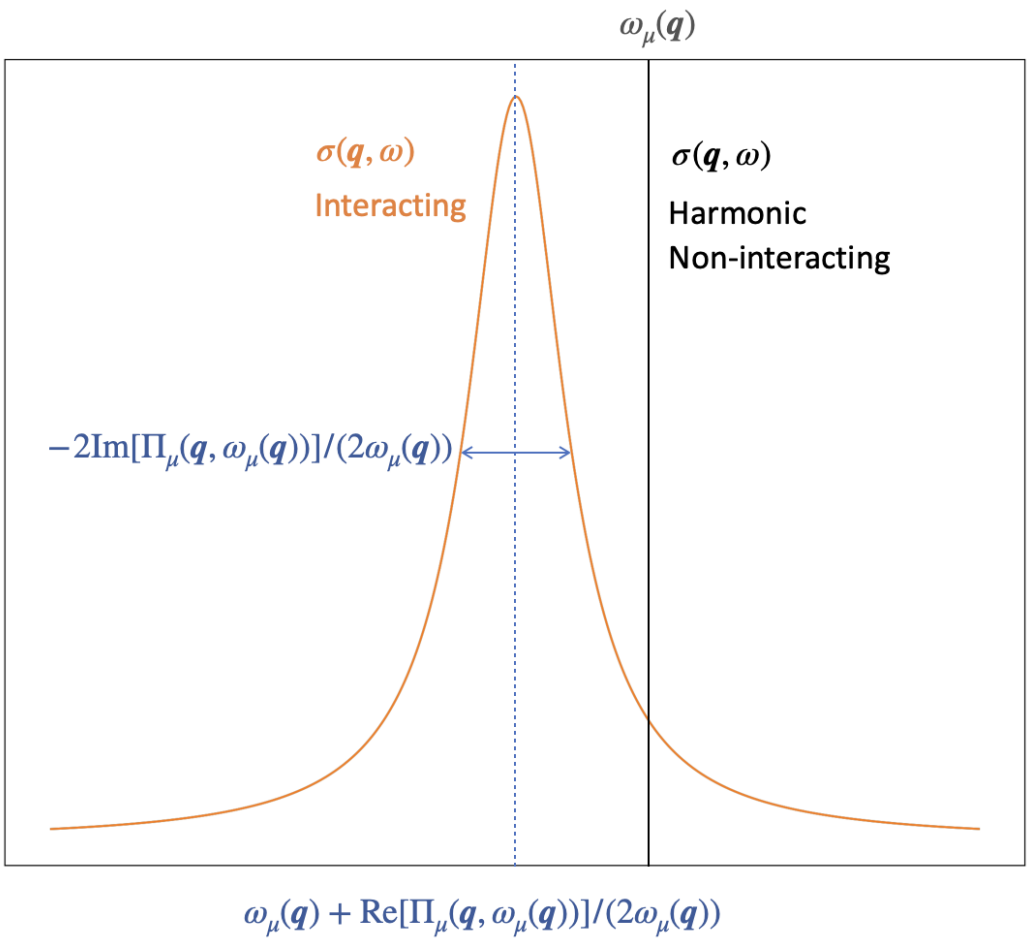
- These force constansts are derivatives of the Born-Oppenheimer potential calculated at the $\boldsymbol{R}_0$ positions that minimize it:

$$\overset{(n)}{\phi}_{a_1\cdots a_n} = \left[\frac{\partial^n V(\boldsymbol{R})}{\partial R_{a_1}\cdots\partial R_{a_n}}\right]_{\boldsymbol{R}=\boldsymbol{R}_0}$$

The spectral function in the perturbative limit

- Experimental signals are proportional to the spectral function

$$\sigma(\boldsymbol{q},\omega) = -\frac{\omega}{\pi}\sum_{a}\mathrm{Im}\left[G_{aa}(\boldsymbol{q},\omega+i\eta)\right]$$



Obtaining 3rd and 4th order force-constants is complex

$$\overset{(n)}{\phi}_{a_1 \cdots a_n} = \left[\frac{\partial^n V(\boldsymbol{R})}{\partial R_{a_1} \cdots \partial R_{a_n}} \right]_{\boldsymbol{R}=\boldsymbol{R}_0}$$

- Density Functional Perturbation Theory and the $2n+1$ theorem to obtain 3rd order force-constants

  Paulatto *et al.*, PRB (2013)

- Finite difference approaches (very tedious)

  Errea *et al.*, PRL (2011)

- Empirical potentials

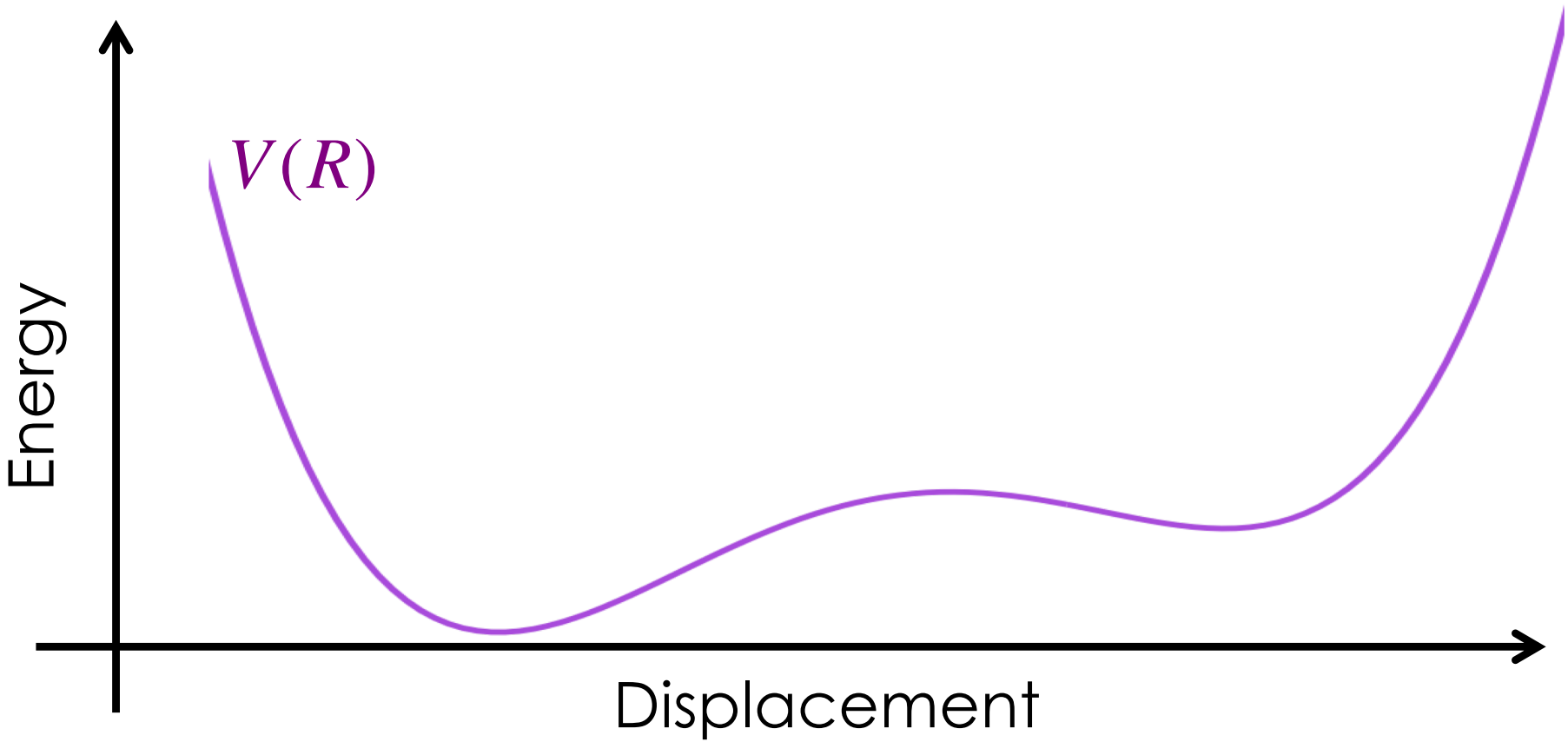
  Chen *et al.*, PRL (2014)

- Compressive sensing lattice dynamics

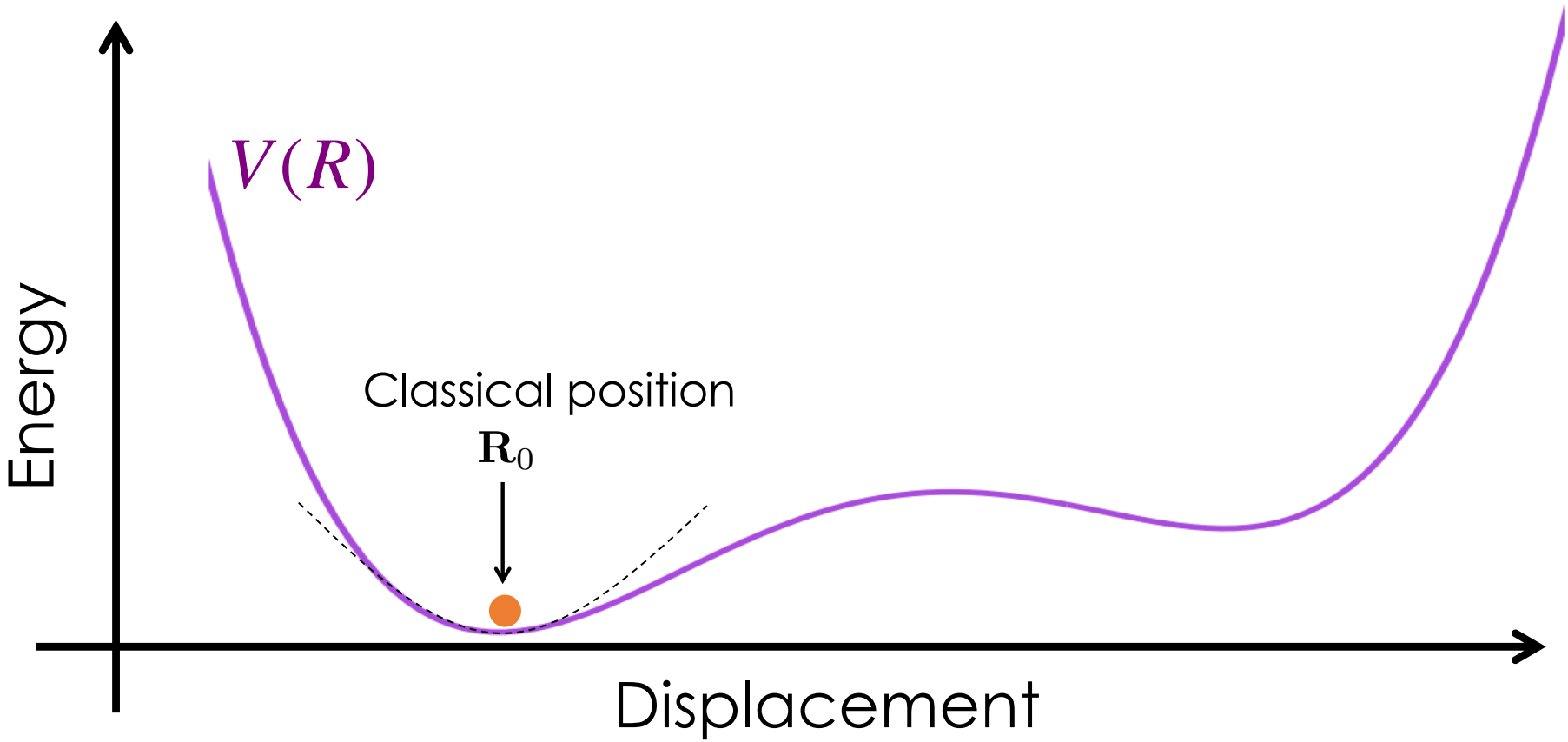
  Zhou *et al.*, PRL (2014)

Outline

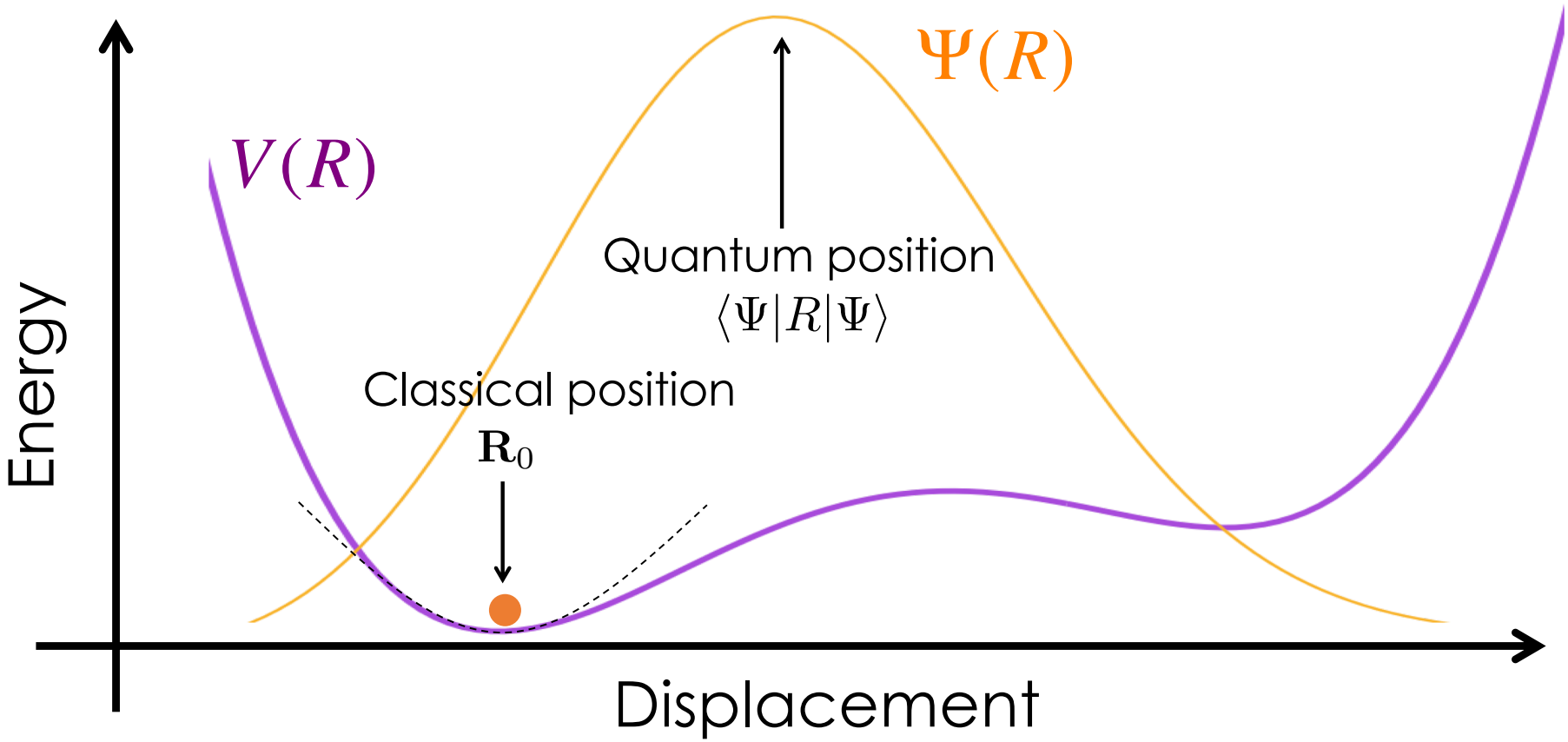
Quantum and non-perturbative anharmonic effects



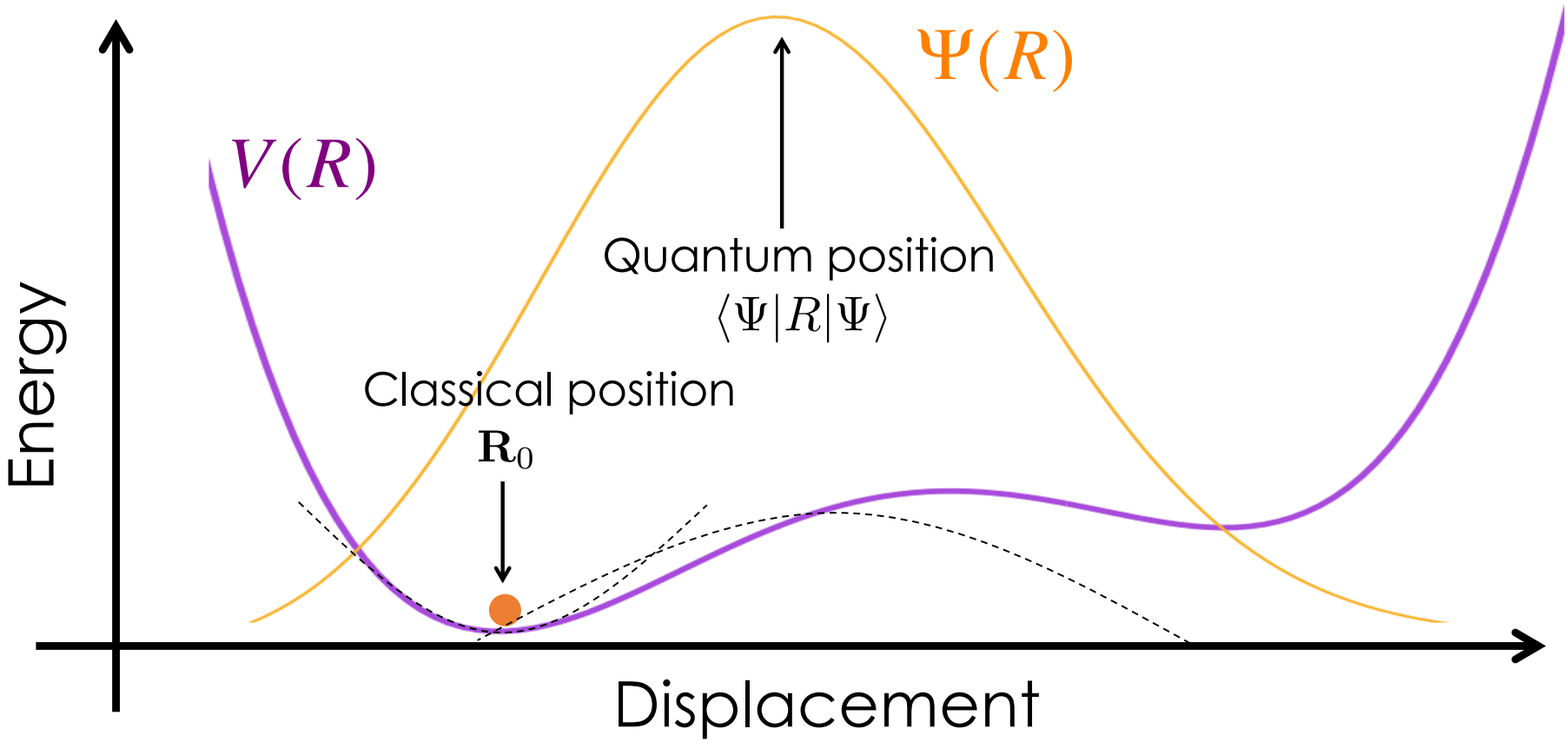
Quantum and non-perturbative anharmonic effects



Quantum and non-perturbative anharmonic effects



Quantum and non-perturbative anharmonic effects



Non-perturbative anharmonic regime occurs in many systems

Compounds with light atoms

- Hydrogen storage materials
- Hydrogen-based superconductors
- Hydrogen at high pressures
- ...

At very high temperatures

- Close to melting
- ...

Second-order structural displacive phase transitions in

- Charge-density wave (CDW) materials
- Ferroelectrics
- Thermoelectrics
- Multiferroics
- ...

How to deal with non-perturbative anharmonicity from first-principles

- *Ab initio* molecular dynamics (AIMD): Newtonian mechanics with DFT forces
  - Phonons from velocity autocorrelation functions

    Zhang *et al.*, PRL (2014)
  - TDEP: effective temperature dependent V_2 and V_3 from AIMD

    Hellman *et al.*, PRB (2011)
- Path integral molecular dynamics (PIMD): quantum dynamics with DFT forces
- Variational methods:
  - VSCF: Variational self-consistent field equations

    Bowman, J. Chem. Phys. (1978); Monserrat *et al.*, PRB (2013)
  - SCHA: Minimization of the free energy with a trial harmonic density matrix

    Hooton, Philos. Mag. Ser. (1955)

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    Hooton, Philos. Mag. Ser. (1955)
  - SSCHA: Stochastic implementation of the SCHA

Outline

SSCHA

Stochastic Self-Consistent
Harmonic Approximation

`sscha.eu`

Journal of Physics: Condensed Matter 33, 363001 (2021)

The stochastic self-consistent harmonic approximation (SSCHA)

- The idea of the SSCHA is to obtain the *harmonic* density matrix $\tilde{\rho}$ that minimizes the total free energy

$$\mathcal{F}[\tilde{\rho}] = \langle T_i + V \rangle_{\tilde{\rho}} + \frac{1}{\beta} \langle \ln \tilde{\rho} \rangle_{\tilde{\rho}}$$

- The probability distribution function that $\tilde{\rho}$ defines, $\tilde{\rho}_{\boldsymbol{\mathcal{R}},\boldsymbol{\Phi}}(\boldsymbol{R})$, is a Gaussian and can be parametrized by *centroid* positions $\boldsymbol{\mathcal{R}}$ and *auxiliary* second-order force constants $\boldsymbol{\Phi}$
- It is like a Hartree-Fock theory but for the phonons

$$\begin{aligned} \Psi_{\alpha_1 \ldots \alpha_n}(\boldsymbol{r}) &= \frac{1}{\sqrt{N!}} \begin{vmatrix} \psi_{\alpha_1}(\boldsymbol{r}_1) & \ldots & \psi_{\alpha_1}(\boldsymbol{r}_N) \\ \vdots & \vdots & \vdots \\ \psi_{\alpha_N}(\boldsymbol{r}_1) & \ldots & \psi_{\alpha_N}(\boldsymbol{r}_N) \end{vmatrix} \\ E &= \langle \Psi_{\alpha_1 \ldots \alpha_n} | \left(T_e + V_{ee} \right) | \Psi_{\alpha_1 \ldots \alpha_n} \rangle \end{aligned}$$

The SSCHA is a quantum variational method

The exact problem

- The exact density matrix

$$H = T_i + V(\boldsymbol{R}) \quad \rho_H = e^{-\beta H} / Z_H$$

- The exact free energy

$$F = \langle T_i + V \rangle_{\rho_H} + \frac{1}{\beta} \langle \ln \rho_H \rangle_{\rho_H}$$

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The variational problem

- Trial density matrix $\tilde{\rho}_{\mathcal{H}}$ from a trial Hamiltonian

$$\mathcal{H} = T_i + \mathcal{V}(\boldsymbol{R}) \quad \tilde{\rho}_{\mathcal{H}} = e^{-\beta \mathcal{H}}/Z_{\mathcal{H}}$$

- The variational free energy

$$\mathcal{F}[\mathcal{H}] = \langle T_i + V \rangle_{\tilde{\rho}_{\mathcal{H}}} + \frac{1}{\beta} \langle \ln \tilde{\rho}_{\mathcal{H}} \rangle_{\tilde{\rho}_{\mathcal{H}}}$$

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$$\mathcal{F}[\mathcal{H}] = \langle T_i + V \rangle_{\tilde{\rho}_{\mathcal{H}}} + \frac{1}{\beta} \langle \ln \tilde{\rho}_{\mathcal{H}} \rangle_{\tilde{\rho}_{\mathcal{H}}}$$

Variational principle

$$\mathcal{F}[\mathcal{H}] \geq F$$

The SSCHA trial Hamiltonian

- The trial Hamiltonian is harmonic and is parametrized with the *centroid* positions $\boldsymbol{\mathcal{R}}$ and *auxiliary* second-order force constants $\boldsymbol{\Phi}$

$$\mathcal{V}(\boldsymbol{R}) = \frac{1}{2} \sum_{ab} \Phi_{ab} (R_a - \mathcal{R}_a)(R_b - \mathcal{R}_b)$$

- Note that this potential is different from the harmonic potential

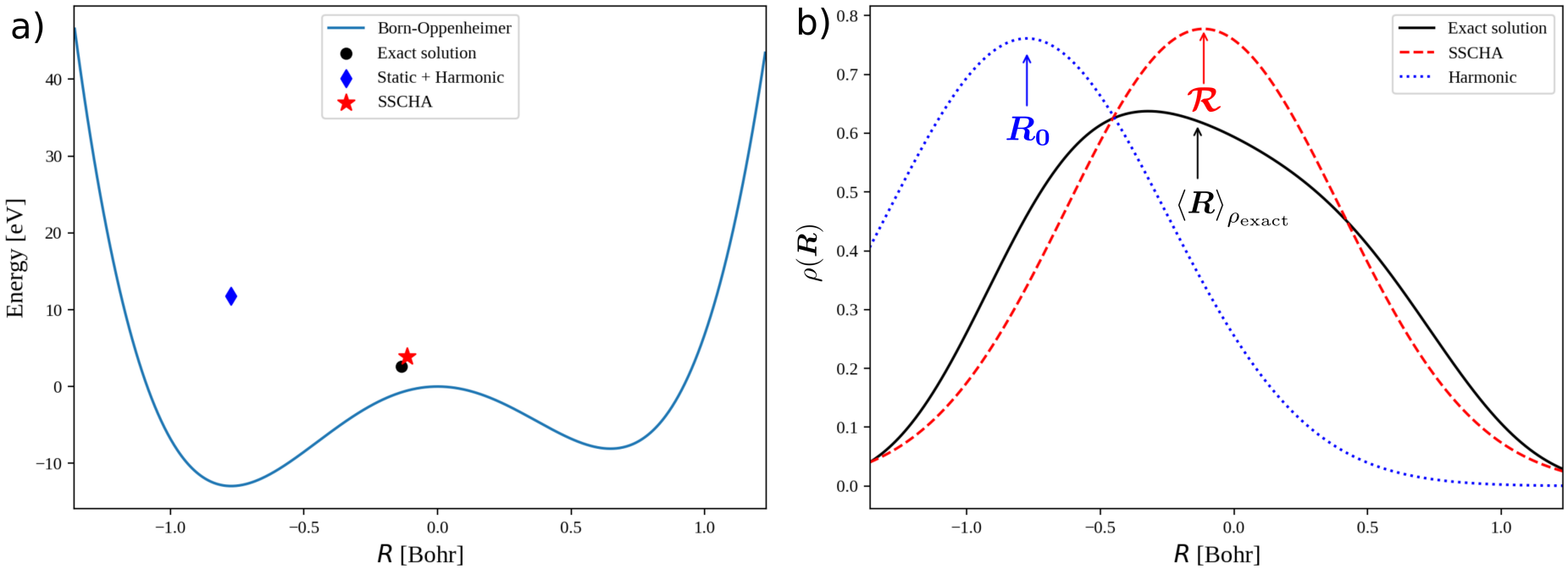
$$V_2(\boldsymbol{R}) = \frac{1}{2} \sum_{ab} \overset{(2)}{\phi}_{ab} (R_a - R_{0a})(R_b - R_{0b})$$

- The variational free energy will depend only on $\boldsymbol{\mathcal{R}}$ and $\boldsymbol{\Phi}$ so we will write $\tilde{\rho}_{\mathcal{H}} \rightarrow \tilde{\rho}_{\boldsymbol{\mathcal{R}},\boldsymbol{\Phi}}$ and $\mathcal{F}[\mathcal{H}] \rightarrow \mathcal{F}[\boldsymbol{\mathcal{R}}, \boldsymbol{\Phi}]$
- The goal of the SSCHA is to minimize $\mathcal{F}[\boldsymbol{\mathcal{R}}, \boldsymbol{\Phi}]$ with respect to $\boldsymbol{\mathcal{R}}$ and $\boldsymbol{\Phi}$
- It is easy to show that the SSCHA free energy can be written as

$$\mathcal{F}[\boldsymbol{\mathcal{R}}, \boldsymbol{\Phi}] = F_{\mathcal{H}} + \langle V - \mathcal{V} \rangle_{\tilde{\rho}_{\boldsymbol{\mathcal{R}},\boldsymbol{\Phi}}}$$

where $F_{\mathcal{H}}$ is the harmonic free energy given by the trial harmonic Hamiltonian

The SSCHA solution in a 1D example



The SSCHA probability distribution function

- The SSCHA probability distribution function is a product of Gaussians, exactly as the harmonic probability distribution function

$$\tilde{\rho}_{\boldsymbol{\mathcal{R}},\boldsymbol{\Phi}}(\boldsymbol{R}) = \langle \boldsymbol{R} | \tilde{\rho}_{\boldsymbol{\mathcal{R}},\boldsymbol{\Phi}} | \boldsymbol{R} \rangle = \sqrt{\det[\boldsymbol{\Psi}^{-1}/(2\pi)]} e^{-\frac{1}{2}\sum_{ab}(R_a - \mathcal{R}_a)\Psi^{-1}_{ab}(R_b - \mathcal{R}_b)}$$

$$\Psi^{-1}_{ab} = \sqrt{M_a M_b} \sum_{\mu} \frac{\mathrm{e}^a_\mu \mathrm{e}^b_\mu}{\mathrm{a}^2_\mu} \qquad \mathrm{a}_\mu = \frac{\hbar}{2\mathtt{w}_\mu}\left[1 + 2n_B(\mathtt{w}_\mu)\right]$$

- At $T = 0$ K it equals the ground state ionic wave function
- In the equations above the frequencies and the polarization vectors are not the eigenvalues and eigenfunctions of the harmonic force-constants,

$$\sum_b \frac{\overset{(2)}{\phi}_{ab}}{\sqrt{M_a M_b}} \mathrm{e}^b_\mu = \omega^2_\mu \mathrm{e}^a_\mu,$$

but of the auxiliary force-constants

$$\sum_b \frac{\Phi_{ab}}{\sqrt{M_a M_b}} \mathrm{e}^b_\mu = \mathtt{w}^2_\mu \mathrm{e}^a_\mu$$

The SSCHA probability distribution function

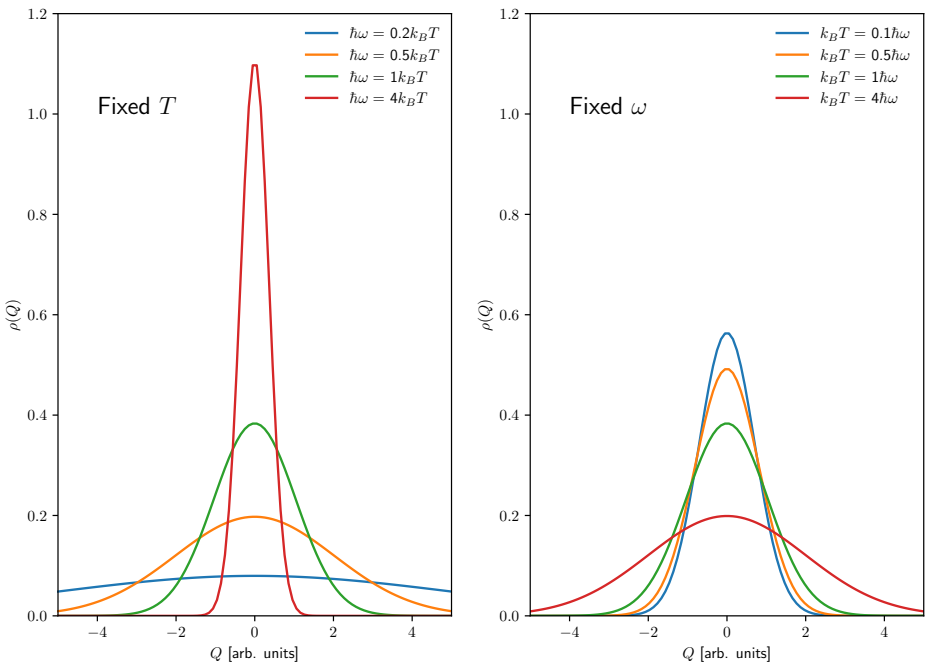
- The auxiliary frequencies $\mathtt{w}_\mu$ are just parameters that describe the SSCHA probability distribution function, not physical quantities, and are positive definite by construction
- The expectation value of the position operator are the centroids since

$$\langle \boldsymbol{R} \rangle_{\tilde{\rho}_{\boldsymbol{\mathcal{R}},\boldsymbol{\Phi}}} = \boldsymbol{\mathcal{R}}$$

- In normal mode basis ($Q_\mu = \sum_a (R_a - \mathcal{R}_a) \frac{\mathrm{e}^a_\mu}{\sqrt{M_a}}$) the probability distribution function is

$$\tilde{\rho}_{\boldsymbol{\mathcal{R}},\boldsymbol{\Phi}}(\boldsymbol{Q}) = \prod_\mu \frac{1}{\sqrt{2\pi \mathrm{a}_\mu^2}} e^{-\frac{Q_\mu^2}{2\mathrm{a}_\mu^2}}$$

- The width of the Gaussian probability is proportional to a
- 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 $O(\boldsymbol{R})$ can be calculated as

$$\langle O \rangle_{\tilde{\rho}_{\boldsymbol{\mathcal{R}},\boldsymbol{\Phi}}} = \mathrm{tr}(O\tilde{\rho}_{\boldsymbol{\mathcal{R}},\boldsymbol{\Phi}}) = \int d\boldsymbol{R} O(\boldsymbol{R}) \tilde{\rho}_{\boldsymbol{\mathcal{R}},\boldsymbol{\Phi}}(\boldsymbol{R})$$

- An example:
  The mean square displacement of an ion

$$\begin{aligned}
\left\langle (R_a - \mathcal{R}_a)^2 \right\rangle_{\tilde{\rho}_{\boldsymbol{\mathcal{R}},\boldsymbol{\Phi}}} &= \int d\boldsymbol{R} (R_a - \mathcal{R}_a)^2 \tilde{\rho}_{\boldsymbol{\mathcal{R}},\boldsymbol{\Phi}}(\boldsymbol{R}) \\
&= \sum_{\mu\nu} \frac{e^a_\mu e^a_\nu}{M_a} \int d\boldsymbol{Q} Q_\mu Q_\nu \tilde{\rho}_{\boldsymbol{\mathcal{R}},\boldsymbol{\Phi}}(\boldsymbol{Q}) \\
&= \sum_{\mu} \frac{e^a_\mu e^a_\mu}{M_a} \frac{\hbar}{2\mathtt{w}_\mu} [1 + 2n_B(\mathtt{w}_\mu)]
\end{aligned}$$

The SSCHA minimization

Conjugate-gradient (CG) minimization of $\mathcal{F}[\boldsymbol{\mathcal{R}}, \boldsymbol{\Phi}]$

- Minimization trajectory in the parameter space $(\boldsymbol{\mathcal{R}}; \boldsymbol{\Phi})$

$$\begin{array}{ccccccccc} \mathcal{H}_0 & \rightarrow & \mathcal{H}_1 & \rightarrow & \mathcal{H}_2 & \rightarrow & \dots & \rightarrow & \mathcal{H}_n \\ (\boldsymbol{\mathcal{R}}; \boldsymbol{\Phi})_0 & \rightarrow & (\boldsymbol{\mathcal{R}}; \boldsymbol{\Phi})_1 & \rightarrow & (\boldsymbol{\mathcal{R}}; \boldsymbol{\Phi})_2 & \rightarrow & \dots & \rightarrow & (\boldsymbol{\mathcal{R}}; \boldsymbol{\Phi})_n \end{array}$$

- At the minimum
  - The eigenvalues $\mathtt{w}_\mu^2$ and the eigenvectors $\mathtt{e}_\mu^a$ of $\boldsymbol{\Phi}$ define the renormalized probability distribution function, not the experimental phonon frequencies
  - $\boldsymbol{\mathcal{R}}$ are the renormalized positions at which the ionic wave function are centered (the centroids)
  - $\mathcal{F}[\boldsymbol{\mathcal{R}}, \boldsymbol{\Phi}]$ is a good variational approximation of the exact free energy

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Conjugate-gradient (CG) minimization of $\mathcal{F}[\boldsymbol{\mathcal{R}}, \boldsymbol{\Phi}]$

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- At the minimum
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  - $\boldsymbol{\mathcal{R}}$ are the renormalized positions at which the ionic wave function are centered (the centroids)
  - $\mathcal{F}[\boldsymbol{\mathcal{R}}, \boldsymbol{\Phi}]$ is a good variational approximation of the exact free energy
- Need the gradient of the functional $\mathcal{F}[\boldsymbol{\mathcal{R}}, \boldsymbol{\Phi}]$

The SSCHA gradients

- The gradients of $\mathcal{F}[\boldsymbol{\mathcal{R}}, \boldsymbol{\Phi}]$ are

$$\frac{\partial \mathcal{F}[\boldsymbol{\mathcal{R}}, \boldsymbol{\Phi}]}{\partial \mathcal{R}_a} = -\left\langle f_a(\boldsymbol{R}) - f_a^{\mathcal{V}}(\boldsymbol{R}) \right\rangle_{\tilde{\rho}_{\boldsymbol{\mathcal{R}}, \boldsymbol{\Phi}}}$$

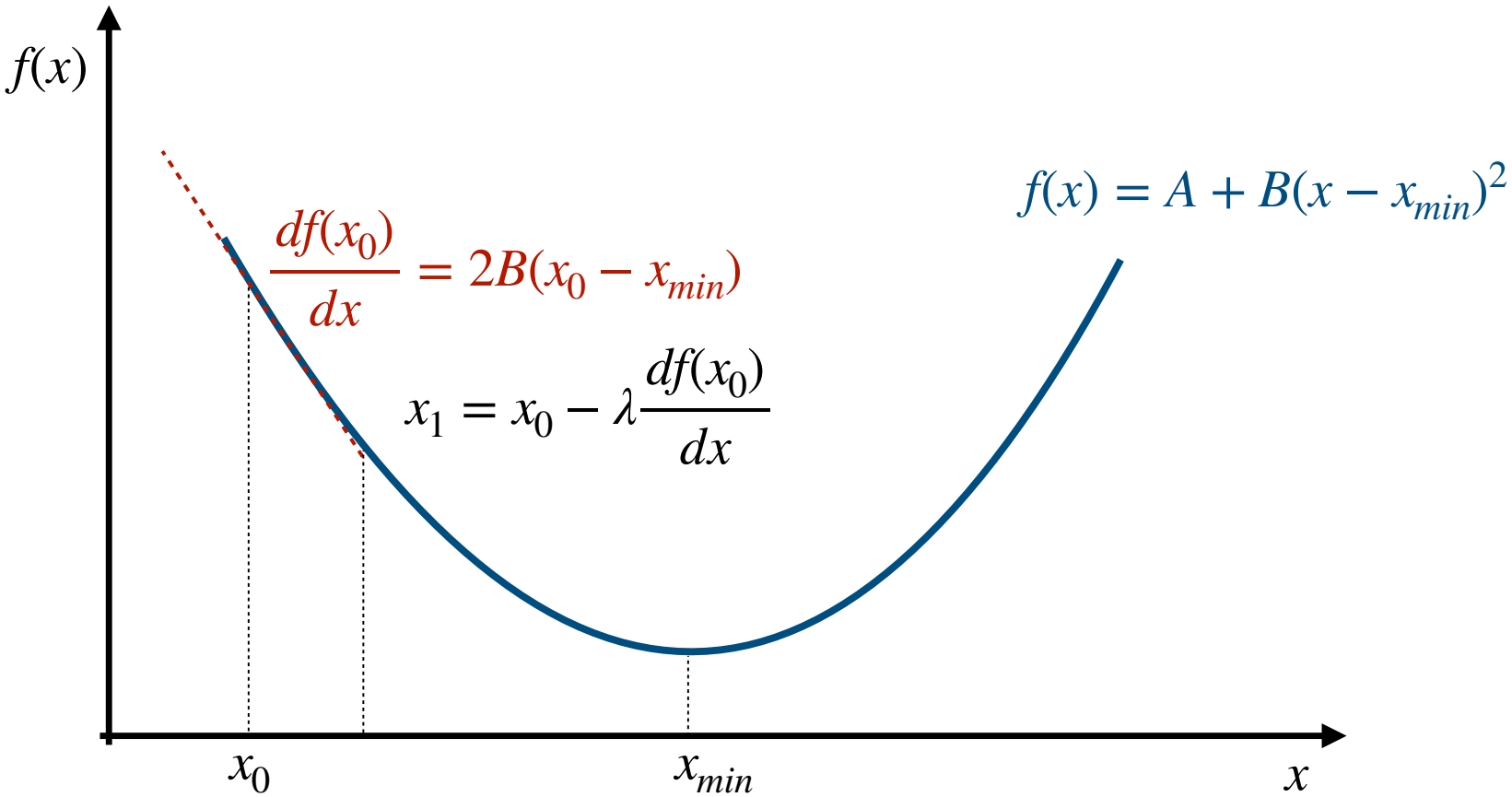
$$\frac{\partial \mathcal{F}[\boldsymbol{\mathcal{R}}, \boldsymbol{\Phi}]}{\partial \Phi_{cd}} = \sum_{ab} \frac{\Lambda[0]^{abcd}}{\sqrt{M_a M_b M_c M_d}} \left\langle \left(f_b(\boldsymbol{R}) - f_b^{\mathcal{V}}(\boldsymbol{R}) \right) \sum_e \Psi^{-1}_{ae} (R_e - \mathcal{R}_e) \right\rangle_{\tilde{\rho}_{\boldsymbol{\mathcal{R}}, \boldsymbol{\Phi}}}$$

- We have quantum statistical averages of BO forces f_a and BO forces times displacements. $f_a^{\mathcal{V}}(\boldsymbol{R}) = -\sum_b \Phi_{ab}(R_b - \mathcal{R}_b)$ is the force derived from the trial potential
- The $\boldsymbol{\Lambda}[0]$ tensor is

$$\Lambda[0]^{abcd} = \sum_{\mu\nu} \frac{\hbar}{4 \mathtt{w}_\nu \mathtt{w}_\mu} \mathrm{e}^a_\nu \mathrm{e}^b_\mu \mathrm{e}^c_\nu \mathrm{e}^d_\mu \begin{cases} \frac{d n_B(\mathtt{w}_\mu)}{d \mathtt{w}_\mu} - \frac{2 n_B(\mathtt{w}_\mu)+1}{2 \mathtt{w}_\mu} & , \mathtt{w}_\nu = \mathtt{w}_\mu \\ \frac{n_B(\mathtt{w}_\mu) - n_B(\mathtt{w}_\nu)}{\mathtt{w}_\mu - \mathtt{w}_\nu} - \frac{1 + n_B(\mathtt{w}_\mu) + n_B(\mathtt{w}_\nu)}{\mathtt{w}_\mu + \mathtt{w}_\nu} & , \mathtt{w}_\nu \neq \mathtt{w}_\mu \end{cases}$$

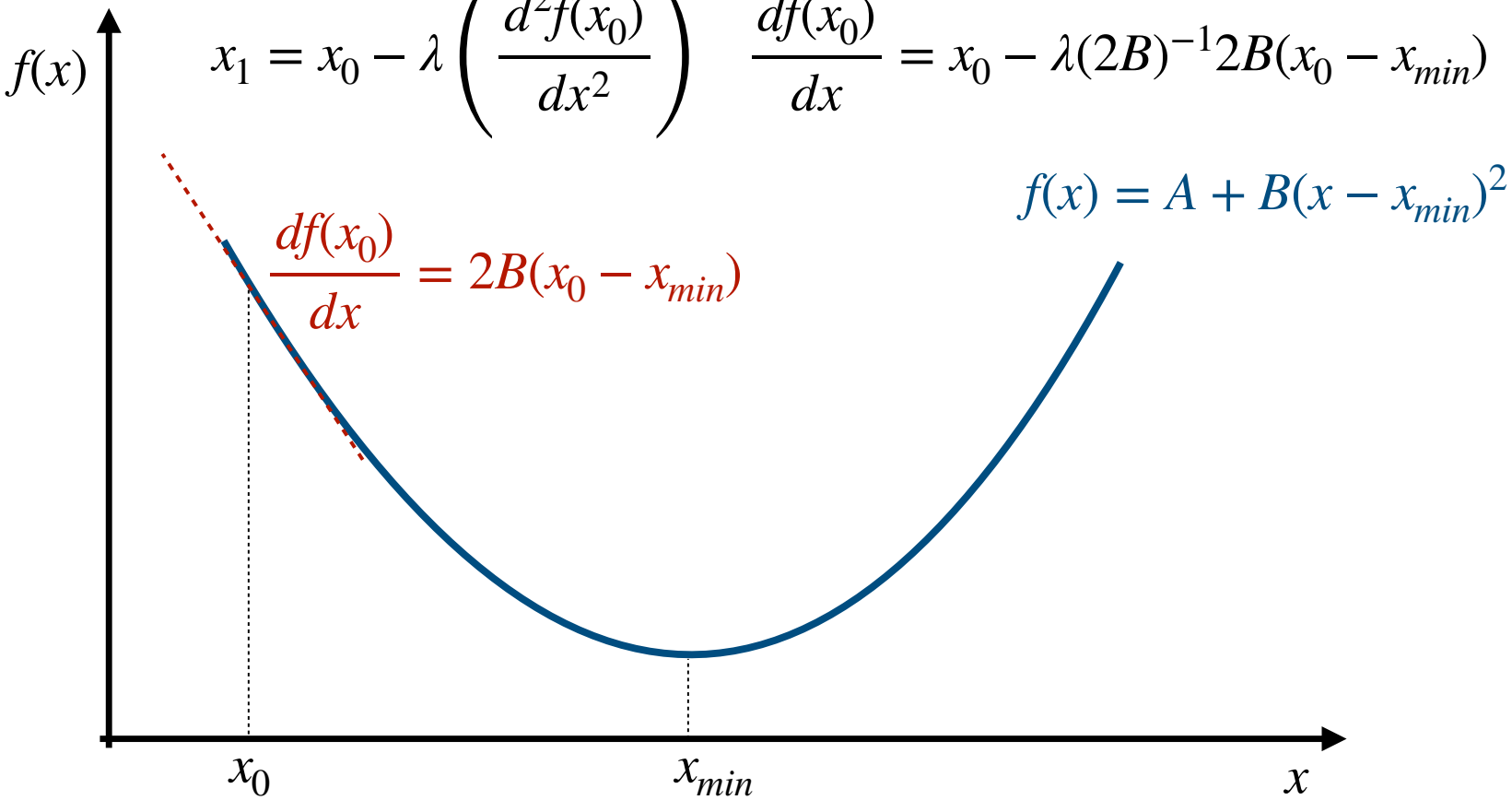
- With the gradients a gradient-descent minimization can be performed
- The gradient is symmetrized at every step, so the minimization is performed respecting the symmetries

A preconditioned gradient descent



A preconditioned gradient descent

$$x_1 = x_0 - \lambda \left(\frac{d^2 f(x_0)}{dx^2} \right)^{-1} \frac{df(x_0)}{dx} = x_0 - \lambda (2B)^{-1} 2B(x_0 - x_{min})$$



A preconditioned gradient descent

- The gradient-descent is much more efficient if the descent is preconditioned and the update of the centroids and auxiliary force constants is performed as

$$\boldsymbol{\Phi}^{(n+1)} = \boldsymbol{\Phi}^{(n)} - \lambda_{\boldsymbol{\Phi}} \sum_{ab} \left(\frac{\partial^2 \mathcal{F}}{\partial \boldsymbol{\Phi} \partial \Phi_{ab}} \right)^{-1} \frac{\partial \mathcal{F}}{\partial \Phi_{ab}}$$

$$\boldsymbol{\mathcal{R}}^{(n+1)} = \boldsymbol{\mathcal{R}}^{(n)} - \lambda_{\boldsymbol{\mathcal{R}}} \sum_{a} \left(\frac{\partial^2 \mathcal{F}}{\partial \boldsymbol{\mathcal{R}} \partial \mathcal{R}_a} \right)^{-1} \frac{\partial \mathcal{F}}{\partial \mathcal{R}_a}.$$

- The steps $\lambda_{\boldsymbol{\mathcal{R}}}$ and $\lambda_{\boldsymbol{\Phi}}$ are adimensional
- It can be shown that in this case

$$\Phi_{ab}^{(n+1)} = \Phi_{ab}^{(n)} - \lambda_{\boldsymbol{\Phi}} \left\langle \left(f_b(\boldsymbol{R}) - f_b^{\mathcal{V}}(\boldsymbol{R}) \right) \sum_c {\Psi^{-1}}_{ac} \left(R_c - \mathcal{R}_c \right) \right\rangle_{\tilde{\rho}_{\boldsymbol{\mathcal{R}},\boldsymbol{\Phi}}}$$

$$\mathcal{R}_a^{(n+1)} = \mathcal{R}_a^{(n)} + \lambda_{\boldsymbol{\mathcal{R}}} \sum_b \Phi_{ab}^{-1} \left\langle f_b(\boldsymbol{R}) - f_b^{\mathcal{V}}(\boldsymbol{R}) \right\rangle_{\tilde{\rho}_{\boldsymbol{\mathcal{R}},\boldsymbol{\Phi}}}$$

The SSCHA self-consistent equation

- The SSCHA minimization can be performed fixing $\boldsymbol{\mathcal{R}}$ and only optimizing the auxiliary force constants
- In that case the SSCHA solution will obey the following self-consistent equation

$$\Phi_{ab}(\boldsymbol{\mathcal{R}}) = \left\langle \frac{\partial^2 V}{\partial R_a \partial R_b} \right\rangle_{\tilde{\rho}_{\boldsymbol{\Phi}(\boldsymbol{\mathcal{R}})}}$$

- This self-consistent equation opens a way to implement the SSCHA without using the gradient-descent approach

Stochastic calculation of the free energy and its gradient

- The calculation of the free energy and the gradient need

$$\langle V(\boldsymbol{R}) - \mathcal{V}(\boldsymbol{R})\rangle_{\tilde{\rho}_{\boldsymbol{\mathcal{R}},\boldsymbol{\Phi}}}, \quad \left\langle f_b(\boldsymbol{R}) - f_b^{\mathcal{V}}(\boldsymbol{R})\right\rangle_{\tilde{\rho}_{\boldsymbol{\mathcal{R}},\boldsymbol{\Phi}}}, \quad \left\langle \left(f_b(\boldsymbol{R}) - f_b^{\mathcal{V}}(\boldsymbol{R})\right)(R_c - \mathcal{R}_c)\right\rangle_{\tilde{\rho}_{\boldsymbol{\mathcal{R}},\boldsymbol{\Phi}}}$$

Importance sampling for the quantum statistical averages

- Quantum statistical averages involve observables that depend on the position

$$\langle O\rangle_{\tilde{\rho}_{\boldsymbol{\mathcal{R}},\boldsymbol{\Phi}}} = \mathrm{tr}[\tilde{\rho}_{\boldsymbol{\mathcal{R}},\boldsymbol{\Phi}} O] = \int \mathrm{d}\mathbf{R} O(\mathbf{R})\tilde{\rho}_{\boldsymbol{\mathcal{R}},\boldsymbol{\Phi}}(\mathbf{R})$$

- Create N_c ionic configurations in a supercell according to $\tilde{\rho}_{(\boldsymbol{\mathcal{R}},\boldsymbol{\Phi})_0}(\mathbf{R})$: $\{\mathbf{R}_I\}_{I=1,\ldots,N_c}$
- Stochastic evaluation of the integral: $\langle O\rangle_{\rho_{\mathcal{H}_0}} \simeq \frac{1}{N_c}\sum_{I=1}^{N_c} O(\mathbf{R}_I)$

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$$\langle V(\boldsymbol{R}) - \mathcal{V}(\boldsymbol{R})\rangle_{\tilde{\rho}_{\boldsymbol{\mathcal{R}},\boldsymbol{\Phi}}}, \quad \left\langle f_b(\boldsymbol{R}) - f_b^{\mathcal{V}}(\boldsymbol{R})\right\rangle_{\tilde{\rho}_{\boldsymbol{\mathcal{R}},\boldsymbol{\Phi}}}, \quad \left\langle \left(f_b(\boldsymbol{R}) - f_b^{\mathcal{V}}(\boldsymbol{R})\right)(R_c - \mathcal{R}_c)\right\rangle_{\tilde{\rho}_{\boldsymbol{\mathcal{R}},\boldsymbol{\Phi}}}$$

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- Create N_c ionic configurations in a supercell according to $\tilde{\rho}_{(\boldsymbol{\mathcal{R}},\boldsymbol{\Phi})_0}(\mathbf{R})$: $\{\mathbf{R}_I\}_{I=1,\ldots,N_c}$
- Stochastic evaluation of the integral: $\langle O\rangle_{\rho_{\mathcal{H}_0}} \simeq \frac{1}{N_c}\sum_{I=1}^{N_c} O(\mathbf{R}_I)$
- Requires to evaluate forces and energies in supercells: $\mathbf{f}(\mathbf{R}_I), V(\mathbf{R}_I)$

Stochastic calculation of the free energy and its gradient

- The calculation of the free energy and the gradient need

$$\langle V(\boldsymbol{R}) - \mathcal{V}(\boldsymbol{R})\rangle_{\tilde{\rho}_{\boldsymbol{\mathcal{R}},\boldsymbol{\Phi}}}, \quad \left\langle f_b(\boldsymbol{R}) - f_b^{\mathcal{V}}(\boldsymbol{R})\right\rangle_{\tilde{\rho}_{\boldsymbol{\mathcal{R}},\boldsymbol{\Phi}}}, \quad \left\langle \left(f_b(\boldsymbol{R}) - f_b^{\mathcal{V}}(\boldsymbol{R})\right)(R_c - \mathcal{R}_c)\right\rangle_{\tilde{\rho}_{\boldsymbol{\mathcal{R}},\boldsymbol{\Phi}}}$$

Reweighting for the quantum statistical averages for CG step $n > 0$

- The calculated forces and energies can be recycled throughout the CG minimization

$$\int \mathrm{d}\mathbf{R} O(\mathbf{R}) \tilde{\rho}_{(\boldsymbol{\mathcal{R}},\boldsymbol{\Phi})_n}(\mathbf{R}) = \int \mathrm{d}\mathbf{R} O(\mathbf{R}) \frac{\tilde{\rho}_{(\boldsymbol{\mathcal{R}},\boldsymbol{\Phi})_n}(\mathbf{R})}{\tilde{\rho}_{(\boldsymbol{\mathcal{R}},\boldsymbol{\Phi})_0}(\mathbf{R})} \tilde{\rho}_{(\boldsymbol{\mathcal{R}},\boldsymbol{\Phi})_0}(\mathbf{R}) \simeq$$
$$\frac{1}{N_c} \sum_{I=1}^{N_c} O(\mathbf{R}_I) \frac{\tilde{\rho}_{(\boldsymbol{\mathcal{R}},\boldsymbol{\Phi})_n}(\mathbf{R}_I)}{\tilde{\rho}_{(\boldsymbol{\mathcal{R}},\boldsymbol{\Phi})_0}(\mathbf{R}_I)}$$

- The reweighting procedure is valid as long as

$$\frac{1}{N_c} \sum_{I=1}^{N_c} \frac{\tilde{\rho}_{(\boldsymbol{\mathcal{R}},\boldsymbol{\Phi})_n}(\mathbf{R}_I)}{\tilde{\rho}_{(\boldsymbol{\mathcal{R}},\boldsymbol{\Phi})_0}(\mathbf{R}_I)} \sim 1$$

Stochastic calculation of the free energy and its gradient

- The calculation of the free energy and the gradient need

$$\langle V(\boldsymbol{R}) - \mathcal{V}(\boldsymbol{R}) \rangle_{\tilde{\rho}_{\boldsymbol{\mathcal{R}},\boldsymbol{\Phi}}}, \quad \left\langle f_b(\boldsymbol{R}) - f_b^{\mathcal{V}}(\boldsymbol{R}) \right\rangle_{\tilde{\rho}_{\boldsymbol{\mathcal{R}},\boldsymbol{\Phi}}}, \quad \left\langle \left(f_b(\boldsymbol{R}) - f_b^{\mathcal{V}}(\boldsymbol{R}) \right) (R_c - \mathcal{R}_c) \right\rangle_{\tilde{\rho}_{\boldsymbol{\mathcal{R}},\boldsymbol{\Phi}}}$$

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$$\frac{1}{N_c} \sum_{I=1}^{N_c} O(\mathbf{R}_I) \frac{\tilde{\rho}_{(\boldsymbol{\mathcal{R}},\boldsymbol{\Phi})_n}(\mathbf{R}_I)}{\tilde{\rho}_{(\boldsymbol{\mathcal{R}},\boldsymbol{\Phi})_0}(\mathbf{R}_I)}$$

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- The SSCHA can be applied at any degree of theory
  - empirical potentials
  - DFT *ab initio*
  - Beyond DFT (Monte Carlo, GW, ...)

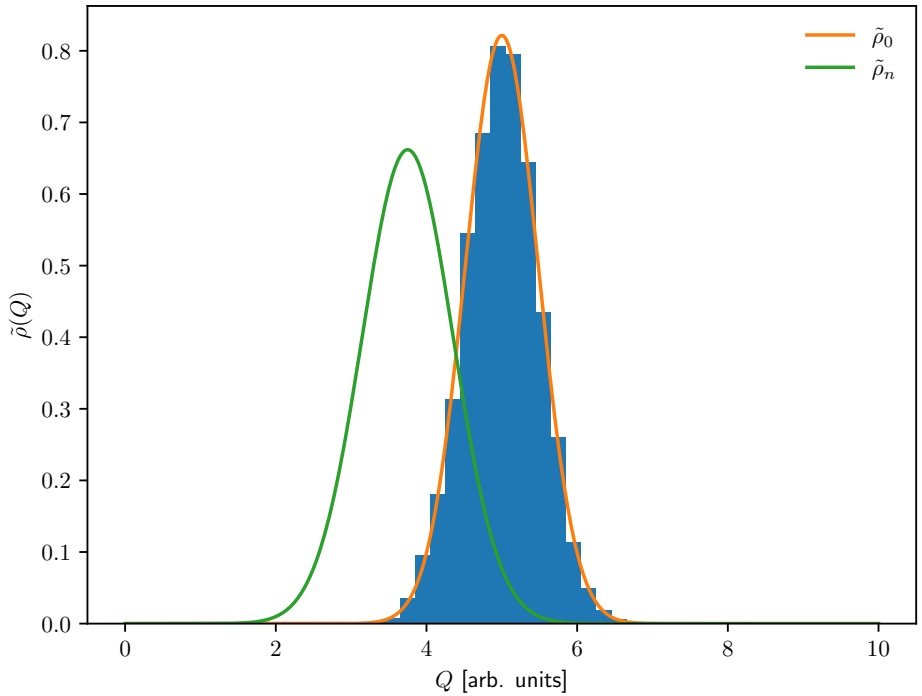
The SSCHA coming out of statistical range

- The SSCHA stops the minimization if the created set of configurations no longer resembles $\tilde{\rho}_{(\boldsymbol{\mathcal{R}},\boldsymbol{\Phi})_n}$
- This is detected according to the Kong-Liu criteria that sets the number of effective configurations at step n

$$N_n^{eff} = \frac{\sum_{I=1}^{N_c} \rho_n^2(I)}{\left(\sum_{I=1}^{N_c} \rho_n(I)\right)^2}$$

where the weights are

$$\rho_n(I) = \frac{\tilde{\rho}_{(\boldsymbol{\mathcal{R}},\boldsymbol{\Phi})_n}(\mathbf{R}_I)}{\tilde{\rho}_{(\boldsymbol{\mathcal{R}},\boldsymbol{\Phi})_0}(\mathbf{R}_I)}$$



- If at step n $N_n^{eff}/N_c < \eta$, where η is a number around 0.5, the SSCHA minimization stops and one should create new configurations with the updated $\tilde{\rho}_{(\boldsymbol{\mathcal{R}},\boldsymbol{\Phi})_n}$

The SSCHA convergence threshold

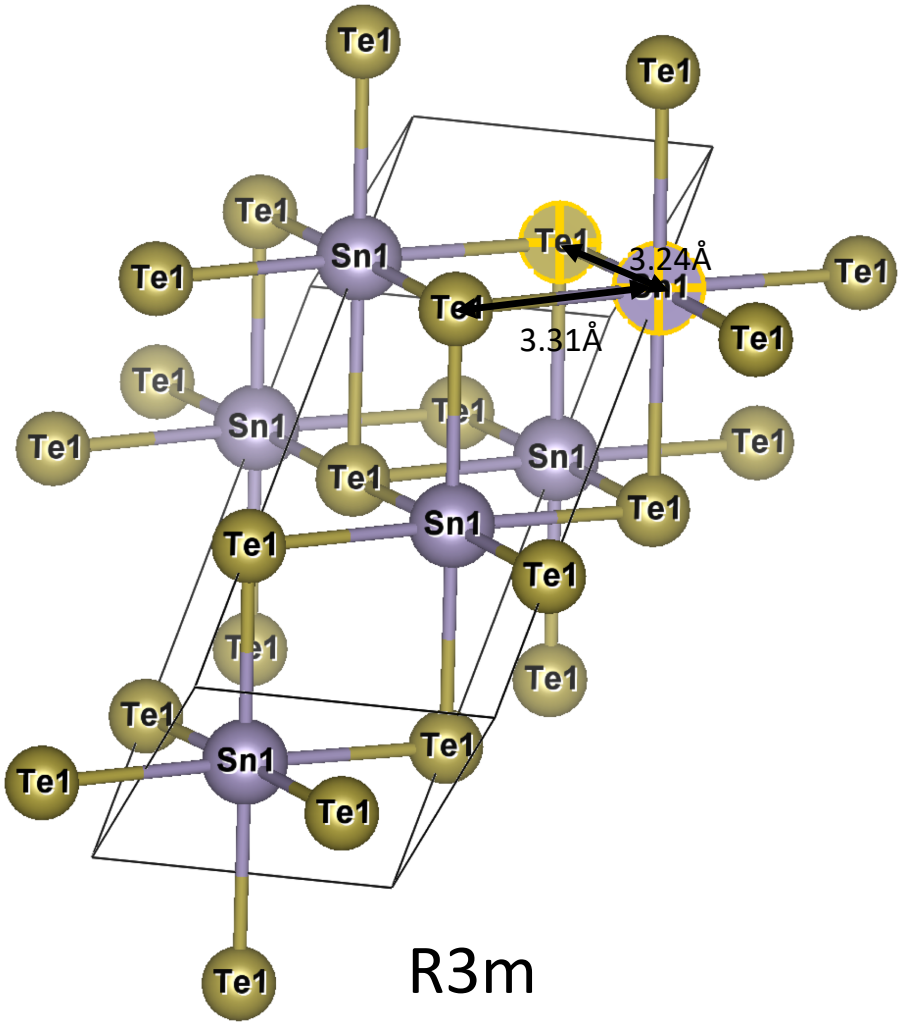
- The SSCHA calculation is stopped when the values of the gradients become smaller than a ratio (δ) of its estimated error

$$\left| \frac{\partial \mathcal{F}[\boldsymbol{\mathcal{R}}, \boldsymbol{\Phi}]}{\partial \boldsymbol{\Phi}} \right| < \delta \left| \Delta \frac{\partial \mathcal{F}[\boldsymbol{\mathcal{R}}, \boldsymbol{\Phi}]}{\partial \boldsymbol{\Phi}} \right|$$

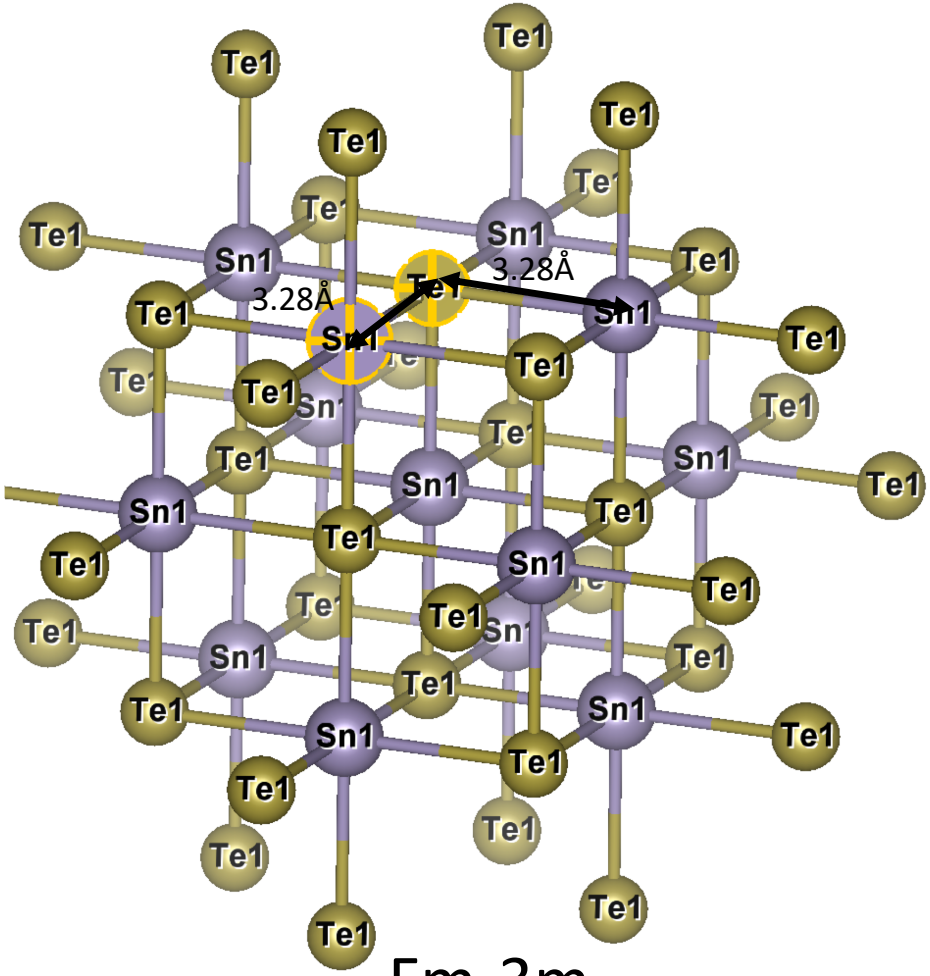
$$\left| \frac{\partial \mathcal{F}[\boldsymbol{\mathcal{R}}, \boldsymbol{\Phi}]}{\partial \boldsymbol{\mathcal{R}}} \right| < \delta \left| \Delta \frac{\partial \mathcal{F}[\boldsymbol{\mathcal{R}}, \boldsymbol{\Phi}]}{\partial \boldsymbol{\mathcal{R}}} \right|$$

- When this criteria is reached in both gradients the calculation is assumed to be converged
- The ideal thing is to use a very small δ and try to reach 0 gradients

SSCHA calculation example



R3m

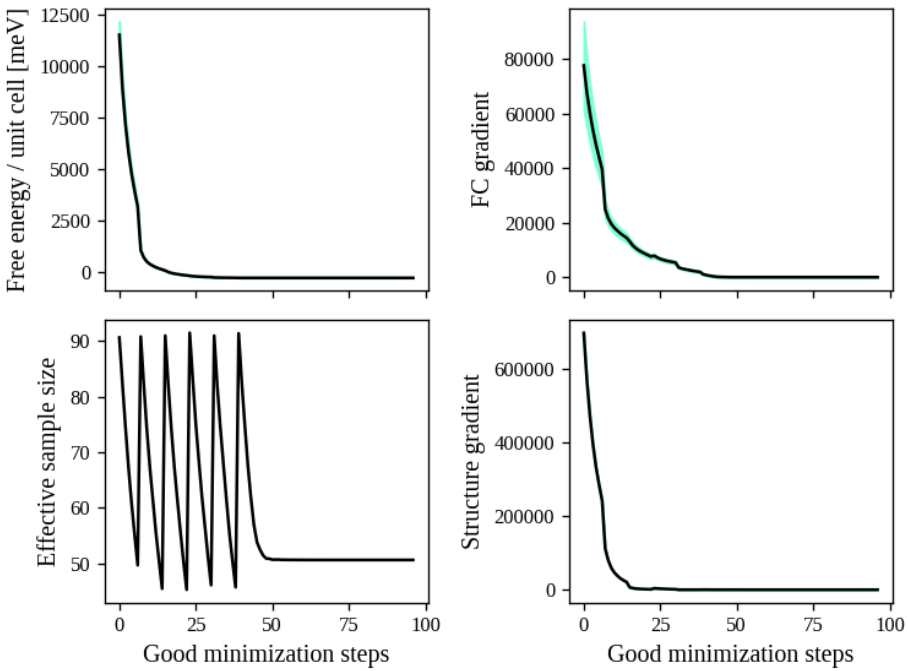


Fm-3m

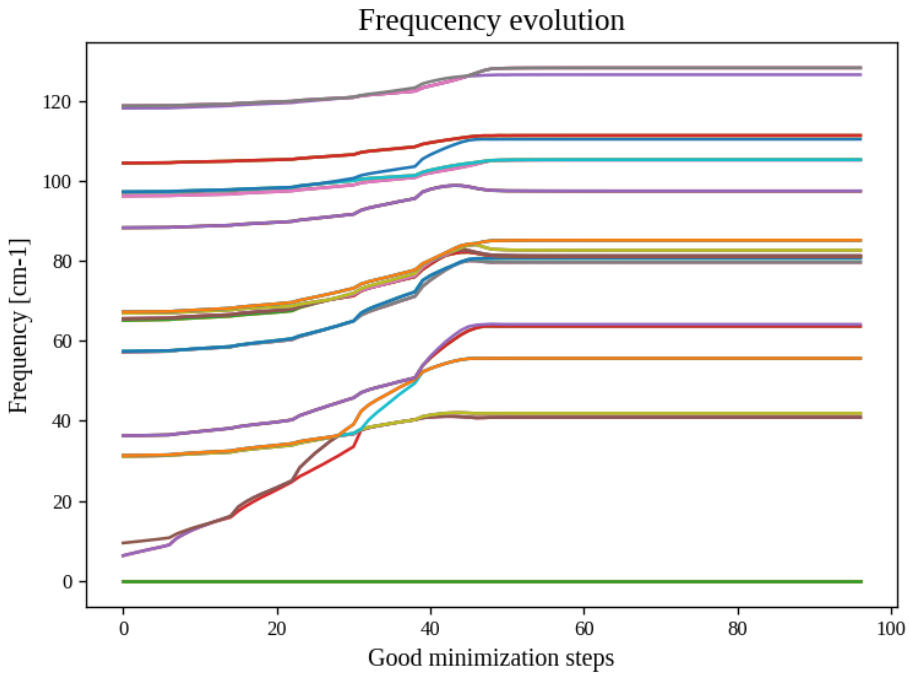
SSCHA calculation example

- First populations with 100 configurations each
- 6 populations to reach convergence

Evolution of the free energy, gradients, and Kong-Liu ratio



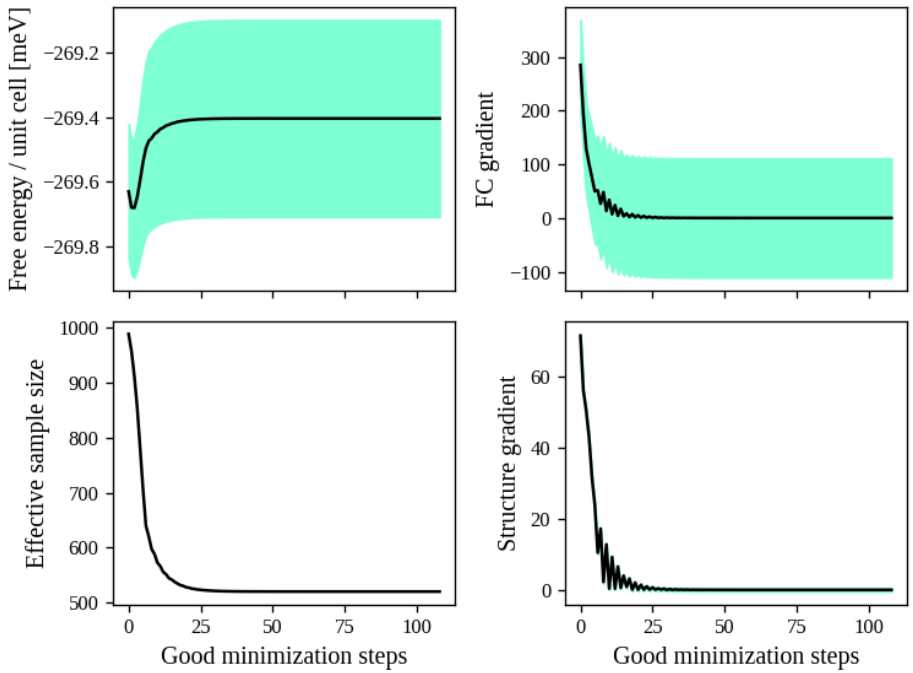
Evolution of the auxiliary frequencies



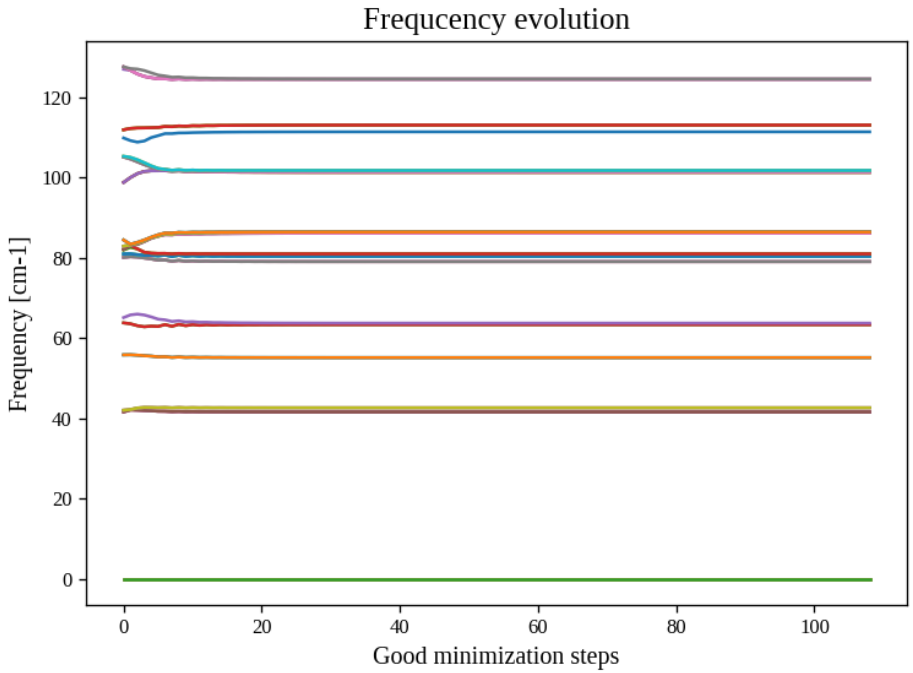
SSCHA calculation example

- Add more configurations for a final run

Evolution of the free energy, gradients, and Kong-Liu ratio



Evolution of the auxiliary frequencies



The optimization of the lattice in the SSCHA

- The SSCHA can be used to relax the lattice parameters of a structure considering quantum and thermal effects, and full anharmonicity
- When a lattice is relaxed in standard methods the contribution of the ions to the energy is neglected as the stress tensor is calculated from $V(\boldsymbol{R})$

$$P^{BO}_{\alpha\beta} = -\frac{N}{\Omega}\left[\frac{\partial V(\boldsymbol{R})}{\partial \varepsilon_{\alpha\beta}}\right]_{\boldsymbol{\varepsilon}=0}$$

- In the SSCHA we can calculate the stress tensor including ionic quantum and thermal effects in the lattice parameters

$$P_{\alpha\beta} = -\frac{N}{\Omega}\left[\frac{\partial \mathcal{F}[\boldsymbol{\mathcal{R}}, \boldsymbol{\Phi}]}{\partial \varepsilon_{\alpha\beta}}\right]_{\boldsymbol{\varepsilon}=0} = \left\langle P^{BO}_{\alpha\beta}(\boldsymbol{R})\right\rangle_{\tilde{\rho}_{\boldsymbol{\mathcal{R}},\boldsymbol{\Phi}}} - \frac{N}{2\Omega}\sum_s \left\langle u_s^\alpha f_s^\beta + u_s^\beta f_s^\alpha \right\rangle_{\tilde{\rho}_{\boldsymbol{\mathcal{R}},\boldsymbol{\Phi}}}$$

- For that, apart from forces, the classical $P^{BO}_{\alpha\beta}$ stresses need to be calculated for each of the structures in the ensemble

The optimization of the lattice in the SSCHA

- The ensemble is created with constant lattice and the lattice vectors $\{\boldsymbol{a}_i\}$ are updated when creating the next ensemble as

$$a'_{i\,\alpha} = a_{i\,\alpha} + \lambda_{\{\boldsymbol{a}_i\}} \sum_{\beta} \varepsilon_{\alpha\beta} a_{i\,\beta},$$

with

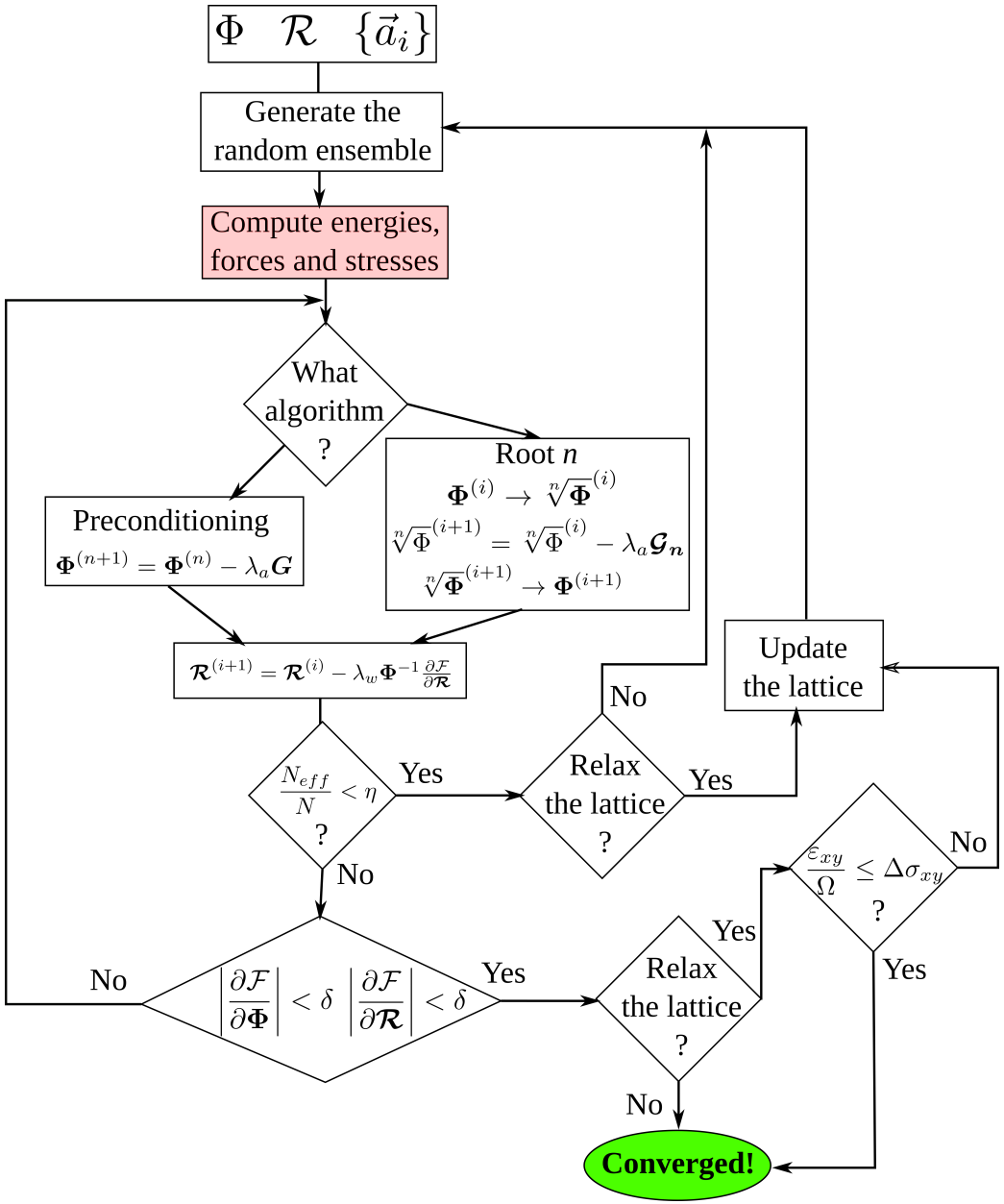
$$\varepsilon_{\alpha\beta} = \frac{\Omega}{N} \left(P_{\alpha\beta} - P^* \delta_{\alpha\beta} \right)$$

- P^* is the target pressure
- The best $\lambda_{\{\boldsymbol{a}_i\}}$ step is obtained with

$$\lambda_{\{\boldsymbol{a}_i\}} = \frac{1}{3\Omega B_0}$$

with B_0 the bulk modulus

SSCHA calculation flowchart with cell relaxation



Take-home message

1. The SSCHA is a variational method based on the thermodynamic free energy
2. The SSCHA can deal with strong anharmonicity in the non-perturbative regime
3. The SSCHA can relax structures, both internal and cell parameters, in the quantum anharmonic energy landscape
4. SSCHA auxiliary frequencies are related to the width of the ionic wave function (probability distribution) and are not in principle physically relevant quantities
5. So far the SSCHA does not describe anharmonic phonon linewidths
6. Lectures 2 and 3 will clarify a lot these issues