From Atoms to Materials: Predictive Theory and Simulations

Week 3: Dynamics of Atoms – Classical Mechanics and MD Simulations

Lecture 3.6: Atomic Dynamics: Final Examples and Review

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Summary: small vibrations

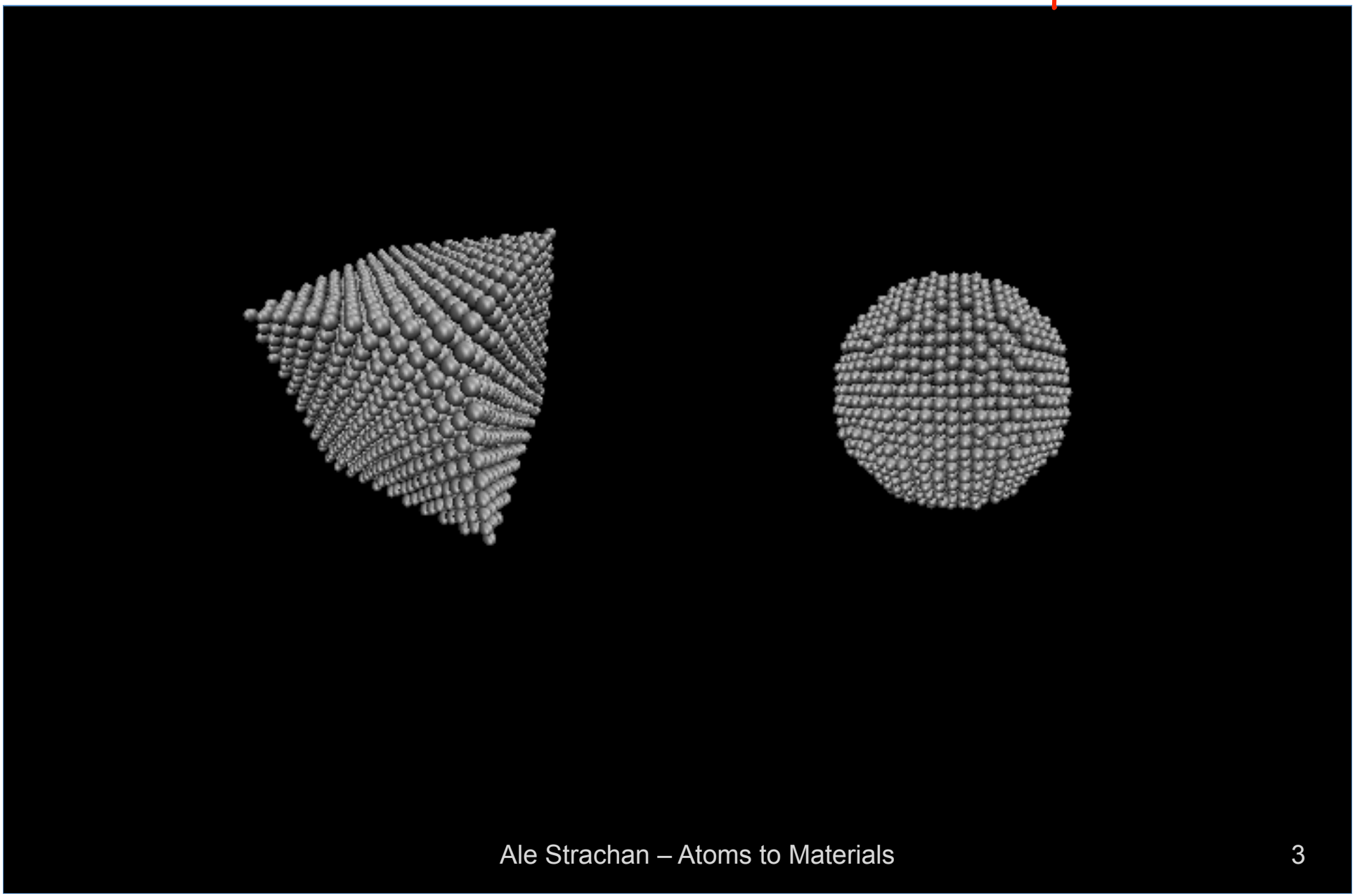
- Molecules
  - Eigenvalues of the Hessian matrix: vibrational frequencies
  - Eigenvectors of the Hessian matrix: normal modes

$$\begin{bmatrix} K_{ij} / \sqrt{M_i M_j} \end{bmatrix} \qquad \omega_\alpha^2 \qquad \rho_\alpha \qquad \Delta R_{\alpha,i} = \frac{\rho_{\alpha,i}}{\sqrt{M_i}} e^{i\omega_\alpha t}$$

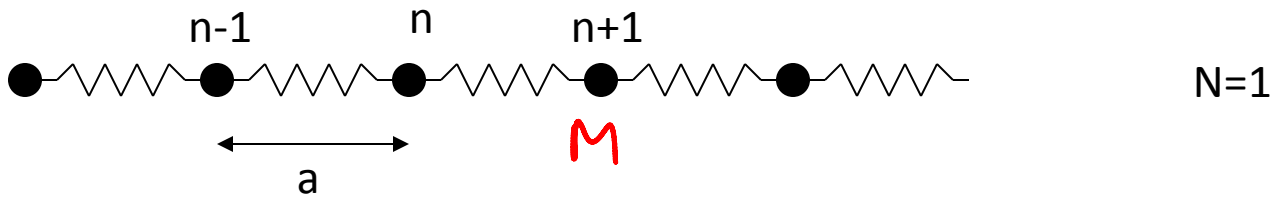
- Crystals
  - Eigenvalues of the Dynamical matrix: vibrational frequencies
  - Eigenvectors of the Dynamical matrix: normal modes

$$H_{ij}(k) = \sum_J^{N_{cell}} \frac{K_{i0,jJ}}{\sqrt{M_j M_i}} e^{ikR_J} \qquad \omega_\alpha^2(k) \qquad u_\alpha(k) \qquad \Delta R_{\alpha,i,I}(k) = \frac{u_{\alpha,i}}{\sqrt{M_i}} e^{i\left(kR_I + \omega_\alpha(k)t\right)}$$

Molecular dynamics



Example of phonon calculation



N=1

$$V\left(\left\{\Delta R_{i,I}\right\}\right)=\frac{1}{2}K\sum_{I}\left(\Delta R_{1I}-\Delta R_{1I+1}\right)^{2}$$

Equation of motion: $$\omega^{2}u_{i}=\sum_{j}^{3N}u_{j}\sum_{J}^{N_{cell}}\frac{K_{i0,jJ}}{\sqrt{M_{j}M_{i}}}e^{ikR_{J}}=\sum_{j}^{3N}u_{j}H_{ij}\left(k\right)$$

$$K_{1I,1J}=\begin{cases}2K & for\ I=J\\ -K & for\ \left|I-J\right|=1\end{cases}$$

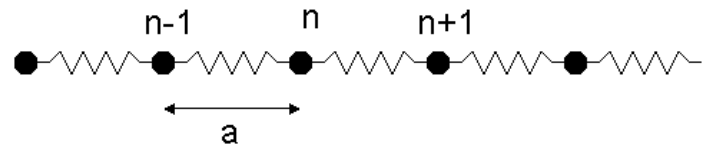
$$H_{ij}\left(k\right)=-\frac{K}{M}e^{ika}+2\frac{K}{M}-\frac{K}{M}e^{-ika}=$$

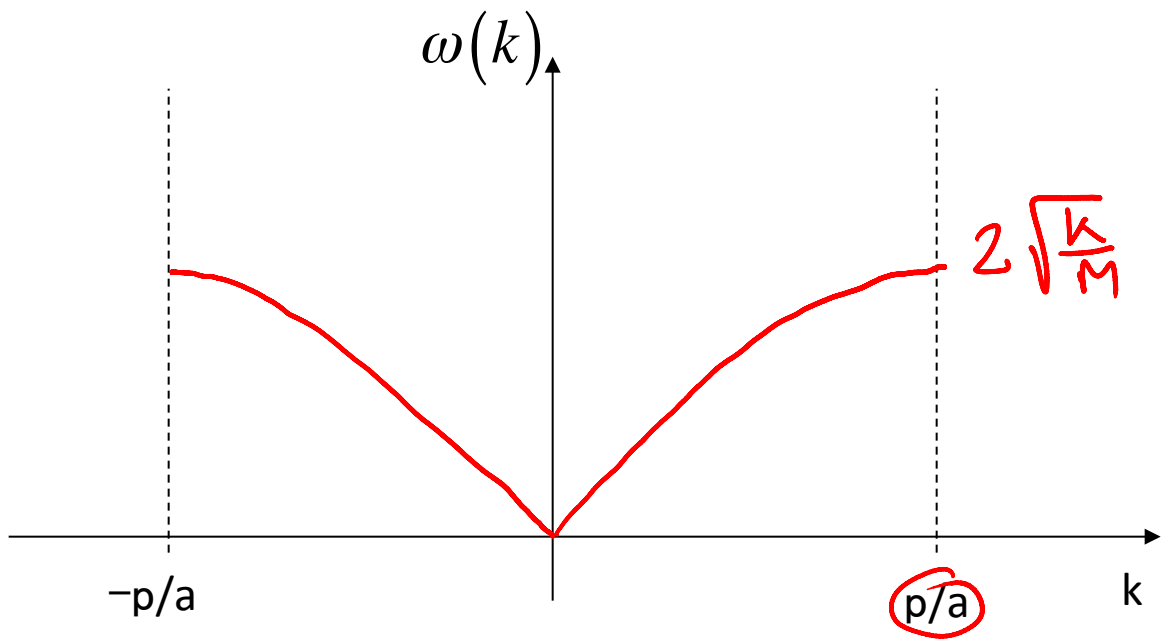
$$\frac{2K}{M}\left[1-\cos\left(ka\right)\right]=4\frac{K}{M}\sin^{2}\left(\frac{ka}{2}\right)$$

$$\omega^{2}u_{i}=4\frac{K}{M}\sin^{2}\left(\frac{ka}{2}\right)u_{i}$$

$$\omega\left(k\right)=2\sqrt{\frac{K}{M}}\left|\sin\left(\frac{ka}{2}\right)\right|$$

Dispersion relationship in 1D chain





$$\omega(k) = 2\sqrt{\frac{K}{M}}\left|\sin\frac{ka}{2}\right|$$

Crystals in 3D

Atoms can now vibrate in three dimensions
Each branch (acoustic and optical) transform into 3 branches

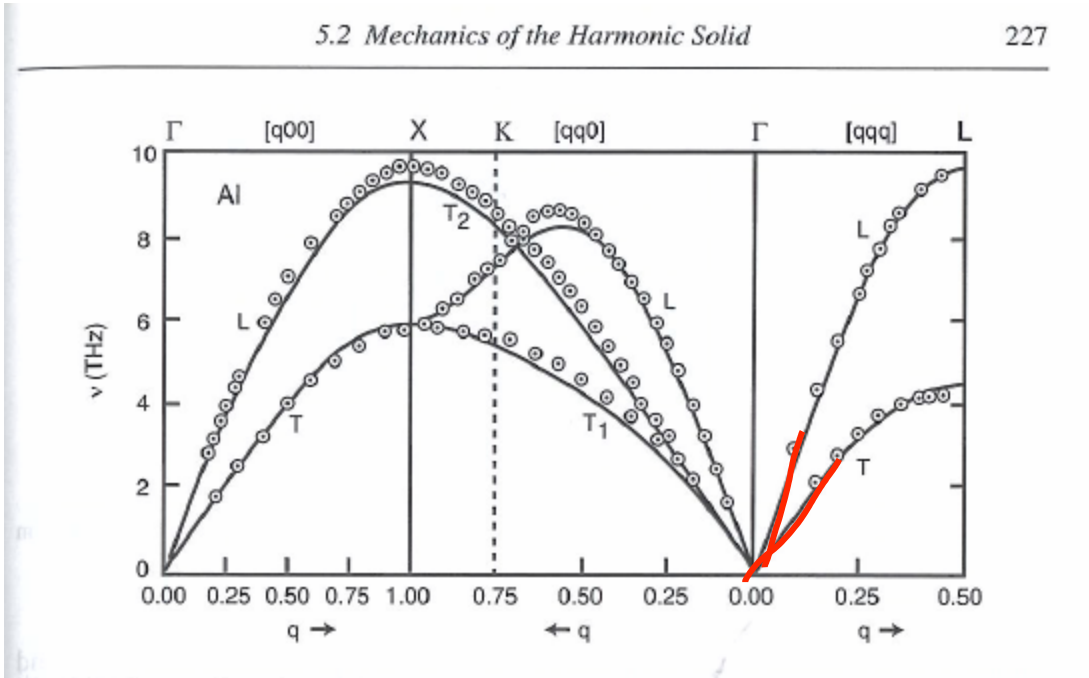


Fig. 5.6. Phonon dispersion relation for Al as computed using pair functional approach (adapted from Mishin *et al.* (1999)). The lines correspond to the theoretical results and the points are experimental data obtained from neutron scattering.

From Rob Phillips: "Crystals, defects and microstructures"

Normal modes and optical properties

A vibrating electric dipole can emit and absorb electromagnetic radiation at their corresponding frequencies

$$Z_{n,\alpha} = \sum_{i,\beta=1}^{N,3} \frac{\rho_{n,j\beta}}{\sqrt{M_j}} Z^*_{j,\beta\alpha}$$

Dipole moment for each normal mode (charge vector) – From DFT

Real part of dielectric constant:

$$\varepsilon'_{\alpha\beta}(\omega) = \varepsilon^{\infty}_{\alpha\beta} - \frac{4\pi}{\Omega} \sum_{n}^{3N} \frac{Z_{n\alpha} Z_{n\beta}}{\omega^2 - \omega_n^2}$$

Imaginary part of dielectric constant:

$$\varepsilon''_{\alpha\beta}(\omega) = \frac{4\pi^2}{\Omega} \sum_{n}^{3N} \frac{Z_{n\alpha} Z_{n\beta}}{2\omega_n} \frac{1}{\sqrt{2\pi}\gamma} e^{-(\omega-\omega_n)^2/\gamma^2}$$

Week 3 summary

Follow the dynamics (motion) of all the atoms in your material

Numerically solve classical equations of motion (Newton's):

Approximation

$$\vec{F}_i = m_i \vec{A}_i \quad \text{or} \quad \begin{cases} \dot{\vec{R}}_i = \dfrac{\vec{P}_i}{M_i} \\ \dot{\vec{P}}_i = \vec{F}_i \end{cases}$$

Forces on atoms come from the interaction with other atoms:

$$\vec{F}_i = -\vec{\nabla}_{R_i} V\left(\{R_j\}\right)$$

Approximated
(in almost all cases)

Total potential energy

- Eigenvalue in the time-independent Schrodinger Eq.
- An empirical potential energy function