FRIEDRICH-ALEXANDER
UNIVERSITÄT
ERLANGEN-NÜRNBERG
FACULTY OF SCIENCES

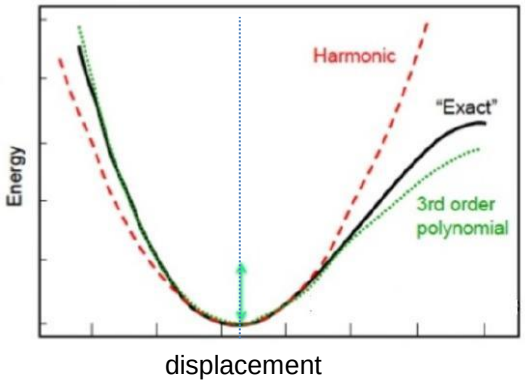
Density functional theory in solid state physics

Lecture 12

Summary

- DFT allow access to vibrational (phononic) spectra of materials within harmonic approximation
- DFT is quite accurate for phonons
- Need dynamical matrix of material
  - Finite displacement method: build force constants/dynamical matrix by successive small displacement of atoms in the unit cell and numerical differentiation
  - Density functional perturbation theory (DFPT): directly calculate dynamical matrix by calculating derivatives of the total energy using perturbation theory.
  - Result: Phonon frequencies, „normalized displacements“ $A_{\nu i} = \frac{c_\nu}{\sqrt{M_i}}$ (c_ν : eigenvector of the DM)
- Phonon dispersions and vibrational DOS from FD requires supercell method (computationally expensive!) due to periodic boundary conditions
- DFPT is more complex but only requires unit cell to obtain full phonon spectrum (but instead sampling of BZ), also yields dielectric tensor, Raman&infrared spectra etc.

- Harmonic approximation only valid for small displacements, and small temperatures,
- no volume dependence of thermal properties, no interaction between phonons

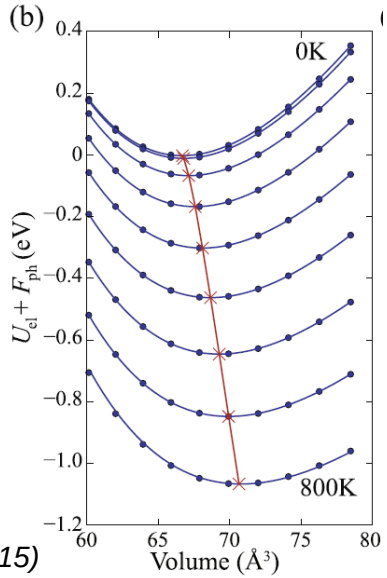


- Quasiharmonic approximation: introduce volume dependence into harmonic approximation

Helmholtz free energy $F^{QHA}(T,V) = \underbrace{U^0(V)}_{=E^{KS}} + F_{vib}^{QHA}(T,V)$

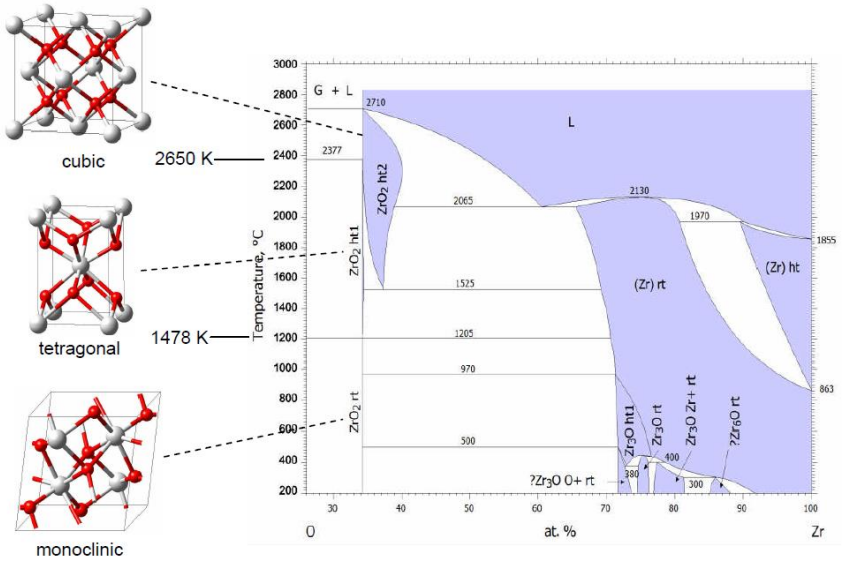
Calculated from phonon frequencies

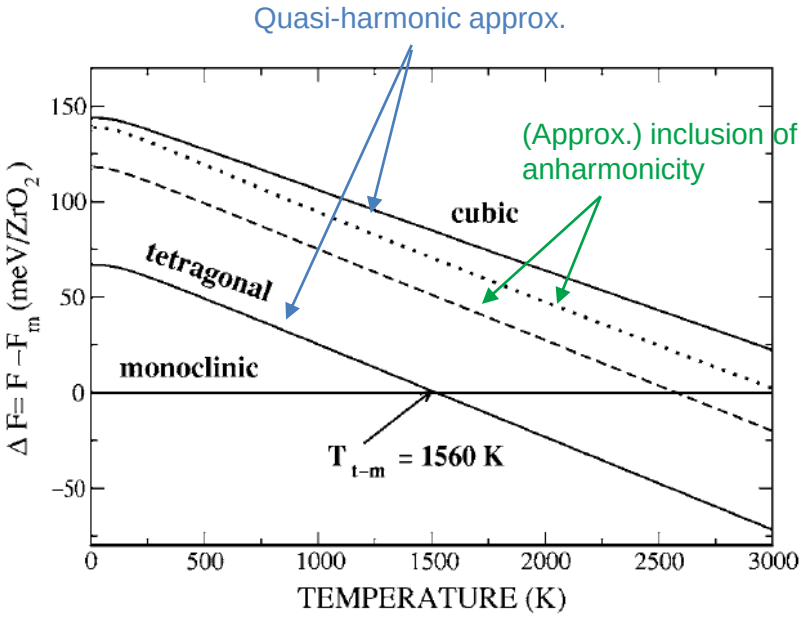
- Allow access to thermal lattice expansion (see exercise sheet 4), temperature-induced phase transitions etc.



Scripta Materialia 108, 1 (2015)

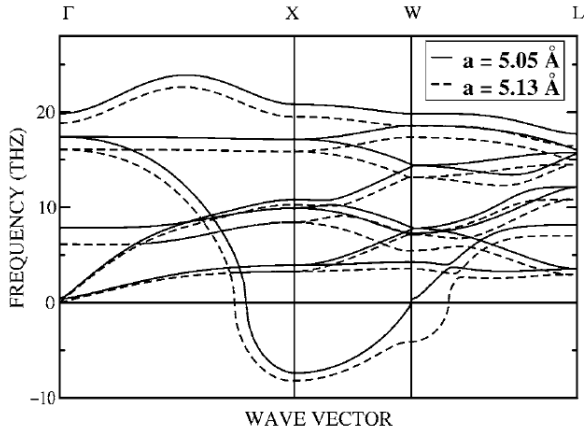
- Example: phase transition in ZrO_2





http://archive.materialsdesign.com/system/files/appnotes/ZrO2_phase_transition.pdf

- QHA works well for monoclinic-tetragonal transition
- ZrO_2 has „soft“ phonon mode, requiring inclusion of anharmonic effects for tetra-cubic transition



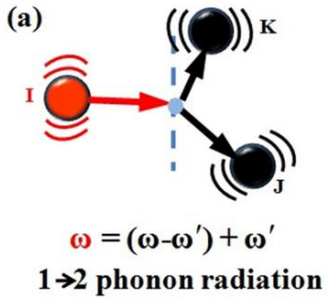
J. Chem Phys. 123, 204708 (2005)

- Expansion of lattice potential energy to include anharmonic effects (1D case)

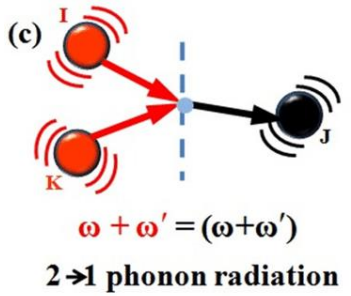
$$U(u) \approx U(0) + \frac{1}{2}\frac{\partial^2 U}{\partial u^2}u^2 + \underbrace{\frac{1}{6}\frac{\partial^3 U}{\partial u^3}u^3}_{U_3} + \underbrace{\frac{1}{24}\frac{\partial^4 U}{\partial u^4}u^4}_{U_4} + \cdots$$

- U_3, U_4, etc correspond to effect of phonon-phonon interaction

$$U_3 = \frac{N^{-0.5}}{n!}\sum_{q_1,q_2,q_3,} \Phi^{lj,l'j',l''j''}_{\alpha,\alpha',\alpha''}(\vec{q}_1,\vec{q}_2,\vec{q}_3)u_{lj\alpha}(\vec{q}_1)u_{l'j'\alpha'}(\vec{q}_2)u_{l''j''\alpha''}(\vec{q}_3)$$



- Can calculate force constants from DFPT, implemented in D3Q code of Quantum Espresso; expensive, as all q_1,q_2,q_3 triples have to be calculated



- Can also do it with supercell method, but complex to handle

- Phonons are important for heat conduction through a material

- Flux of heat for temperature gradient is given by perturbed phonon population $N_{q\nu}$

$$\sum_{\nu} \int_{BZ} \hbar \omega_{q\nu} \vec{c}_{q\nu} N_{q\nu} \, dq = -\kappa \nabla T \qquad \text{(Fourier's law)}$$

- Boltzmann Transport Equation for phonons: flow of phonon population

$$\frac{\partial N_{q\nu}}{\partial t} = -\left[\vec{c}_{q\nu} \cdot \nabla T \left(\frac{\partial N_{q\nu}(r,t)}{\partial T} \right) + \hbar^{-1} \nabla_q N_{q\nu}(r,t) \cdot \vec{F} \right] + \left(\frac{\partial N_{q\nu}}{\partial t} \right)_{scat}$$

Diffusion terms — External field — scattering

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Steady-state

Absence of external fields

- $\left(\frac{\partial N_{q\nu}}{\partial t}\right)_{scat}$ derived from phonon-phonon scattering rate (three-phonon case)

$$\Gamma_{q\nu}^{ph-ph} = \frac{18\pi}{\hbar^2} \sum_{q_1\nu_1, q_2\nu_2} \left|V^{(3)}\right|^2 \delta_{\vec{q}+\vec{q}_1+\vec{q}_2,+\vec{G}} \cdot \left[\left(N_{q_1\nu_1} + N_{q_2\nu_2} + 1\right) \delta\left(\omega_{q\nu} - \omega_{q_1\nu_1} - \omega_{q_2\nu_2}\right) \right.$$
$$\left. + \left(N_{q_1\nu_1} - N_{q_2\nu_2}\right) \left(\delta\left(\omega_{q\nu} + \omega_{q_1\nu_1} - \omega_{q_2\nu_2}\right) - \delta\left(\omega_{q\nu} - \omega_{q_1\nu_1} + \omega_{q_2\nu_2}\right) \right) \right]$$

Three-phonon coupling, depends on $\phi_{\alpha,\alpha',\alpha''}^{lj,l'j',l''j''}$

Eur. Phys. J 89, 239 (2016)

- Small perturbations: $N_{q\nu} \approx N_{q\nu}^{eq} + \left.\frac{\partial N_{q\nu}}{\partial(\hbar\omega'_{q\nu})}\right|_{\omega'_{q\nu}=\omega_{q\nu}} \vec{F}_{q\nu} \cdot \nabla T$

Leads to linearized BTE and the approximation $\frac{\partial N_{q\nu}(r,t)}{\partial T} \approx \frac{\partial N_{q\nu}^{eq}(r,t)}{\partial T}$

- Solving BTE iteratively for $\vec{F}_{q\nu}$ allows for following phonon population with time

- Can get several properties from this, e.g. thermal conductivity tensor:

$$\kappa_{\alpha\beta} = \frac{\hbar}{k_B T^2 V_{uc}} \sum_{q\nu} \omega_{q\nu} c_\alpha N_{q\nu}^{eq}\left(N_{q\nu}^{eq} + 1\right) F_{q\nu,\beta}$$

- Most expensive part: Calculating the phonon-phonon scattering matrix elements

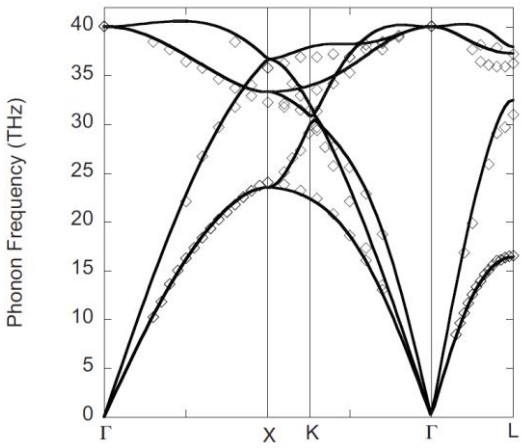
- Additional simplification: Relaxation time approximation (RTA)

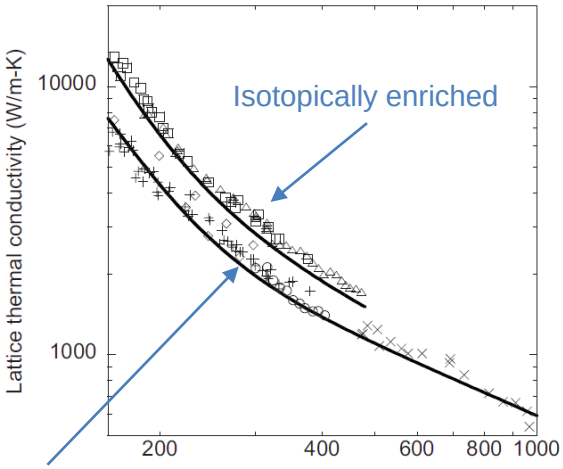
$$\left(\frac{\partial N_{q\nu}}{\partial t}\right)_{ph-ph} \approx \left(N_{q\nu} - N_{q\nu}^{eq}\right) \underbrace{\tau_{q\nu}^{-1}}_{=\Gamma_{q\nu}^{ph-ph}}$$

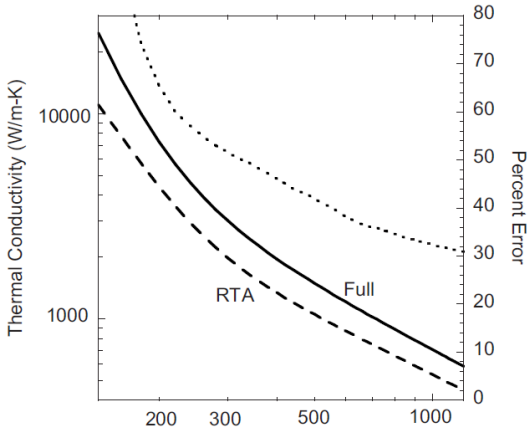
Could also include defect and/or four-phonon scattering here

Eur. Phys. J 89, 239 (2016)
Phys. Rev. B 93, 024307 (2016)

- Example: Thermal conductivity in diamond *Phys. Rev. 80, 125203 (2009)*







- Three-phonon scattering and elastic scattering on isotopic impurities included, iterative solution of the BTE

- Solution of the BTE (both iterative and in the RTA) are implemented in a few freely available packages

- Now coupling between electronic and phononic subsystem:

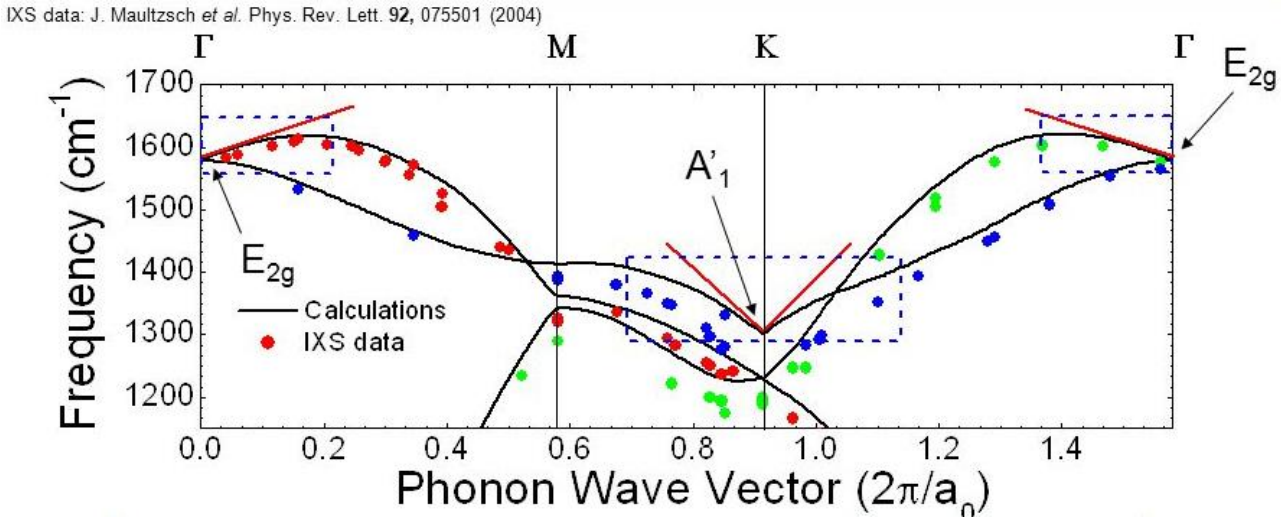
$$H = H^{KS} + H^{phon} + \underbrace{H^{el-phon}}_{\sum_{q\nu} g^{q\nu}_{mk+q,nk} \hat{c}^{\dagger}_{mk+q} \hat{c}_{nk} (\hat{a}_{q\nu} + \hat{a}^{\dagger}_{-q\nu})} \left(+H^{el-2phon} + \cdots\right)$$

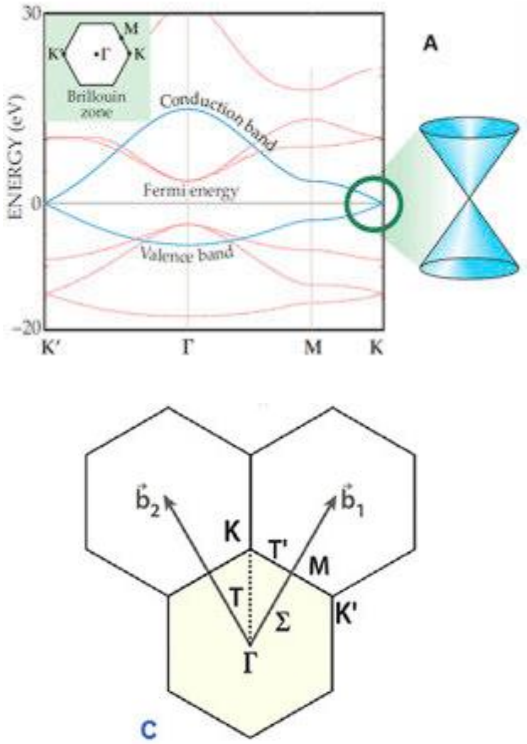
- Matrix element for scattering of electron from state φ_{nk} to state φ_{mk+q} by phonon

$$g^{q\nu}_{mk+q,nk} = \sum_{l,i} \sum_{\alpha=1}^{3} \frac{A^{q\nu}_{li\alpha}}{\sqrt{M_i \omega_{qv}}} \underbrace{\left\langle \varphi_{mk+q} \left| \frac{\partial v_{KS}}{\partial \tilde{u}_{0i,\alpha}(q)} \right| \varphi_{nk} \right\rangle_{uc}}_{M^{\alpha}_{mk+q,nk}}$$

- Here: include the reaction („screening“) of the electronic structure to lattice distortion
- Straight-forward to calculate from DFT because electronic part (Kohn-Sham wavefunctions) and phononic part (DFPT) are separated.
- Readily available in several DFT codes, such as Quantum Espresso, Elk, GPAW etc.
- Review and more details of EPC in Rev. Mod. 89, 015003 (2017)

- Electron-phonon coupling crucial for correct description of effect of Kohn anomalies on phonon spectrum
- Kohn anomaly: phonons can couple two points on Fermi surface, reducing phonon frequency
- Prominent example: Graphene





2 sharp kinks for modes at Γ and K

Kohn anomaly ↔ EPC≠0

Mat. Today Pys. 3, 93 (2017)

Phys. Rev. Lett. 93, 185503 (2004)

- Phonon self-energy from EPC:

$$\Pi_{q\nu}(\omega) = \frac{2}{V_{BZ}} \sum_{m,n} \int_{BZ} \left| g^{q\nu}_{mk+q,nk} \right|^2 \frac{f_{nk}(T) - f_{mk+q}(T)}{\varepsilon_{nk} - \varepsilon_{mk+q} - \omega - i\delta} dk$$

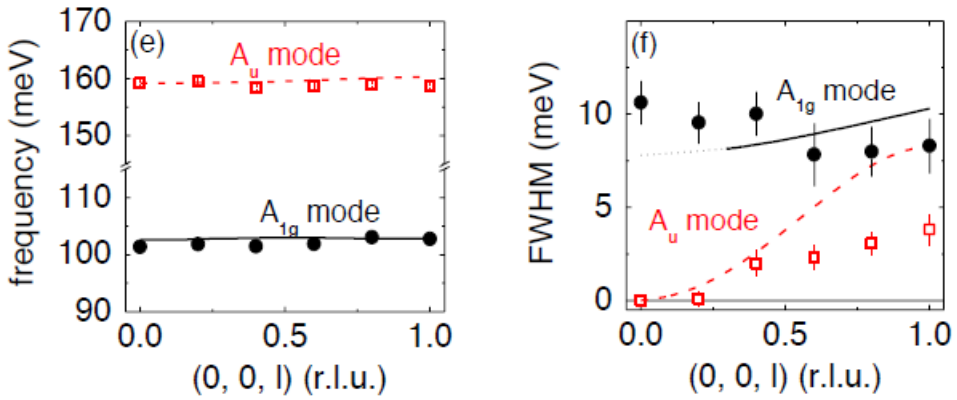
- Renormalization of phonon frequencies:

$$\tilde{\omega}^2_{q\nu} = \omega^2_{q\nu} - 2\omega_{q\nu} Re\left(\Pi_{q\nu}(\tilde{\omega}_{q\nu}, T)\right)$$

- EPC induced phonon linewidths for small T (experimentally measureable from, e.g. neutron or x-ray scattering):

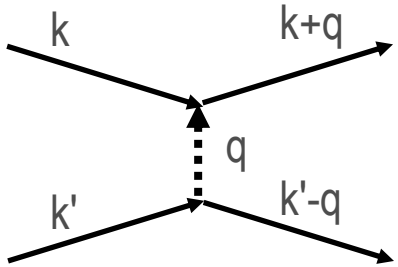
$$\gamma_{q\nu} = -2\pi Im\left(\Pi_{q\nu}\right)$$

YNi_2B_2C



Phys. Rev. Lett. 109, 057001 (2012)

- Superconductivity: Phonon-mediated electron-electron interaction



- Migdal-Eliashberg theory: extension of BCS theory framework to strong coupling regime

- Quasiparticle spectrum is gapped (Eliashberg gap equations, see https://www.cond-mat.de/events/correl13/manuscripts/ummarino.pdf for details)

- Important ingredient: Eliashberg function for coupling between two electronic states:

$$\alpha^2 F_{mk+q,nk}\,(\omega) = \frac{N(E_F)}{V_{BZ}} \sum_{\nu} \int_{BZ} \left| g^{q\nu}_{mk+q,nk} \right|^2 \delta\left(\omega - \omega_{q\nu}\right) dq$$

$N(E_F)$: electronic DOS at E_F

- Electron-phonon coupling strength for phonon branch ν:

$$\lambda_{q\nu} = \frac{1}{N(E_F)\omega_{q\nu}} \sum_{m,n} \int_{BZ} \left| g^{q\nu}_{mk+q,nk} \right|^2 \delta(\varepsilon_{nk} - E_F)\delta\left(\varepsilon_{mk+q} - E_F\right) dk$$

- Superconducting gap surprisingly isotropic: Isotropic Eliashberg function

$$\alpha^2 F(\omega) = \frac{1}{N(E_F)V_{BZ}} \sum_{\nu} \int_{BZ} \omega_{q\nu}\lambda_{q\nu}\, \delta\left(\omega - \omega_{q\nu}\right) dq$$

- Isotropic EPC strength: $\lambda = 2\int \frac{\alpha^2 F(\omega)}{\omega} d\omega$ $\lambda < 0.5$: weak coupling, $\lambda > 1$: strong coupling

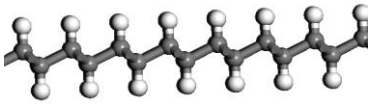
- All ingredients (with full momentum dependence) readily available from ab initio using DFT+DFPT approach

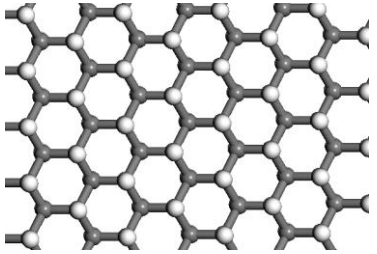
- Can be used to estimate critical temperature: $T_c = \frac{\omega_{ph}^{eff}}{1.2} exp\left(-\frac{1.04(1+\lambda)}{\left(\lambda - \mu^*(1-0.62\lambda)\right)}\right)$

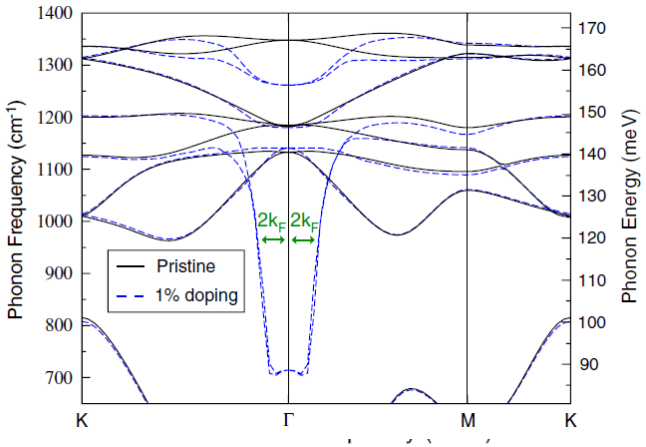
$$\omega_{ph}^{eff} = \frac{2}{\lambda}\int \alpha^2 F(\omega)\, d\omega$$

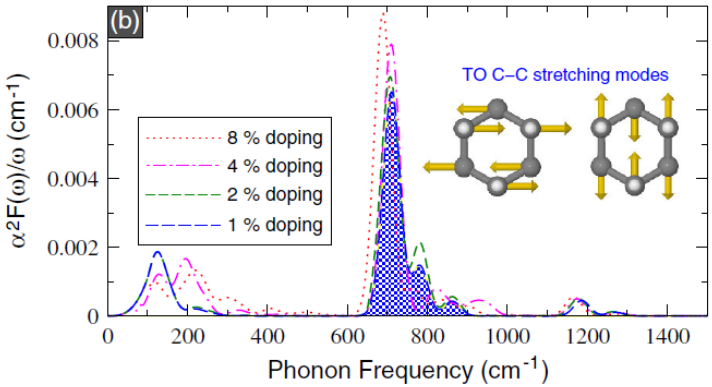
„Coulomb pseudopotential“, can be measured accurately experimentally

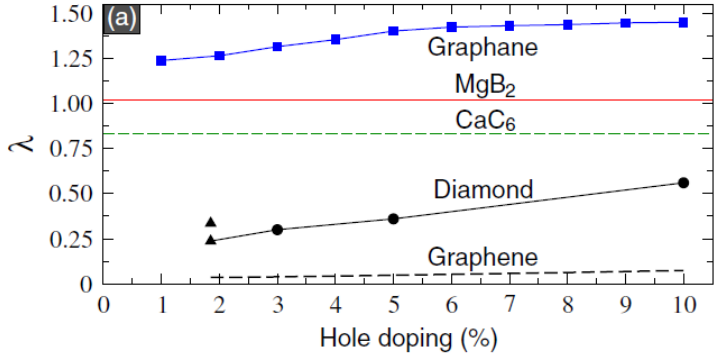
- Example: p-doped graphane *Phys. Rev. Lett. 105, 037002 (2010)*
- Calculated with Quantum Espresso, LDA

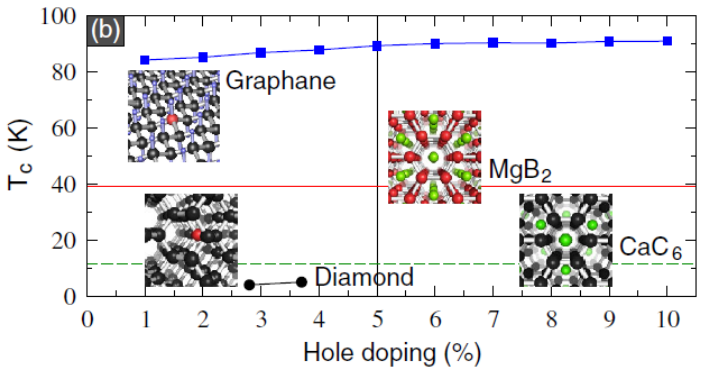












- BCS like superconductivity with high T_c, could be achieved by gate doping

- On the other hand: effect on „conventional“ electronic structure as well

- Electron self-energy from EPC:

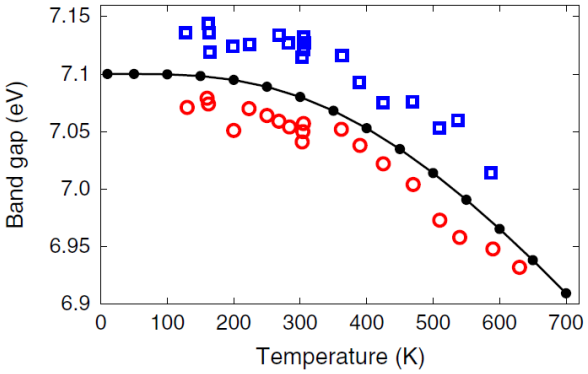
$$\Sigma_{nk}(\omega,T) \approx \underbrace{\sum_{q\nu}\frac{1}{2\omega_{q\nu}}\sum_{m}\left|g^{q\nu}_{mk+q,nk}\right|^2\left[\frac{N_{q\nu}(T)+f_{mk+q}(T)}{\omega-\varepsilon_{mk+q}+\omega_{q\nu}+i\eta}+\frac{N_{q\nu}(T)+1-f_{mk+q}(T)}{\omega-\varepsilon_{mk+q}-\omega_{q\nu}+i\eta}\right]}_{\Sigma^{Fan}_{nk}(\omega,T)} + \Sigma^{DW}_{nk}(T)$$

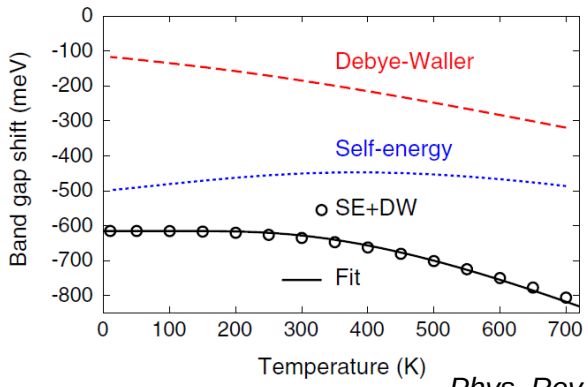
Electron-2 phonon scattering

- Temperature-induced renormalization of band gaps:

$$\tilde{\varepsilon}_{nk}(T) = \varepsilon_{nk}(T) + Re[\Sigma_{nk}(\varepsilon_{nk},T)]$$

- For example: Direct band gap in diamond





Phys. Rev. Lett. 105, 265501 (2010)

- Phonons also affect the resistivity of a material through scattering of carriers

- First principle carrier dynamics using calculated electron-phonon matrix elements

- Boltzmann-Transport Equation (BTE): flow of electron occupations $f_{nk}(r,t)$

$$\frac{\partial f_{nk}(r,t)}{\partial t} = -\left[\nabla_r f_{nk}(r,t)\cdot\vec{v}_{nk} + \hbar^{-1}\nabla_k f_{nk}(r,t)\cdot\vec{F}\right] + I[f_{nk}]$$

Drift terms — Collision term

- Collision term describes scattering of charge carriers, for scattering from EPC

$$I^{el-phon}[f_{nk}] = -\frac{2\pi}{\hbar}\frac{1}{N_q}\sum_{m,q}\left|g^{q\nu}_{mk+q,nk}\right|^2\{\delta\left(\varepsilon_{nk}-\varepsilon_{mk+q}-\hbar\omega_{q\nu}\right)\cdot F_{em} + \\ +\delta\left(\varepsilon_{nk}-\varepsilon_{mk+q}+\hbar\omega_{q\nu}\right)\cdot F_{abs}\}$$

$$F_{em} = f_{nk}\left(1-f_{mk+q}\right)N_{q\nu} - f_{mk+q}(1-f_{nk})\left(N_{q\nu}+1\right)$$ Phonon emission

$$F_{abs} = f_{nk}\left(1-f_{mk+q}\right)\left(N_{q\nu}+1\right) - f_{mk+q}(1-f_{nk})N_{q\nu}$$ Phonon absorption

Eur. Phys. J. B 89, 239 (2016)

- Solve BTE iteratively by updating f_{nk}, but keeping N_{qv} constant

- Simple and easier: Relaxation time approximation (RTA)

$$I[f_{nk}] = -\frac{f_{nk}(r,t) - f_{nk}^{eq}(r,t)}{\tau_{nk}^{el-phon}} + \text{other terms}$$

- Relaxation time for electron state *n*,*k*: $\tau_{nk}^{el-phon} = \left(\frac{2}{\hbar} Im[\Sigma_{nk}]\right)^{-1}$

- From (iterative) solution of the BTE:

Conductivity tensor

$$\sigma_{\alpha\beta} \propto \sum_{nk} v_{nk}^{\alpha} F_{nk}^{\beta} \left(-\frac{\partial f_{nk}^{eq}}{\partial \varepsilon_{nk}}\right)$$

Mobility tensor

$$\mu_{\alpha\beta} = \frac{\sigma_{\alpha\beta}}{e n_{carrier}}$$

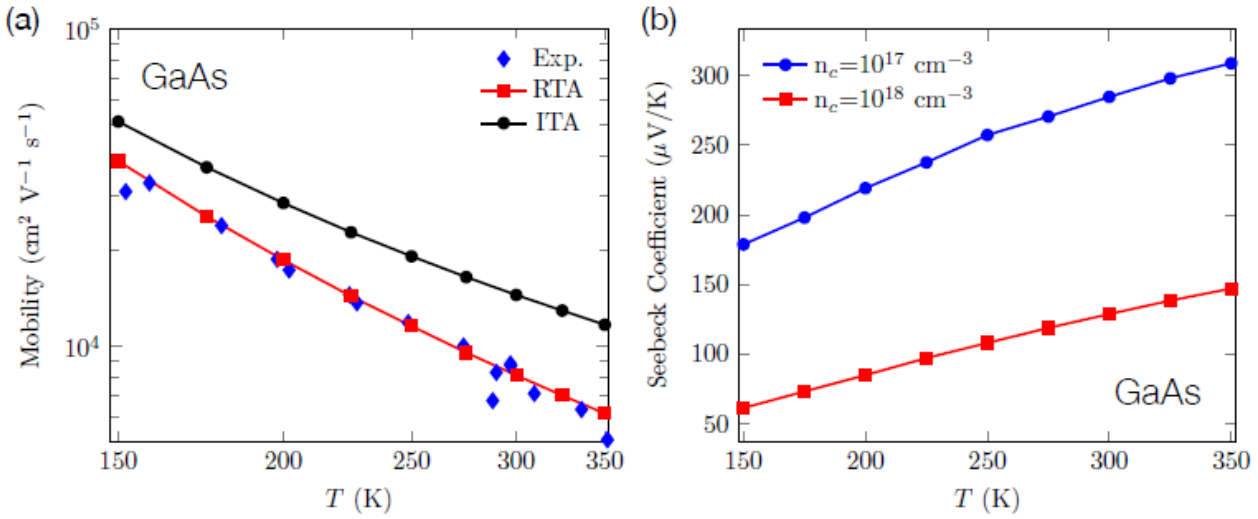
Other properties

- Also several codes available nowadays that solve the BTE based on DFT input

EPW®

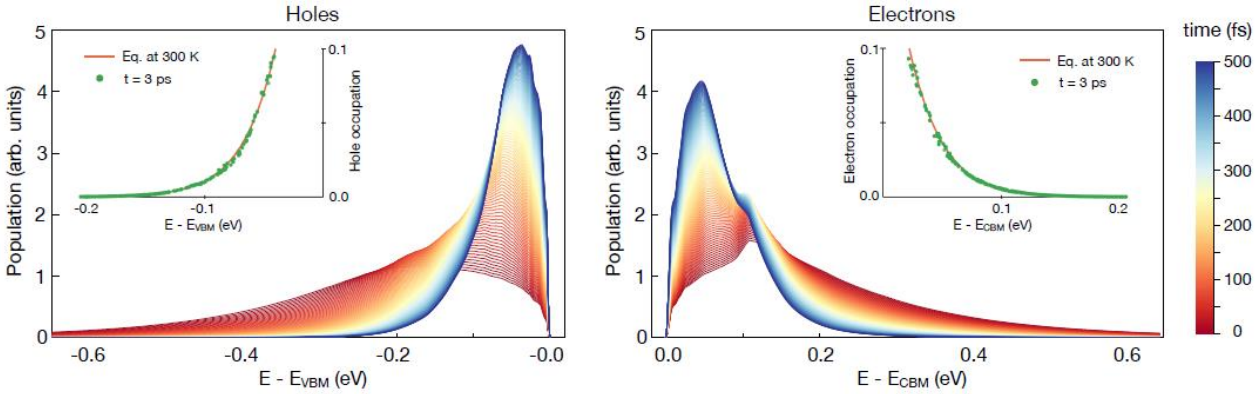
Perturbo

- Mobility and Seebeck coefficient in GaAs



- We also have access to „ultrafast carrier dynamics“

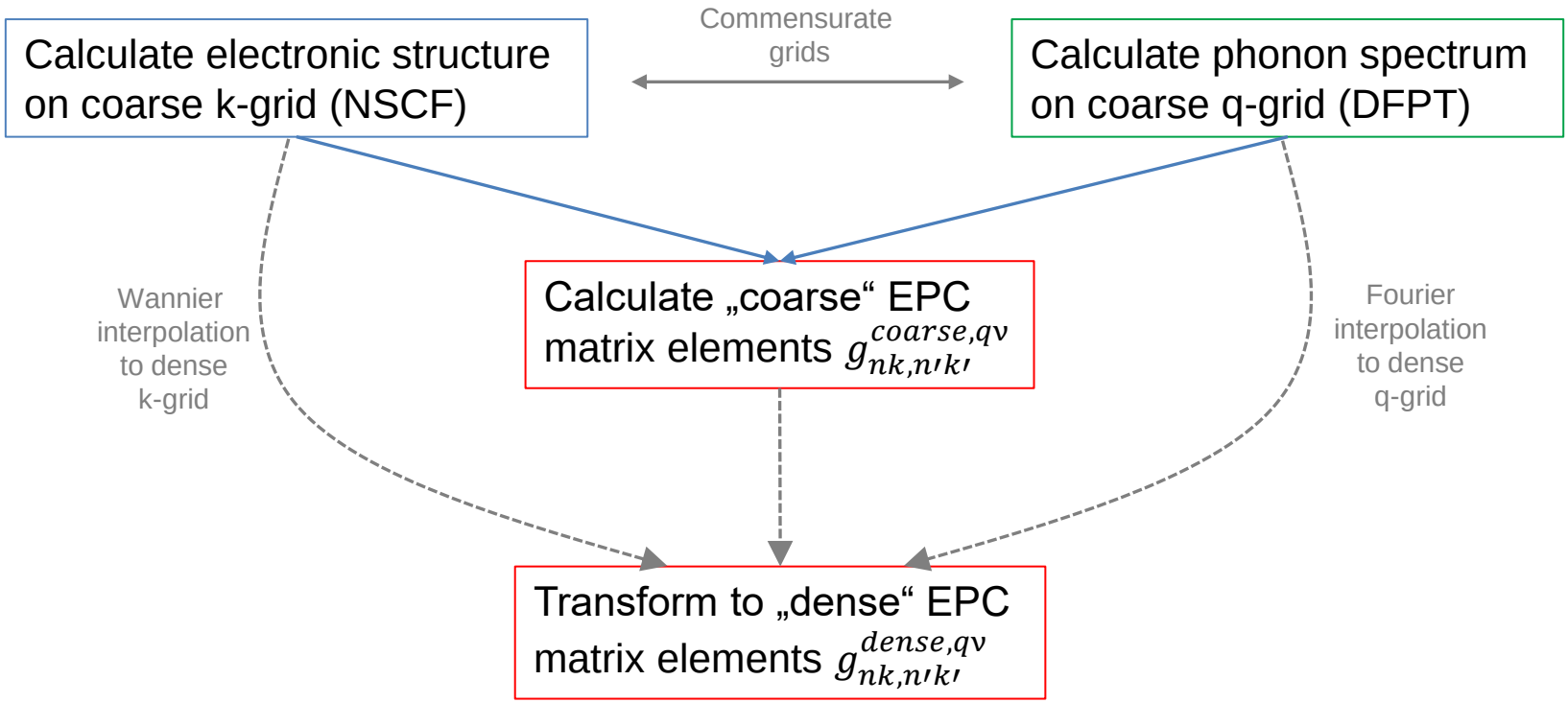
Silicon



arXiv:2002.02045v1

- EPC related properties often require very dense k-point and q-point samplings, of order 100x100x100 points

- Modern approach: use Wannier interpolation for electrons and Fourier interpolation of phonons



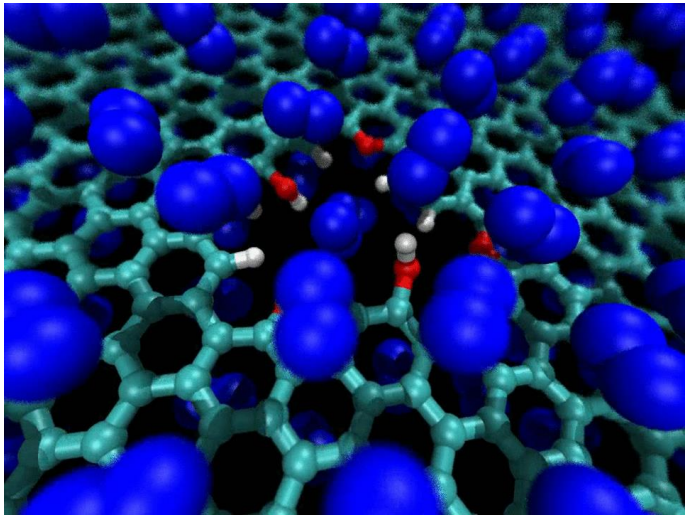
- Let‘s talk about a more ‚integrated‘ way to obtain physical properties of materials

- BO approximation: Nuclei are supposed to obey classical mechanics, i.e.

$$m_I \ddot{R}_I = -\frac{\partial \phi^{BO}(\{R\})}{\partial R_I} \qquad I = 1, N$$

- Molecular dynamics: Follow the time evolution of the atomic movements („trajectories“) and do statistics
  - Observe dynamics of atoms and molecules
  - Compute ensemble averages

- Access to
  - chemical reactions
  - Adsorption of molecules on surfaces
  - Phonons
  - Phase transitions
  - Diffusion of atoms or defects
  - IR and Raman spectra



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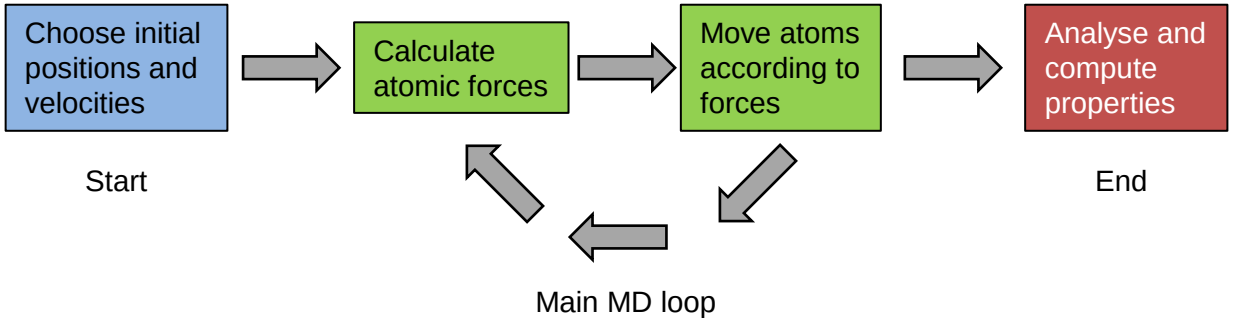
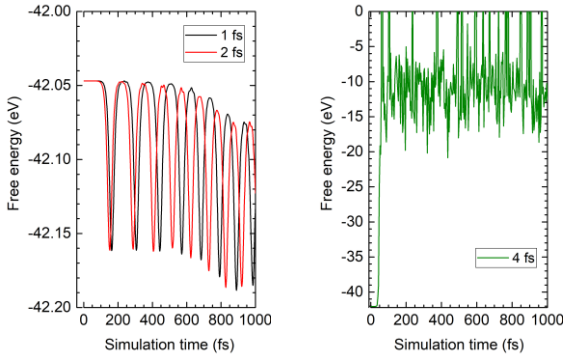
- Goal: „Propagate Newton‘s Equations, use discrete timestep Δt



- Need some „propagator“ (or „integrator“) to do the update
  - Integrator should be time reversible
  - It should conserve phase space volume
  - It should be stable for larger time steps (i.e. allow for longer MD simulation time)



The choice of Δt is crucial!

- Example: „Velocity Verlet“ method, combine forward and backward Taylor expansions

$$R_I(t+\Delta t) = 2R_I(\mathrm{t})\text{-}\ R_I(t-\Delta t)\text{+}\ \ddot{R}_I(\mathrm{t})\frac{(\Delta t)^2}{2}, \qquad v_I(t+\Delta t) = v_I(t)\left[\frac{a(t)+a(t+\Delta t)}{2}\right]\Delta t$$

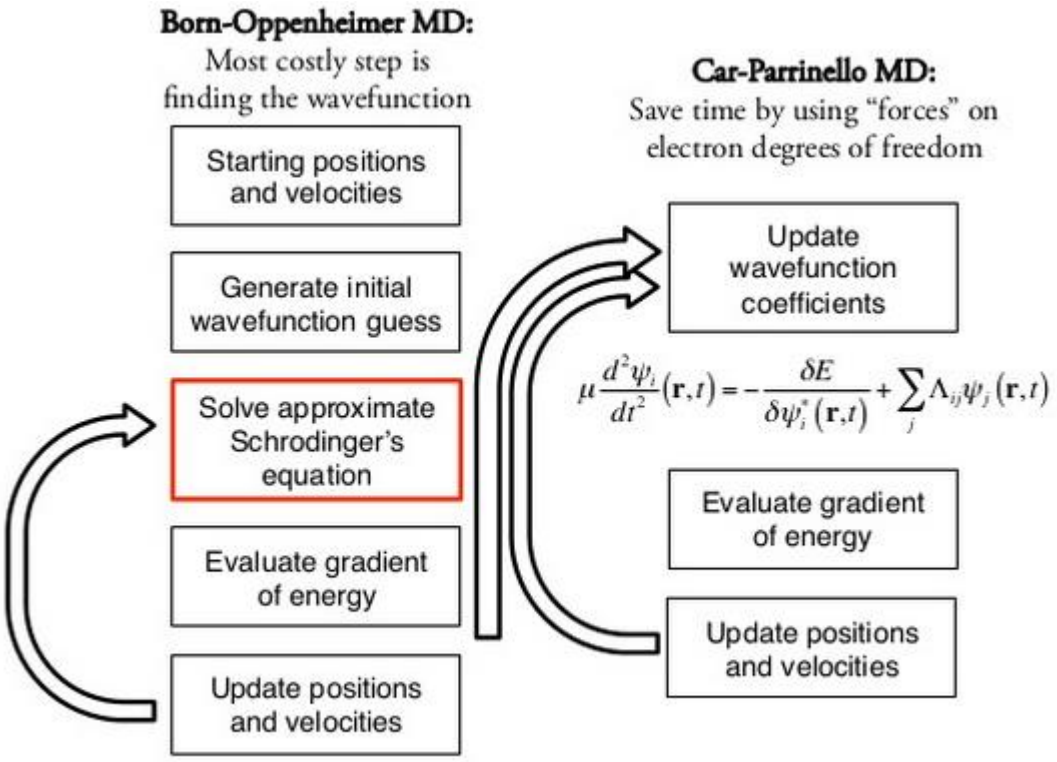
- Need to get interatomic forces
- Ab initio molecular dynamics (AIMD): the potential energy surface is obtained from density functional theory
- Born-Oppenheimer AIMD: $m_i \ddot{R}_i = -\nabla_I \min_n \{\langle \varphi^{GS} | H^{KS} | \varphi^{GS} \rangle\}$
- At each time-step minimize electron density to obtain the current electronic structure and forces
- An alternative: „Car-Parinello“ molecular dynamics (CPMD)

$$m_i \ddot{R}_i = -\nabla_I E[\{\varphi_i\}, \{R_I\}]$$

$$\mu_k \ddot{\varphi}_i(r,t) = -\frac{\delta E^{KS}}{\delta \varphi_i^*} - \sum_j \lambda_{ij} \varphi_j(r,t)$$

ficticious mass — Gradient forces — Orthogonality constraint

- CPMD: Propagate KS orbitals together with nuclei



- Ab initio DFT methods allow for simulation times of a few ps
- CPMD is faster than BOMD, but forces are noisy and require much smaller timestep ($\Delta t \sim 0.1\ fs$) compares to BOMD ($\Delta t \sim 1\ fs$)
- AIMD methods that go beyond Born-Oppenheimer exist (Ehrenfest, Surface hopping)

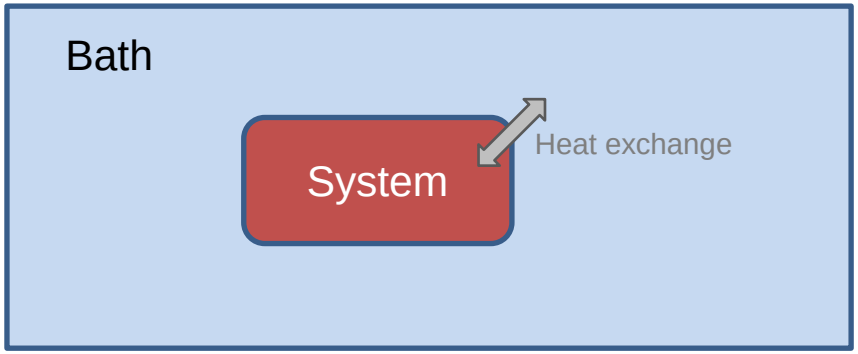
- Can simulate different ensembles:
  - Microcanonical ensemble (NVE): Number of particles, volume and the total energy are conserved, „natural ensemble“ for MD
  - Canonical ensemble (NVT): Number of particles, volume and temperature are conserved → system is in contact with a heat bath
  - NPT, NPH ensembles: number of particles, pressure and enthalpy or temperature are constant, used for studying phase transitions
  - Grand canonical ensemble (μVT): chemical potential is constant, used for adsorption/desorption
- MD allows us to simulate experiments at these conditions

- How to include temperature?
- Simplest way: „velocity rescaling“
  - every *N* steps, rescale the atomic velocities by a factor that creates the desired temperature T

$$v_{new} = \sqrt{\frac{T}{T(t)}} v_{old}$$

  - Easy and stable, but does not correspond to any ensemble
  - Not time-reversible

- Idea: couple the system to a heat bath that acts as a thermostat



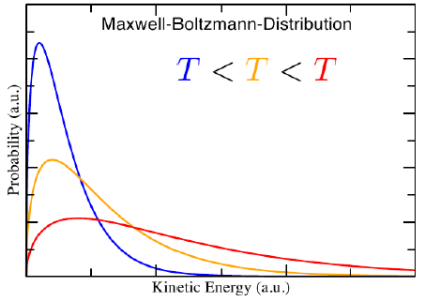
System: energy not conserved
System+bath: Energy conserved

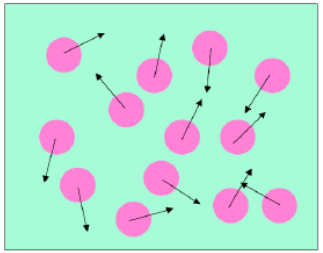
- Weak coupling Berendsen bath: Unit cell immersed in a hypothetical surrounding bath at T_{bath}:
  - More elaborate velocity rescaling, adjust system temperature according to

$$\Delta T = \frac{\Delta t}{\tau}(T_{bath} - T(t))$$

  - Still no real ensemble, but in practice results are close enough
  - Not time-reversible
  - The ‚rise time' τ needs to be chosen to keep the temperature evolution smooth

- Andersen thermostat *J. Chemical Phys. 72, 2384 (1980)*
  - Particles have fixed probability to collide with „Andersen daemon", collision frequency *v*
  - After collision, give velocity according to Maxwell-Boltzmann distribution
  - Samples correctly the NVT ensemble

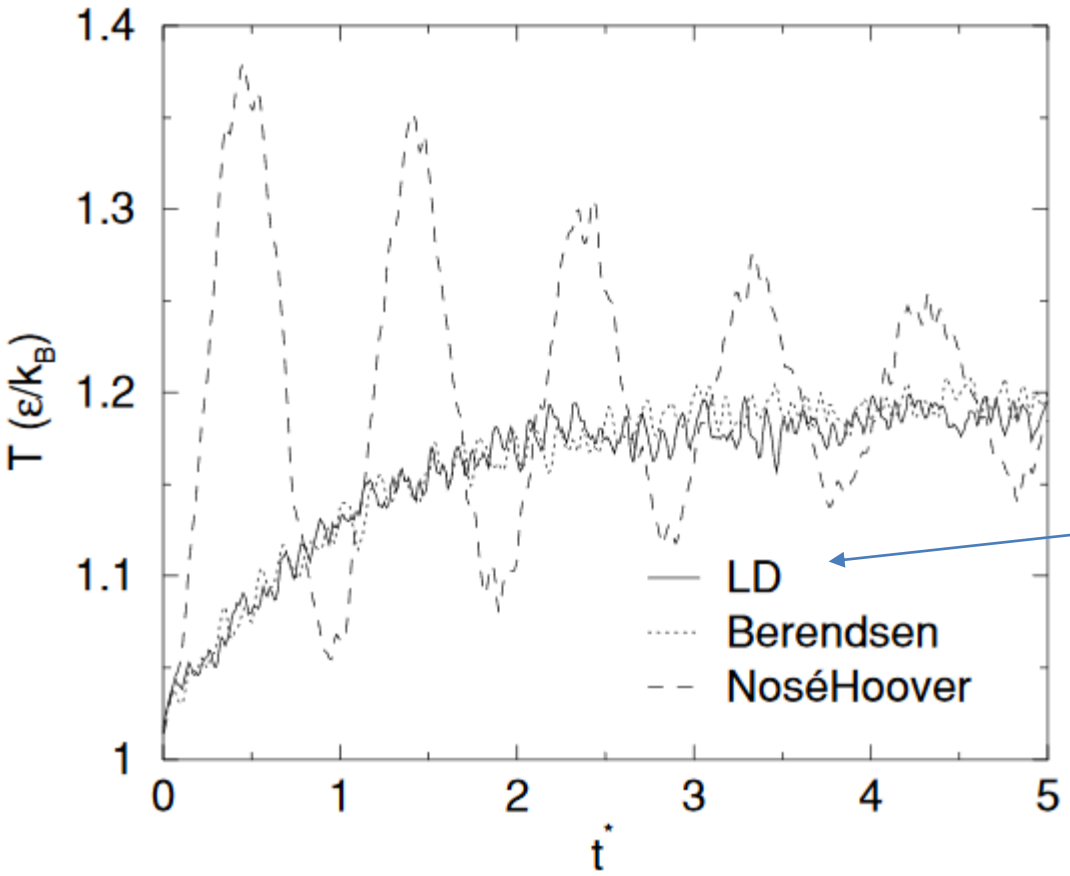




- Nosé-Hoover thermostat *J. Chem. Phys. 81, 511 (1984), Phys. Rev. A. 31, 1695 (1984)*
  - Includes the heat bath explicitly as an additional degree of freedom
  - Introduce artificial ‚time scaling parameter' s, a ficticious mass Q and a friction coefficient ζ
  - Nosé-Hoover Hamiltonian: $H_{N-H} = \sum_{i=1}^{N} \frac{\vec{p}_i^2}{2m_i} + U(\vec{R}) + \frac{\zeta^2 Q}{2} + 3Nk_B T ln\, s$

    Ficticious oscillator
  - Magnitude of Q controls coupling strength
  - Q needs to be carefully chosen: -too large →poor temperature control
    -too small →high frequency T variations
  - Very popular algorithm

- Comparison of thermostats



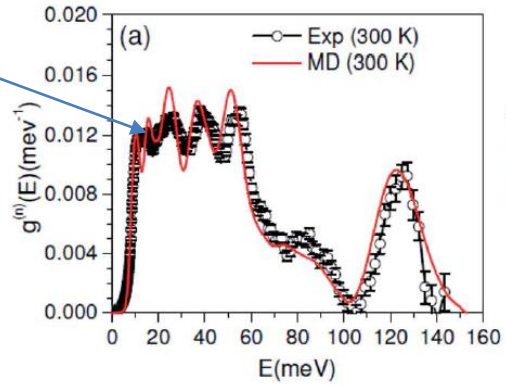
Like Anderson thermostat

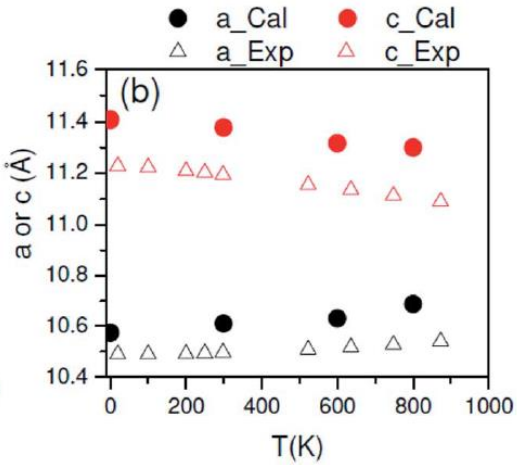
- Each thermostat requires an ‚equilibration phase' to reach desired temperature

- How about constant pressure?
- Barostats:
  - Weak coupling Berendsen *J. Chem. Phys. 81, 3684 (1984)*
    - Similar to thermostat
    - Scale each dimension by $\mu = \left[1 - \frac{\beta \Delta t}{\tau}(P_0 - P)\right]^{1/2}$ where β is an isothermal compressibility (has to be properly chosen)
  - Rahman-Parrinello *J. Appl. Phys. 52, 7182 (1981)*
    - Adaption of Nosé-Hoover thermostat
    - Extension to allow change of cell volume and shape
    - <u>But:</u> Another „cell mass“ to properly choose such that coupling to ‚pressure bath‘ is neither too strong nor to weak
- Combination of barostats and thermostats allows for geometry optimization for a specfic temperature T or for search for global energy minimum → simulated annealing

- Example: 1-D superionic conduction and phase transition β-$AlSiO_4$

Phonon spectrum





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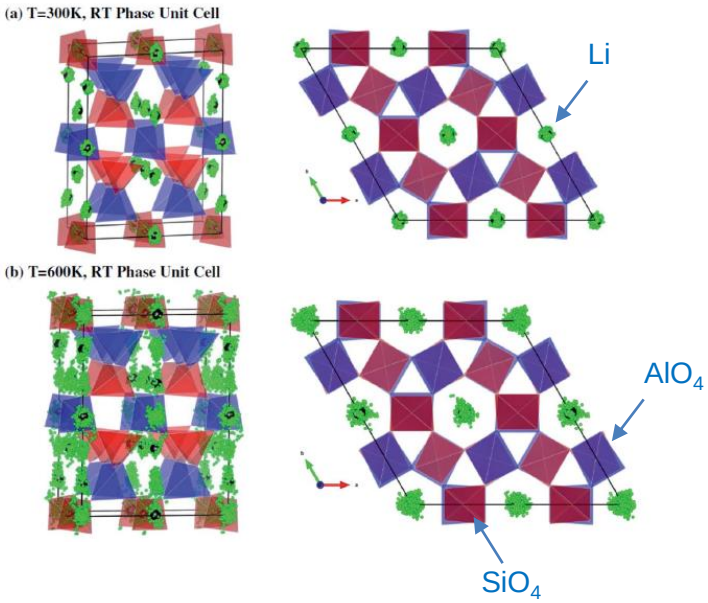

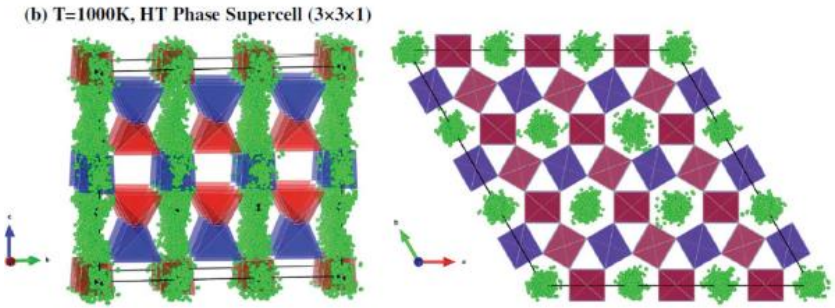

- Superionic phase transition for T>600 K
- Microscopic understanding of 1D Li diffusion along c axis
- Increased Li conduction if Li or O vacancies are introduced