Understanding Phonon Transport Using Lattice Dynamics and Molecular Dynamics

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Outline

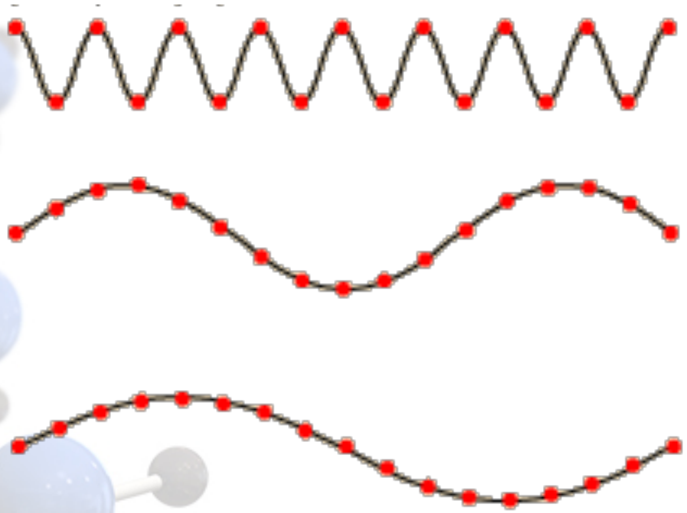
- What is a phonon?
  - What is the phonon gas model (PGM)?
  - What's the problem with the PGM?
- Back to basics – atomic vibration
  - Lattice dynamics (LD)
    - Single harmonic oscillator (SHO)
    - Two oscillators
    - Linear chain of oscillators
    - Generalization to 3D
    - What exactly is a "mode"
  - Molecular dynamics (MD)
    - The connection between phonons and atomic vibration
    - Modal analysis
    - How is this useful?
    - Scattering vs. correlation
    - GKMA & ICMA
    - Interesting results & new insights

Part I

Part II

What is the Phonon Gas Model (PGM)?

What is a phonon?

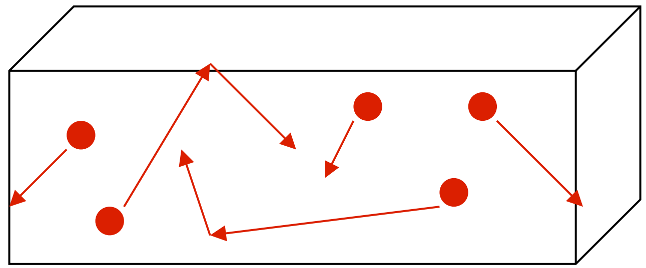


Energy = $\hbar\omega$

Wavelength = $\lambda \rightarrow \mathbf{k} = 2\pi / \lambda$

Speed = $v_p = \omega / \mathbf{k} \quad v_g = d\omega / d\mathbf{k}$

What is the PGM?



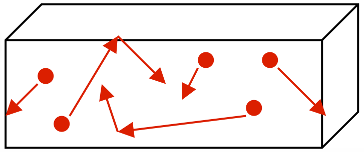
$$\dot{\mathbf{q}} = \left(\frac{1}{2} m v^2\right) \cdot \mathbf{v} / V \rightarrow (\hbar\omega) \cdot \mathbf{v} / V$$

$$\kappa = \frac{1}{3} \sum_p \int_0^{\nu_{max}} C \cdot v \cdot \Lambda \cdot d\nu$$

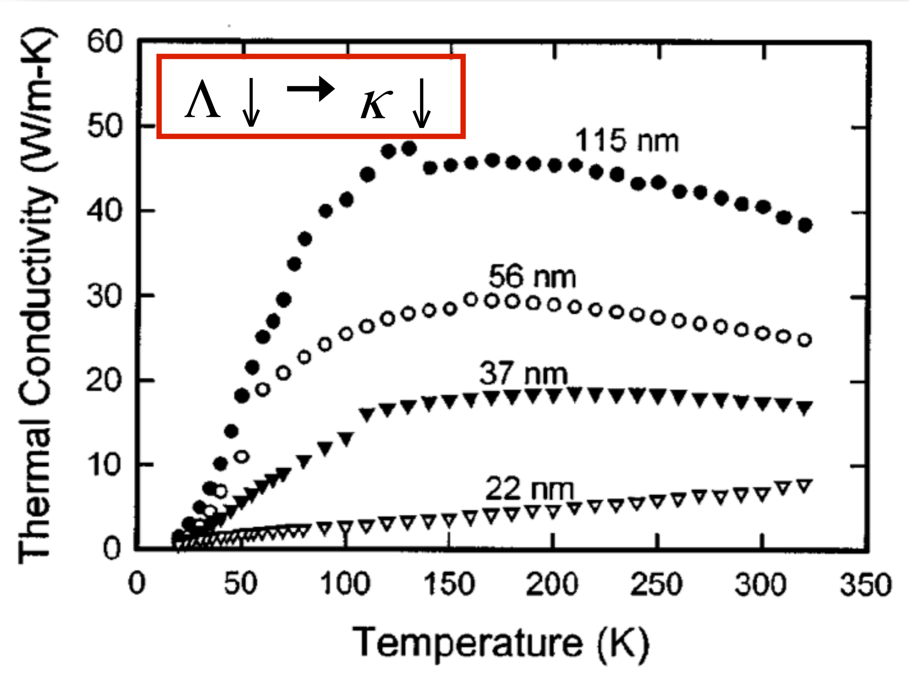
Derived by analogy
NOT basic principles!

It Seems to Work!

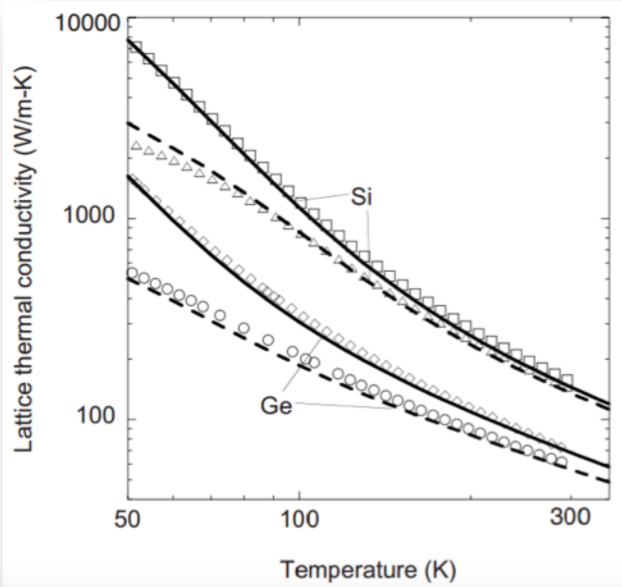
Classical Size Effects

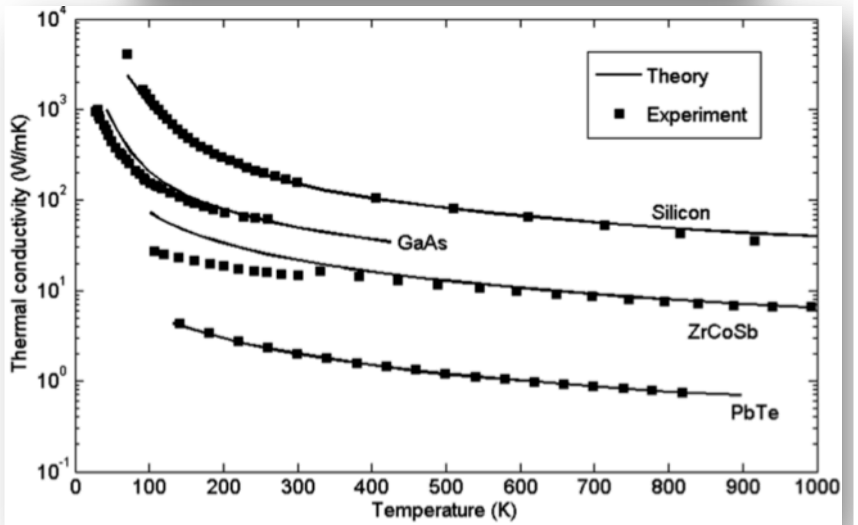


$$\kappa = \frac{1}{3}\sum_{p}\int_{0}^{\nu_{max}} C \cdot v \cdot \Lambda \cdot d\nu$$



D. Li *et al.*, Appl. Phys. Lett. 83, 14, 2934-2936 (2003)





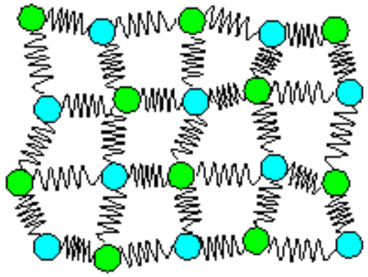
What is the Problem?

- PGM requires phonon velocity
  - Rigorously – requires periodicity, dispersion → velocity
  - PGM assumes plane wave mode character
- Derived by analogy
  - Not based on fundamental principles
  - Is not general
- Disjoint with the atomic level view
  - How long does a scattering event take?
  - Why would only modes with similar λ add together and not others?
- What is the general & rigorous connection between phonons and atomic vibrations?

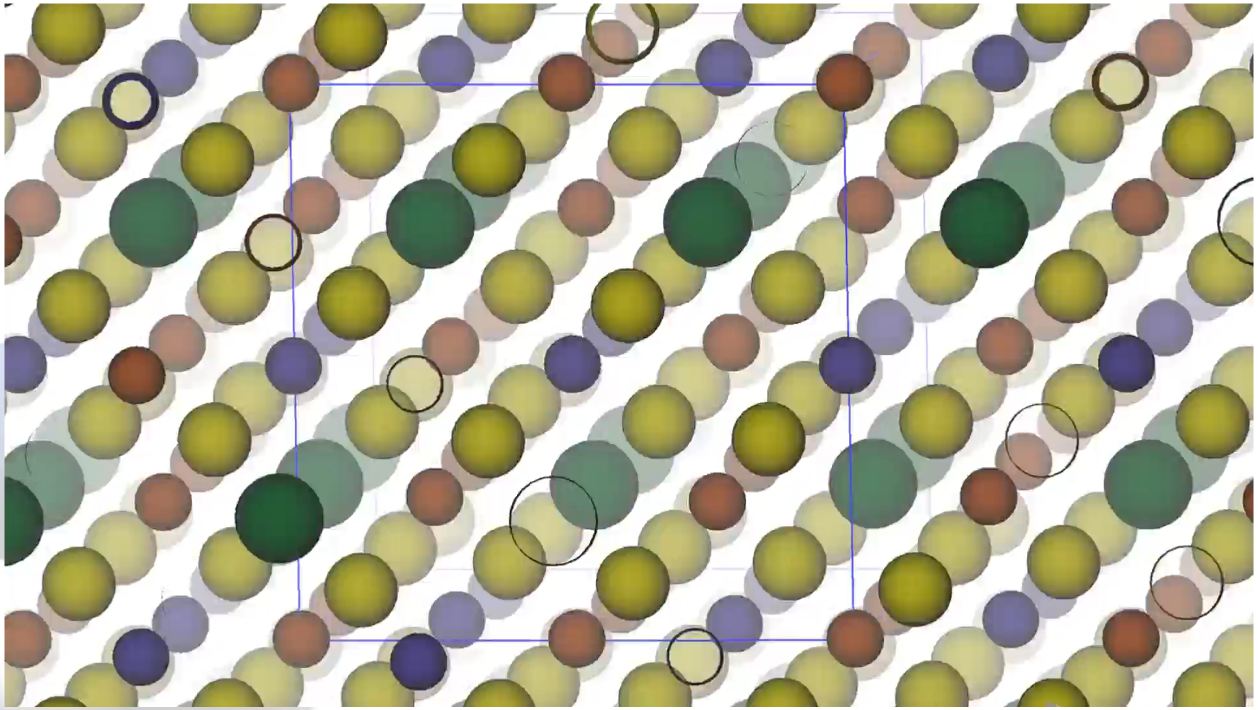
Sound of one Si atom

Sound of one Polythiophene Mode's Heat Flux (~0.02 THz)

Atomic Motions

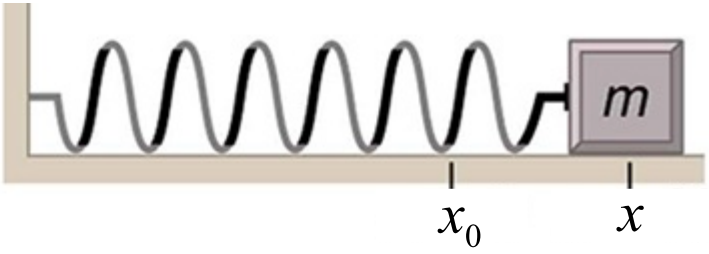


- In rigid bodies → atoms vibrate
- Similar to rigid balls connected by springs
- If springs are linear $E = \frac{1}{2}K(x_1 - x_2)^2 \rightarrow \mathbf{F} = K(x_1 - x_2)$
  - We can solve for the motions of atoms analytically $\mathbf{F} = m\mathbf{a}$



CZTS
MD Simulation

Review: Equations of Motion



[redacted]

$$X = x - x_0$$

$$E = \frac{1}{2}KX^2 \qquad F = -\frac{d}{dx}\left(\frac{1}{2}KX^2\right)$$

$$F = -KX \qquad F = ma$$

$$-KX = m\frac{d^2X}{dt^2} \qquad \frac{d^2X}{dt^2} = -\frac{K}{m}X$$

$$\omega = \omega_0 = \sqrt{\frac{K}{m}}$$

$$\frac{d^2(\sin\omega t)}{dt^2} = -\omega^2 \sin\omega t$$

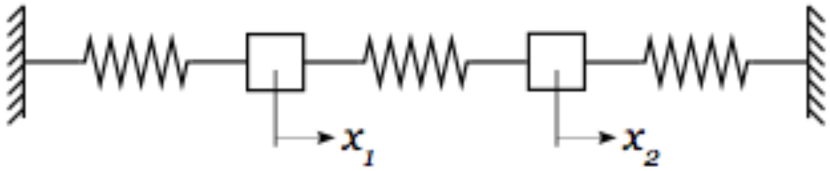
$$\frac{d^2(\cos\omega t)}{dt^2} = -\omega^2 \cos\omega t$$

$$X = \underbrace{A\sin\omega t + B}\cos\omega t = \underbrace{A\cos(\omega t - \phi)}$$

Determined from initial position and velocity

Coupled Vibrations

$$X_1 = x_1 - x_{0:1}$$



$$X_2 = x_2 - x_{0:2}$$

$$m\ddot{X}_1 = -KX_1 + K\left(X_2 - X_1\right)$$

$$m\ddot{X}_2 = -K\left(X_2 - X_1\right) - KX_2$$

$$\ddot{X}_1 = -2\omega_0^2 X_1 + \omega_0^2 X_2$$

$$\ddot{X}_2 = \omega_0^2 X_1 - 2\omega_0^2 X_2$$

$$\omega_0 = \sqrt{\frac{K}{m}}$$

$$X_1 = A_1 \cos\left(\omega t - \phi\right)$$

$$X_2 = A_2 \underbrace{\cos\left(\omega t - \phi\right)}$$

$$\left(\hat{\omega}^2 - 2\right)A_1 + A_2 = 0$$

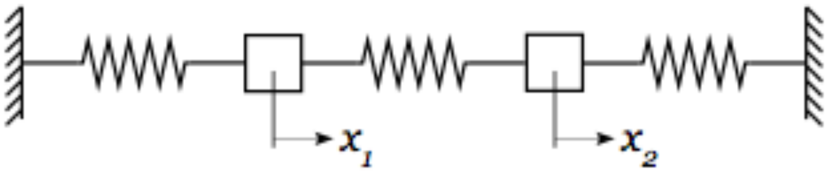
$$A_1 + \left(\hat{\omega}^2 - 2\right)A_2 = 0$$

$$\hat{\omega} = \frac{\omega}{\omega_0}$$

The core oscillatory function is in every term. It factors out!

The differential Eqs. simplify into a series of algebraic Eqs. The roots of the algebraic Eqs. reveal the different characteristic frequencies of vibration

Coupled Vibrations



$$\frac{A_1}{A_2} = \frac{-1}{(\hat{\omega}^2 - 2)} = -(\hat{\omega}^2 - 2)$$

$$(\hat{\omega}^2 - 2)(\hat{\omega}^2 - 2) - 1 = 0$$

$$\begin{pmatrix} \hat{\omega}^2 - 2 & 1 \\ 1 & \hat{\omega}^2 - 2 \end{pmatrix}\begin{pmatrix} A_1 \\ A_2 \end{pmatrix} = \begin{pmatrix} 0 \\ 0 \end{pmatrix}$$

$$X_1 = a_1 \cos(\omega_0 t - \phi_1) + a_2 \cos(\sqrt{3}\omega_0 t - \phi_2)$$

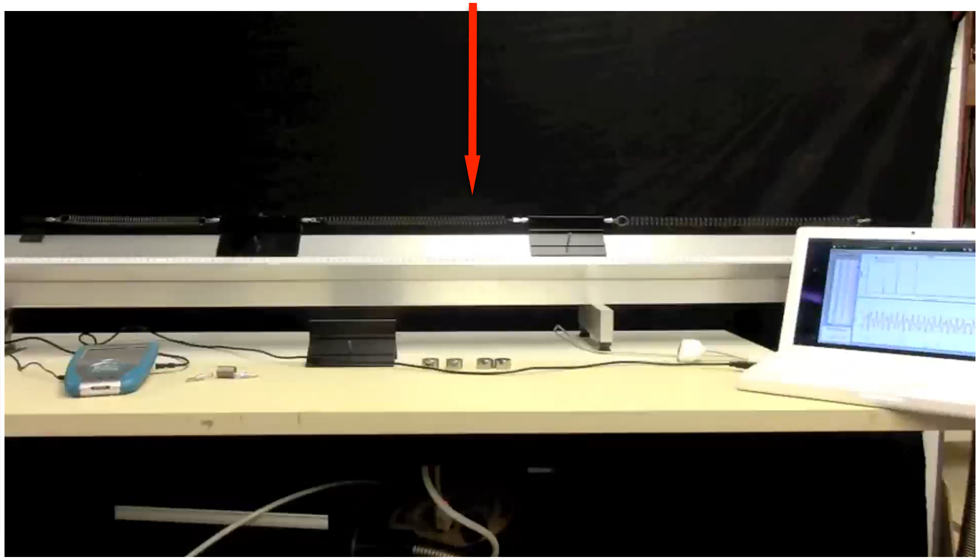
$$X_2 = a_1 \cos(\omega_0 t - \phi_1) - a_2 \cos(\sqrt{3}\omega_0 t - \phi_2)$$

There are two characteristic frequencies of vibration. The new frequency is higher and arises from the relative motion between them.

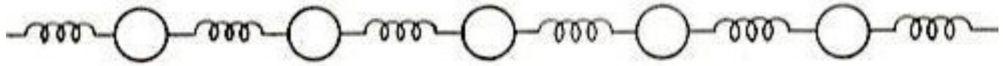
Frequency → $\hat{\omega} = 1$ or $\hat{\omega} = \sqrt{3}$

Direction → $A_1 = A_2$ or $A_1 = -A_2$

Combination of two frequencies can look chaotic!



Linear Chain of Oscillators



Wave Eq.

$$m\frac{\partial^2 X_j}{\partial t^2} = -K\frac{\partial^2 X_j}{\partial x^2}$$

$$m\frac{\partial^2 X_j}{\partial t^2} = -K\left(2X_j - X_{j+1} - X_{j-1}\right)$$

Eq. of Motion Looks Similar

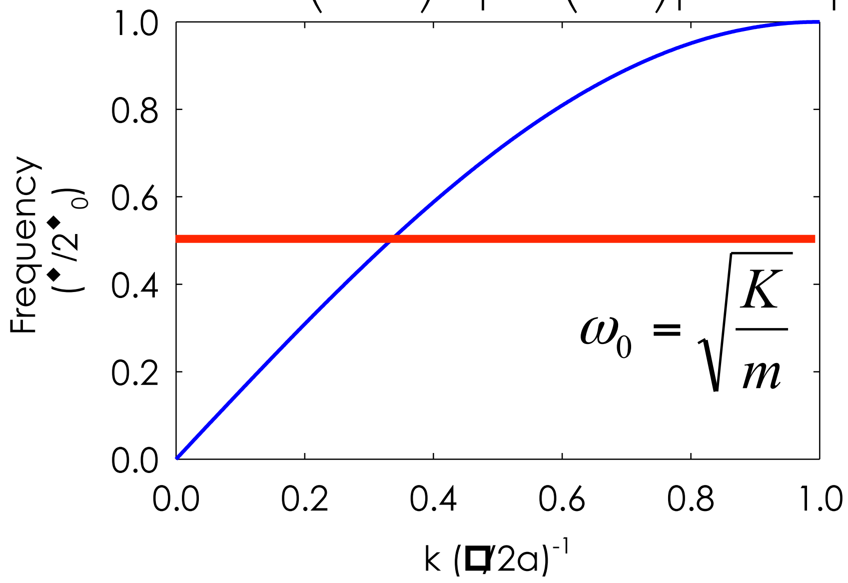
Solutions Become Waves

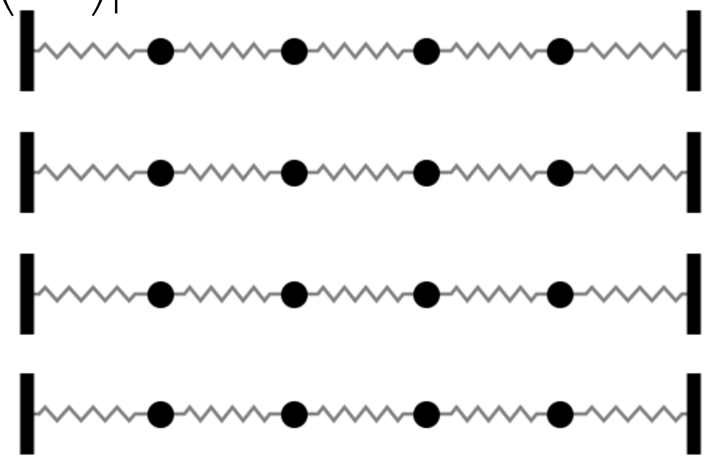
$$X_j = \sum_k \underbrace{A_k \exp(ik \cdot ja)}\exp(-i\omega_k t)$$

Displacement & Velocity Profile

$$\omega_k = \left(\frac{4K}{m}\right)^{1/2}\left|\sin\left(\frac{ka}{2}\right)\right| = 2\omega_0\left|\sin\left(\frac{ka}{2}\right)\right|$$

Dispersion





http://www.acs.psu.edu/drussell/Demos/multi-dof-springs/multi-dof-springs.html

Generalization to 3D

$$K = \Phi_{\underbrace{\alpha,\beta}_{x,y,z}}(j, j') = \frac{\partial^2 E}{\partial X_{j,\alpha} \partial X_{j',\beta}}$$

$$m_j \ddot{\vec{\mathbf{X}}}_j = -\sum_{j'} \Phi(j, j')\left(\vec{\mathbf{X}}_j - \vec{\mathbf{X}}_{j'}\right)$$

$$\vec{\mathbf{X}}_j = \sum_{\mathbf{k},v} \vec{\mathbf{p}}\left(j, \vec{\mathbf{k}}, v\right) \exp\left(i\vec{\mathbf{k}} \cdot \vec{\mathbf{r}}_j - \omega t\right)$$

$$\vec{\mathbf{e}}\left(\vec{\mathbf{k}}, v\right) = \begin{bmatrix} \sqrt{m_1}\, p_x\left(1, \vec{\mathbf{k}}, v\right) \\ \sqrt{m_1}\, p_y\left(1, \vec{\mathbf{k}}, v\right) \\ \sqrt{m_1}\, p_z\left(1, \vec{\mathbf{k}}, v\right) \\ \sqrt{m_2}\, p_x\left(2, \vec{\mathbf{k}}, v\right) \\ \sqrt{m_2}\, p_y\left(2, \vec{\mathbf{k}}, v\right) \\ \downarrow \\ \sqrt{m_j}\, p_x\left(j, \vec{\mathbf{k}}, v\right) \end{bmatrix}$$

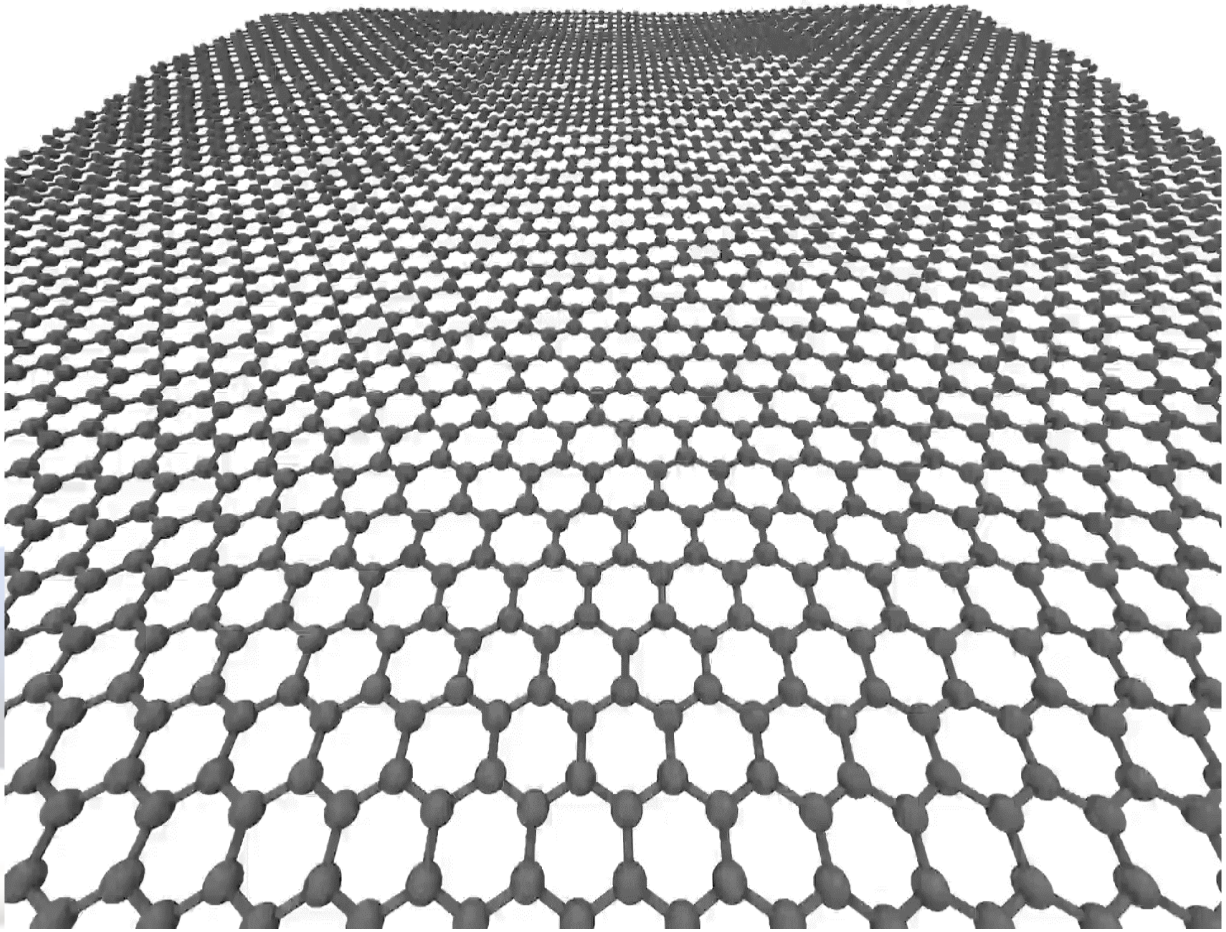
$$m_j \omega^2 \vec{\mathbf{p}}\left(j, \vec{\mathbf{k}}, v\right) = \sum_{j'} \Phi(j, j') \vec{\mathbf{p}}\left(j', \vec{\mathbf{k}}, v\right) \exp\left(i\vec{\mathbf{k}} \cdot \left(\vec{\mathbf{r}}_{j',0} - \vec{\mathbf{r}}_{j,0}\right)\right)$$

$$\omega^2\left(\vec{\mathbf{k}}, v\right) \vec{\mathbf{e}}\left(\vec{\mathbf{k}}, v\right) = D\left(\vec{\mathbf{k}}\right) \cdot \vec{\mathbf{e}}\left(\vec{\mathbf{k}}, v\right)$$

Generalization to 3D

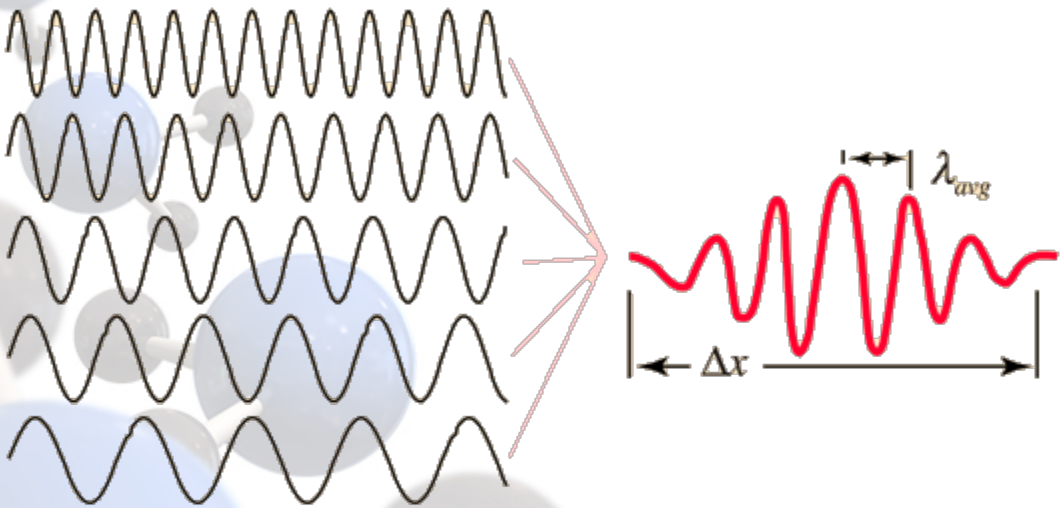
Each solution to the Eqs. of motion = a mode

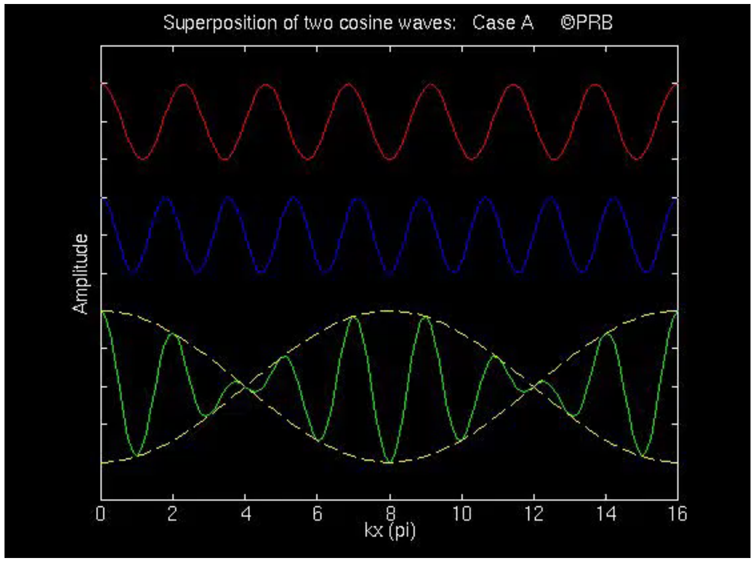
A phonon is a quasi-particle associated with each integer increase in amplitude of a mode → quantum solutions



Wave Packets

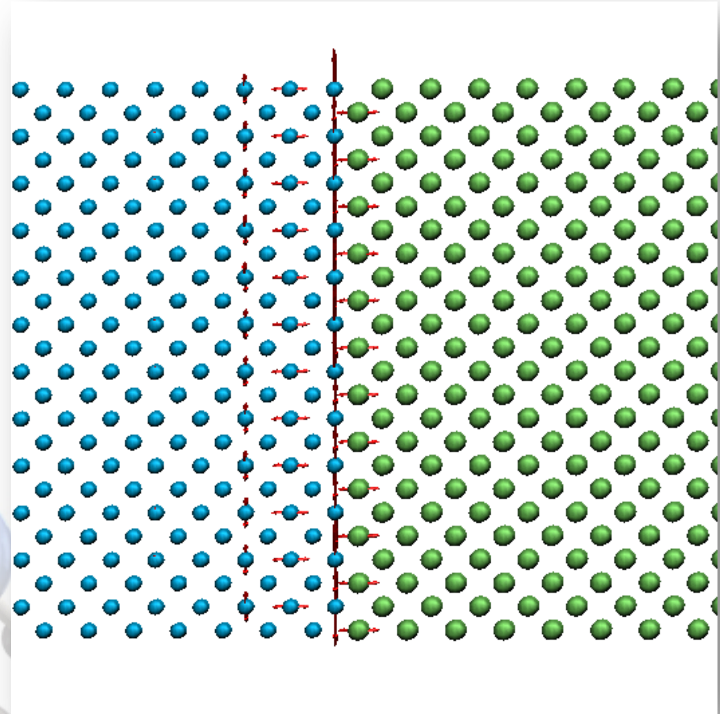
- Addition of waves → localized packet
- Packet travels at group velocity
- Groups of individual modes move energy
- Consistent with the PGM



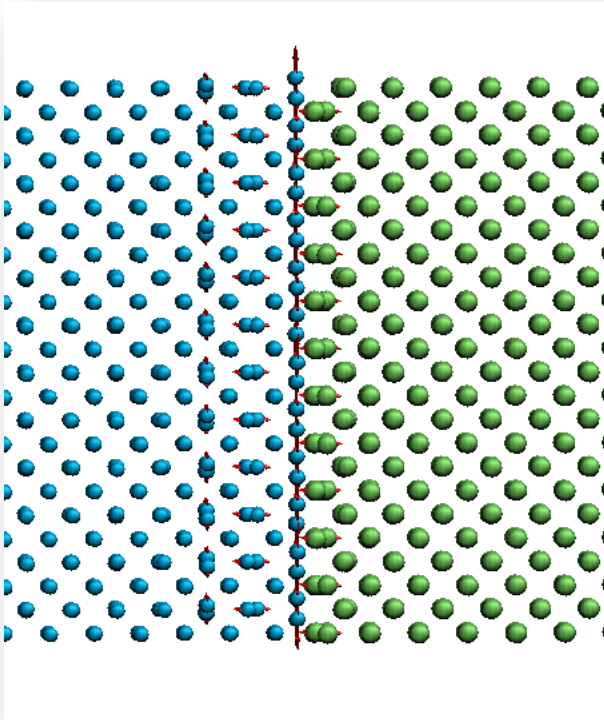


What Exactly is a "Mode"?

Beginning

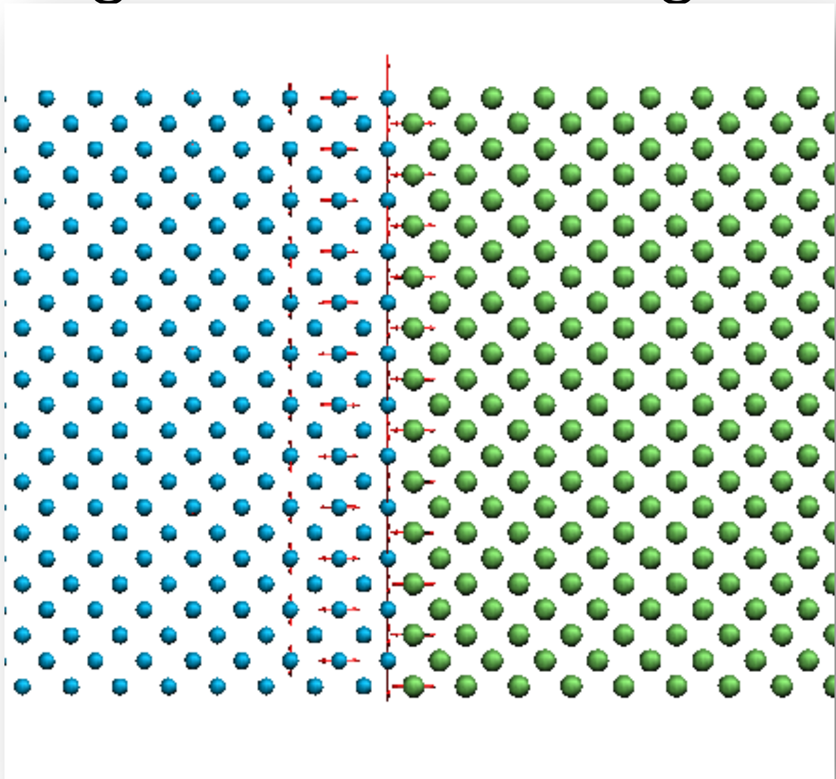


After 1 ns

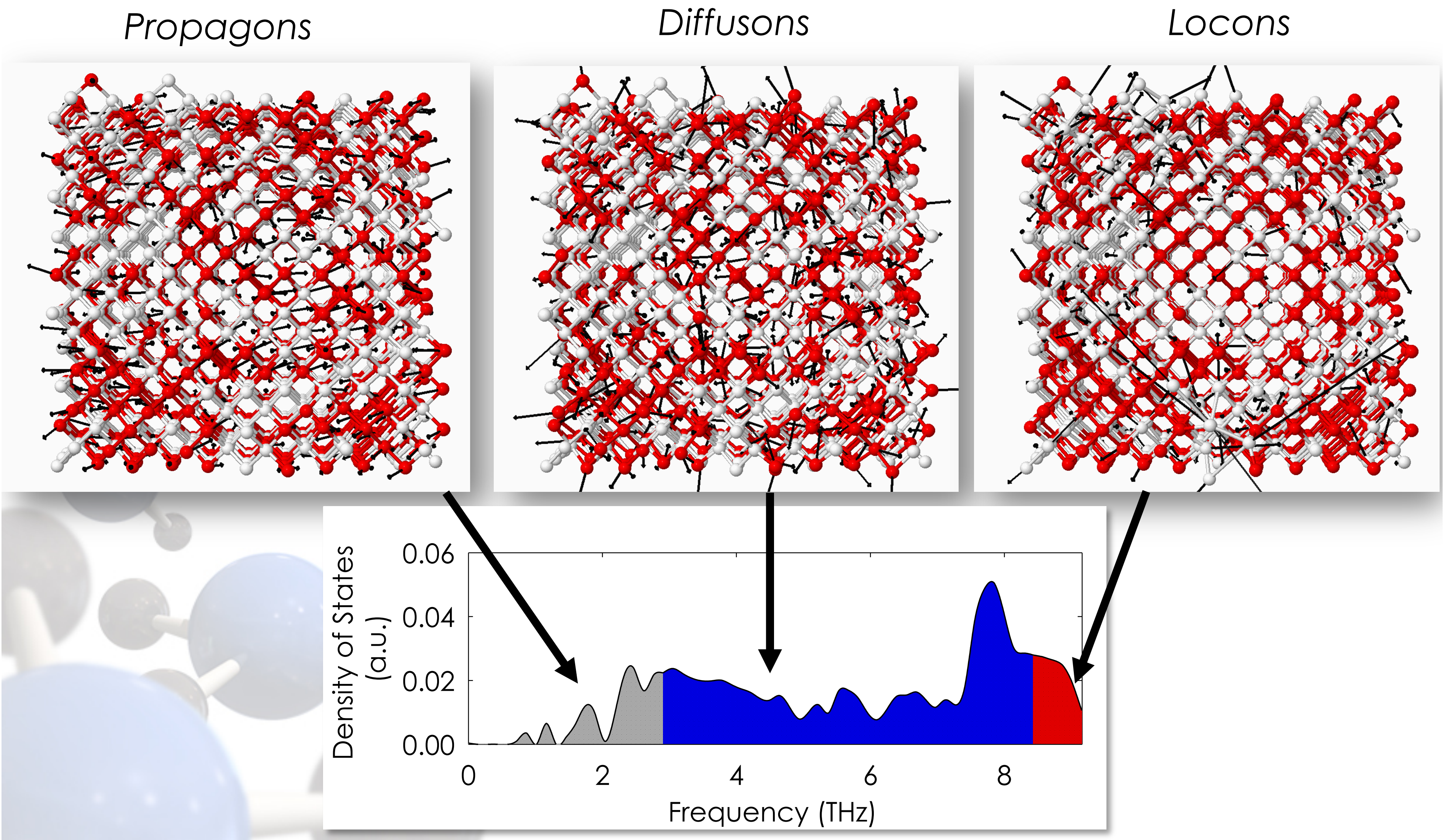


What Exactly is a “Mode”?

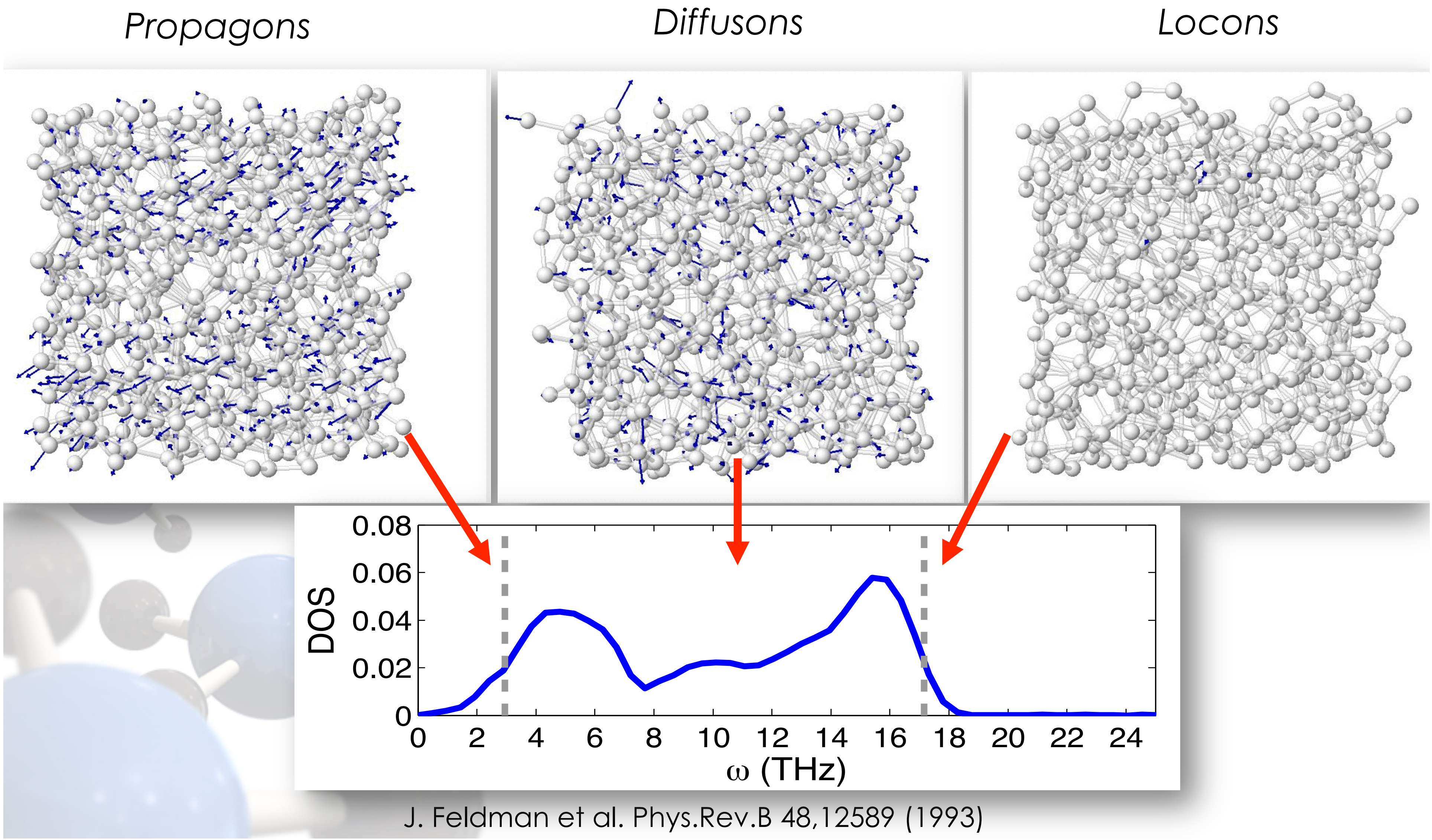
Eigen Vectors Changed



Modes of Vibration in Alloys



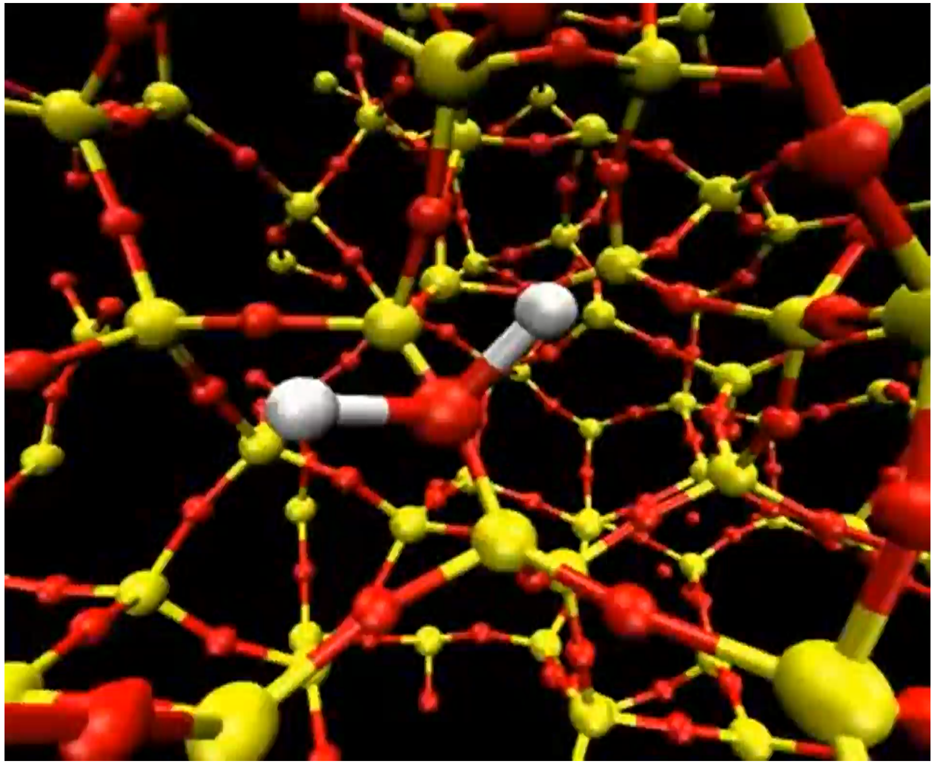
Amorphous Solids



J. Feldman et al. Phys.Rev.B 48,12589 (1993)

Anharmonicity

Purely harmonic interactions → non-interacting modes, mode amplitudes do not change in time.

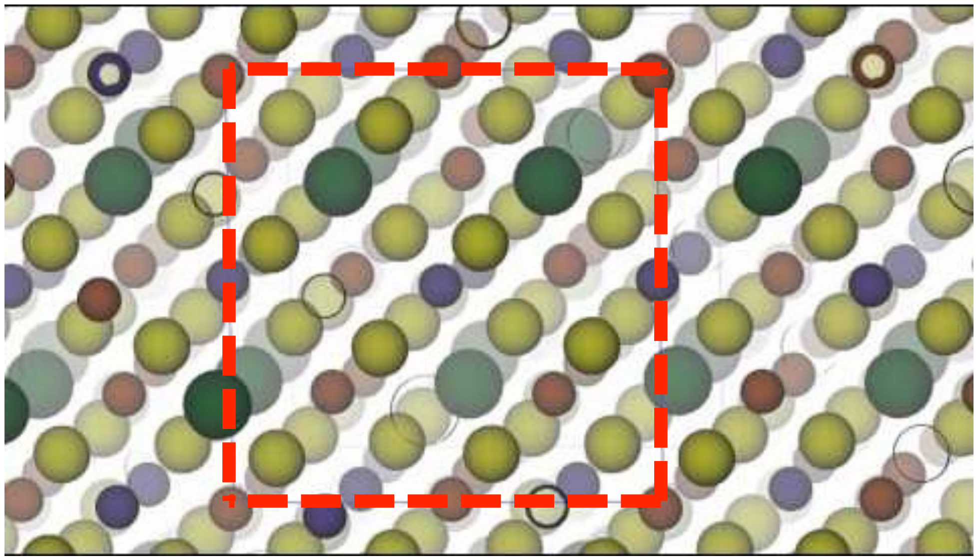


SiO2 Hydration

Finite bonding energy requires potential cannot be symmetric → anharmonicity causes mode interactions, amplitudes are not constant in time

Molecular Dynamics (MD)

- Cannot generally solve anharmonic case
- Solve numerically
  - Model of interactions
  - Classical
  - Atom = point particle
  - Verlet algorithm
  - Small time steps

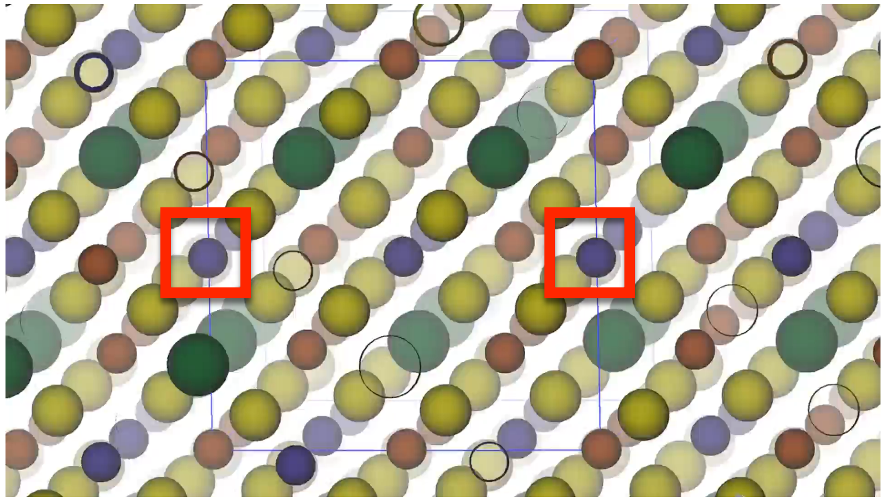


- Output = anharmonic trajectory $\mathbf{x}_j(t)\ \dot{\mathbf{x}}_j(t)$
- Periodic boundary conditions

Molecular Dynamics (MD)

- Simulation procedure
- Initial positions
- Initial velocities
- Positions → potential
- Gradient → Forces
- Calculate acceleration
- Predict new positions
- Update
- Repeat

Periodic Boundary Conditions



Verlet Algorithm

$$\vec{\mathbf{r}}(t+\Delta t) = \vec{\mathbf{r}}(t) + \vec{\mathbf{v}}(t)\Delta t + \tfrac{1}{2}\vec{\mathbf{a}}(t)\Delta t^2$$

$$+\ \vec{\mathbf{r}}(t-\Delta t) = \vec{\mathbf{r}}(t) - \vec{\mathbf{v}}(t)\Delta t + \tfrac{1}{2}\vec{\mathbf{a}}(t)\Delta t^2$$

$$\vec{\mathbf{r}}(t+\Delta t) = 2\vec{\mathbf{r}}(t) - \vec{\mathbf{r}}(t-\Delta t) + \vec{\mathbf{a}}(t)\Delta t^2$$

What is the Connection?

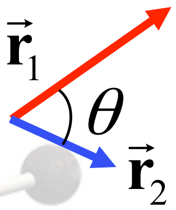
- We know…
  - Harmonic limit solutions → Modes/Phonons
  - Anharmonic motions → Molecular Dynamics
- Mode Amplitudes

$$A_k \begin{cases} \text{Harmonic} \rightarrow A_k = const. \\ \text{Anharmonic} \rightarrow A_k = f(t) \end{cases}$$

- The connection is modal analysis
  - Lattice Dynamics (LD) = Basis
  - Molecular Dynamics (MD) = Signal
  - Modal Analysis = Projection of Signal onto Basis
  - (Similar to a FFT)

Modal Analysis

- Convert trajectory into modal coordinates
- Move from describing:
  - Individual atom motions
  - Collective atom motions
- Projection = multiply then sum
  - Inner product



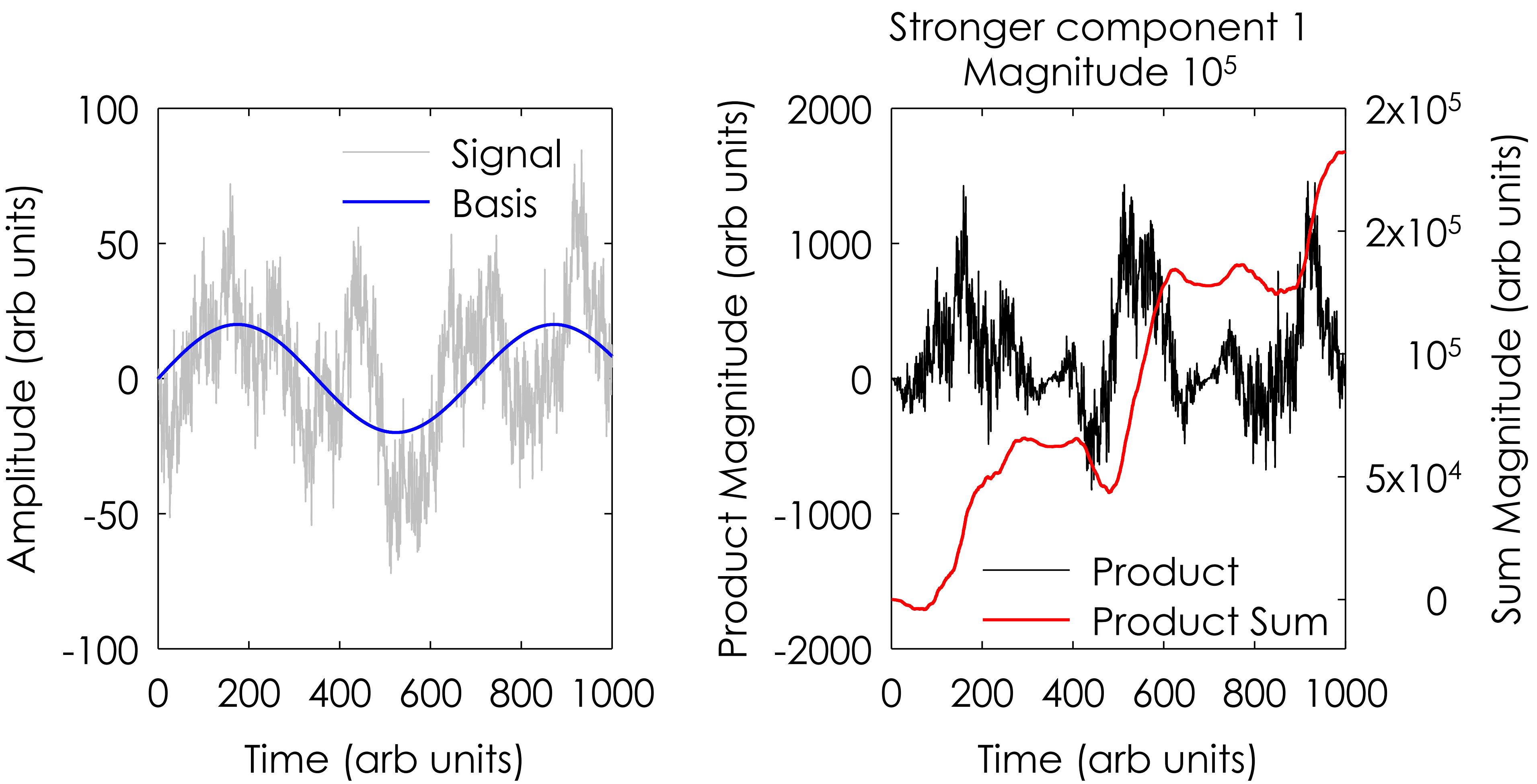
$$\vec{\mathbf{r}}_1 \cdot \vec{\mathbf{r}}_2 = |\vec{\mathbf{r}}_1||\vec{\mathbf{r}}_2|\cos(\theta) \begin{cases} \text{If } \vec{\mathbf{r}}_1 \text{ or } \vec{\mathbf{r}}_2 \text{ is large } \vec{\mathbf{r}}_1 \cdot \vec{\mathbf{r}}_2 = \text{large} \\ \text{If } \vec{\mathbf{r}}_1 \,\&\, \vec{\mathbf{r}}_2 \text{ same dir. } \vec{\mathbf{r}}_1 \cdot \vec{\mathbf{r}}_2 = \text{max} \\ \text{If } \vec{\mathbf{r}}_1 \,\&\, \vec{\mathbf{r}}_2 \text{ opposite } \vec{\mathbf{r}}_1 \cdot \vec{\mathbf{r}}_2 = \text{-max} \\ \text{If } \vec{\mathbf{r}}_1 \text{ or } \vec{\mathbf{r}}_2 \text{ are } \perp \;\; \vec{\mathbf{r}}_1 \cdot \vec{\mathbf{r}}_2 = \text{zero} \end{cases}$$

- Conversion to modal coordinates

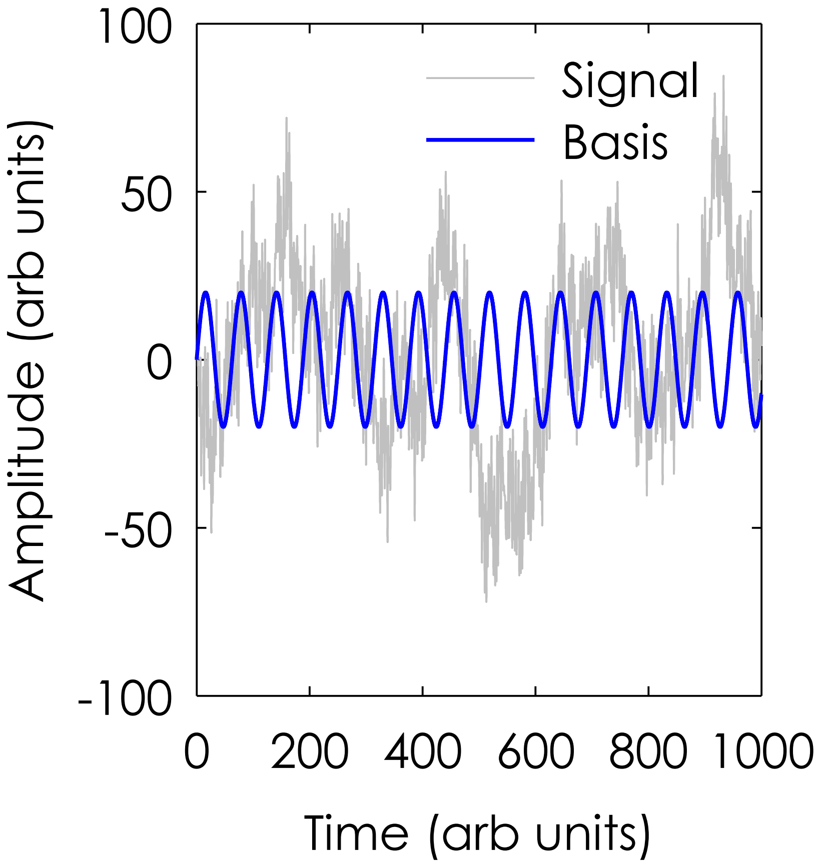
$$X_n(t) = \sum_j \vec{\mathbf{X}}_j(t) \cdot \vec{\mathbf{p}}_j(n) \qquad \vec{\mathbf{X}}_j(t) = \sum_n X_n(t) \cdot \vec{\mathbf{p}}_j(n)$$

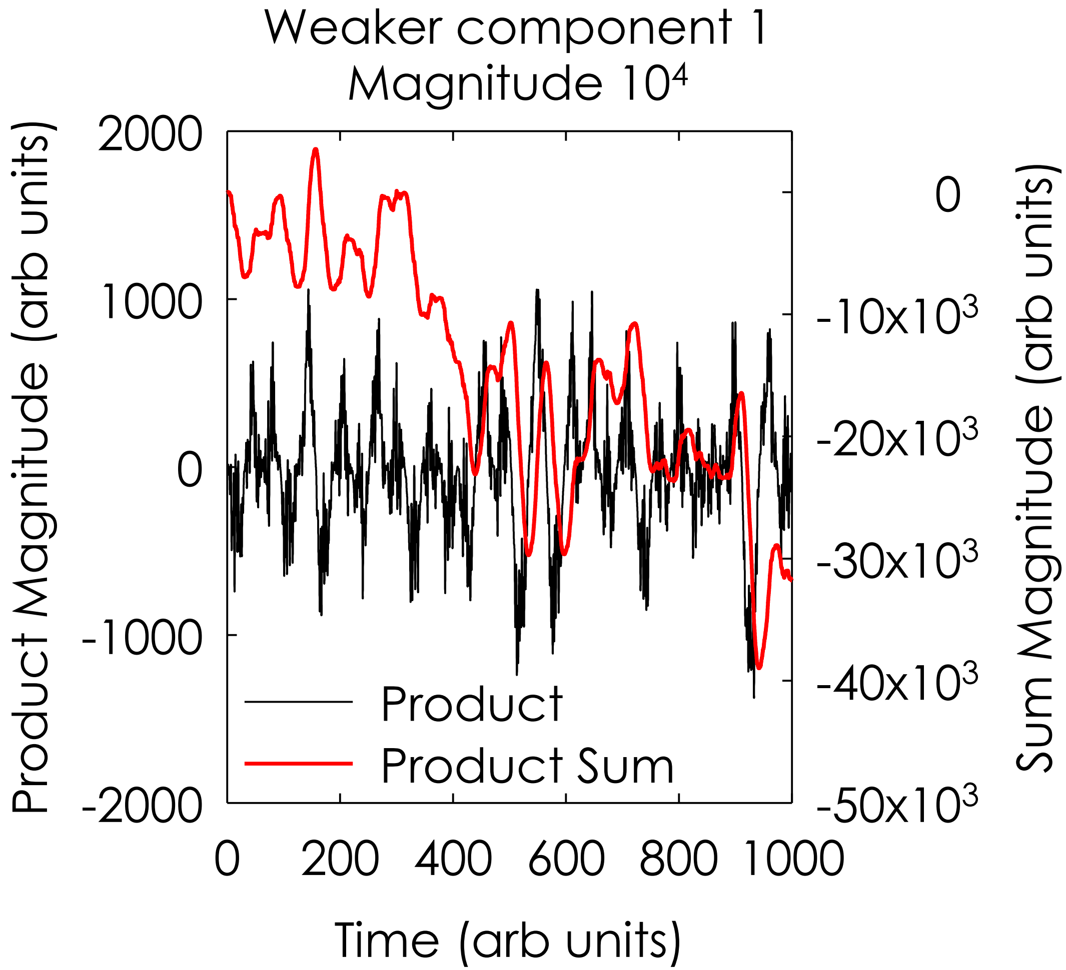
$$\dot{X}_n(t) = \sum_j \dot{\vec{\mathbf{X}}}_j(t) \cdot \vec{\mathbf{p}}_j(n) \qquad \dot{\vec{\mathbf{X}}}_j(t) = \sum_n \dot{X}_n(t) \cdot \vec{\mathbf{p}}_j(n)$$

Projection: Signal onto a Basis

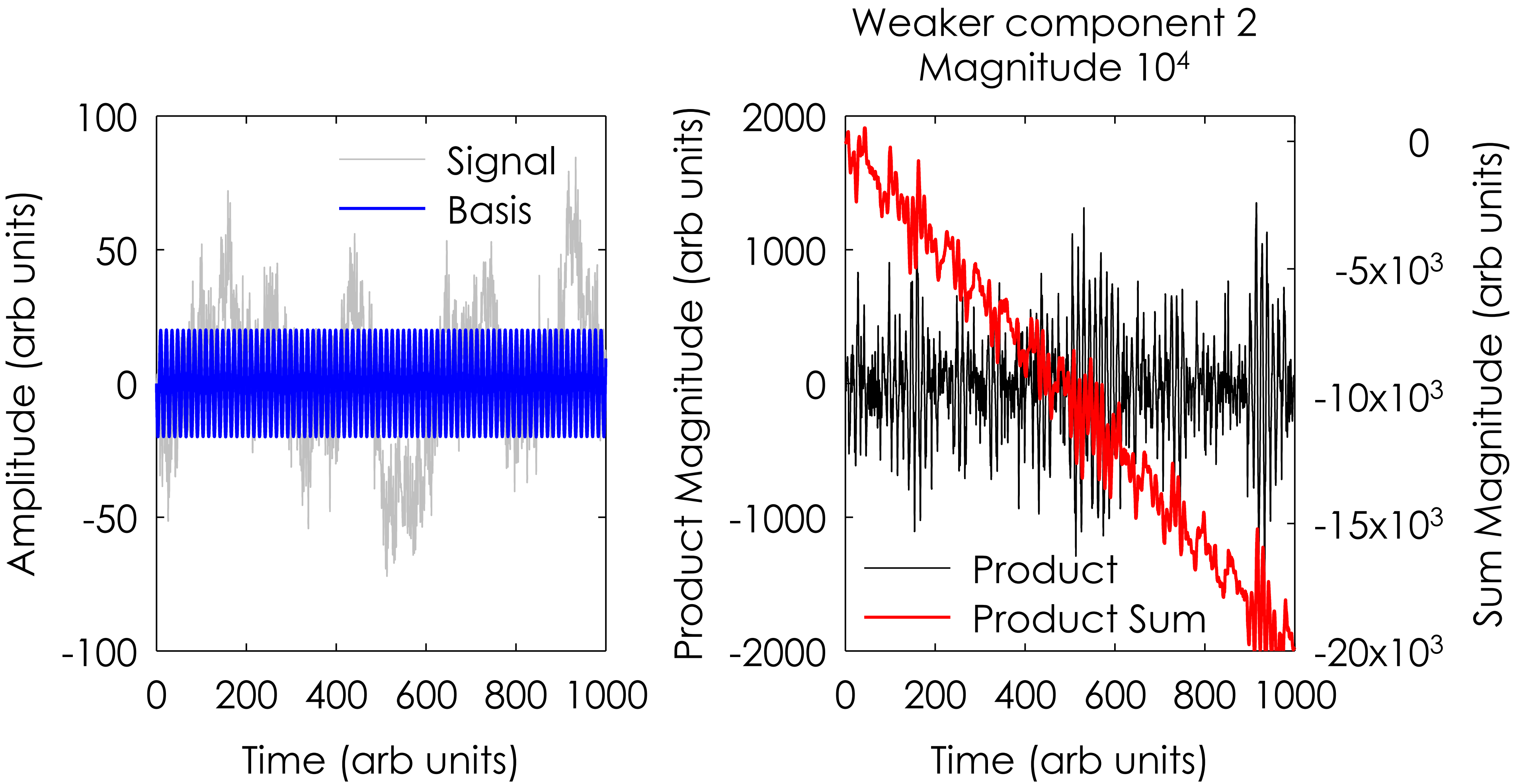


Projection: Signal onto a Basis





Projection: Signal onto a Basis



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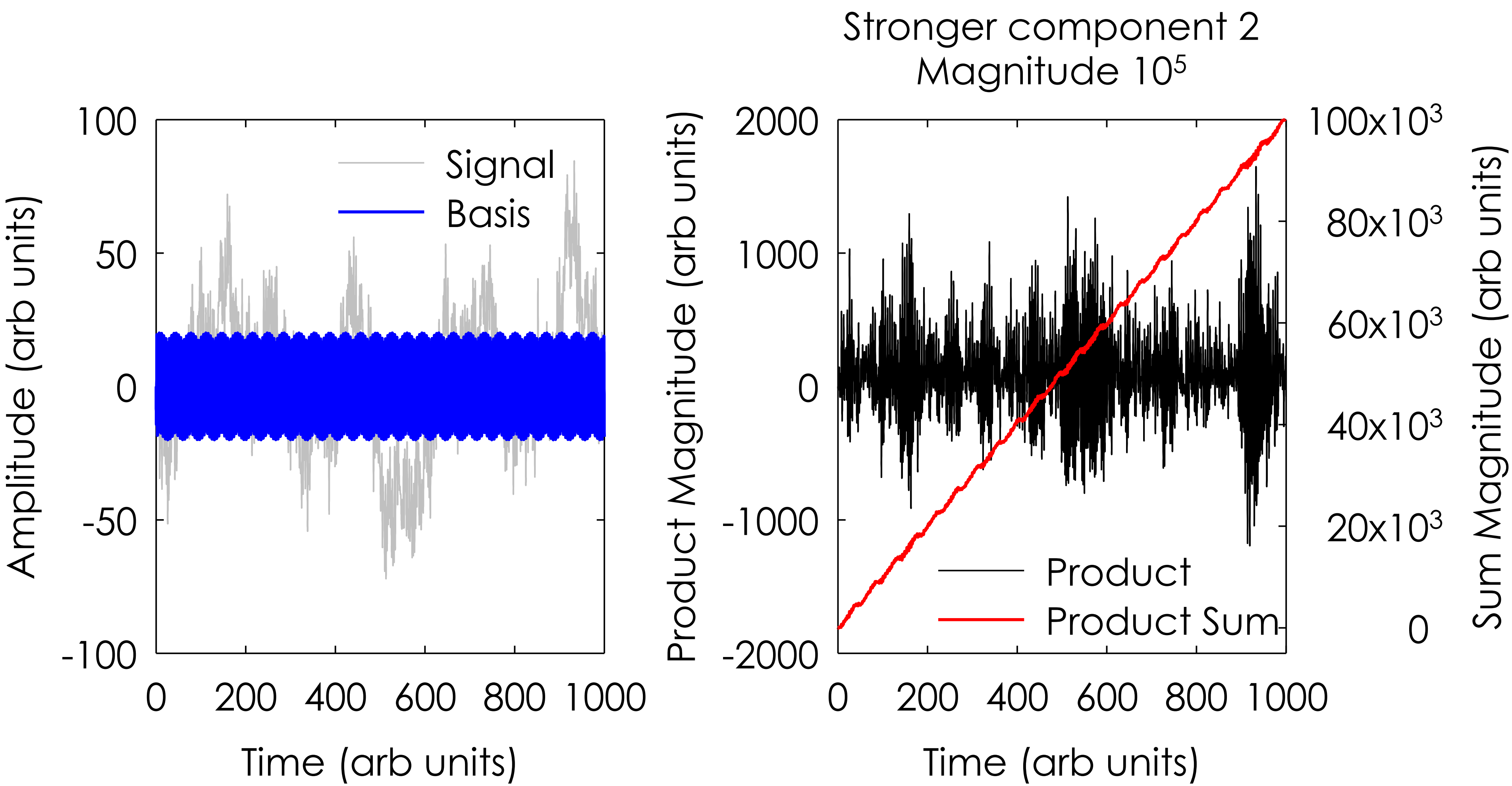
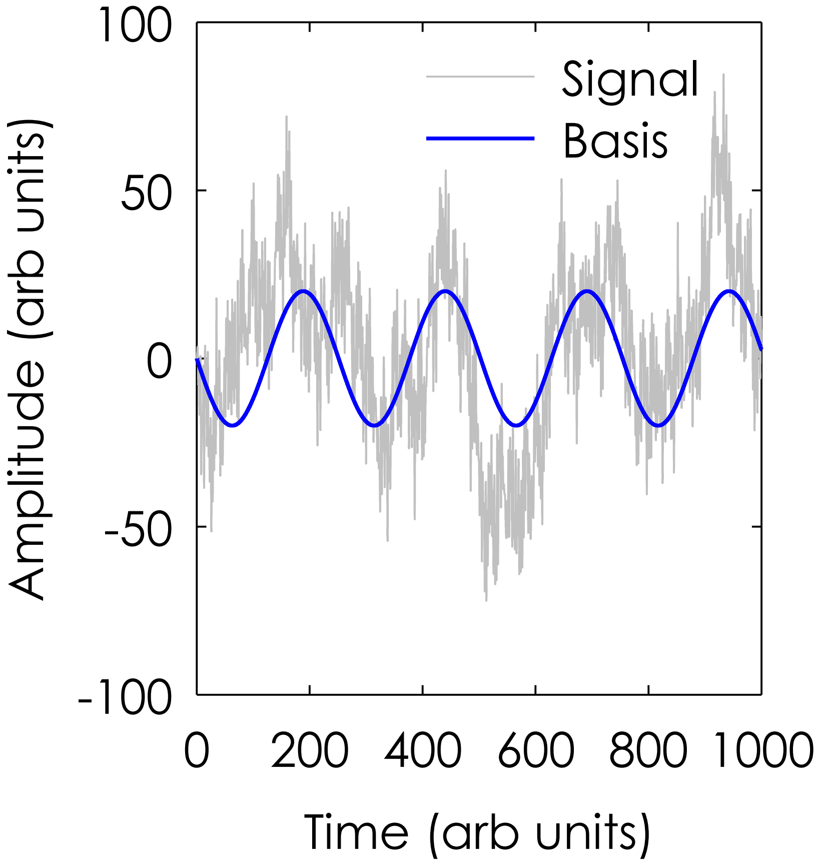
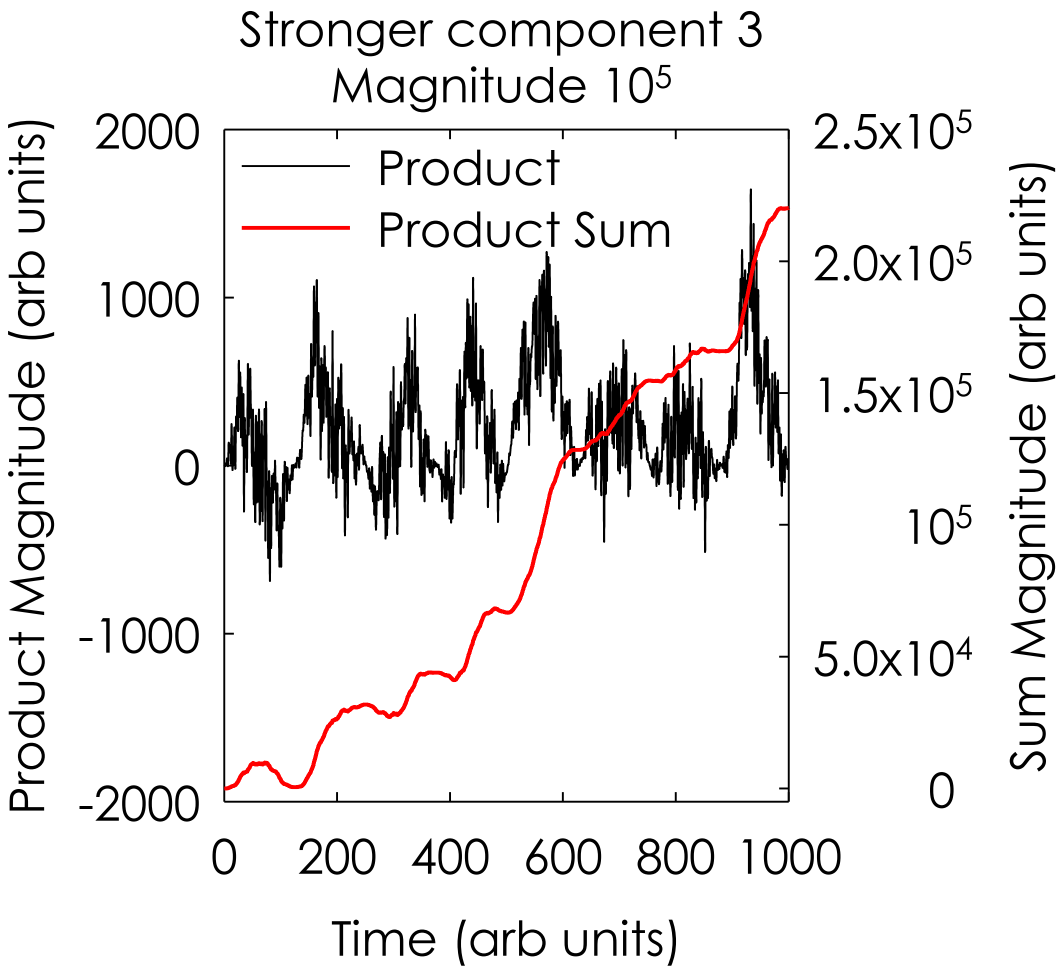


Projection: Signal onto a Basis





How is Modal Analysis Useful?

- We can convert to modal coordinates

$$X_n(t) = \sum_j \vec{\mathbf{X}}_j(t)\cdot\vec{\mathbf{p}}_j(n) \qquad \vec{\mathbf{X}}_j(t) = \sum_n X_n(t)\cdot\vec{\mathbf{p}}_j(n)$$

$$\dot{X}_n(t) = \sum_j \dot{\vec{\mathbf{X}}}_j(t)\cdot\vec{\mathbf{p}}_j(n) \qquad \dot{\vec{\mathbf{X}}}_j(t) = \sum_n \dot{X}_n(t)\cdot\vec{\mathbf{p}}_j(n)$$

- What can we learn that is new?

Correlation Time → Relaxation Times

$$E_P = \tfrac{1}{2}\omega^2 X_n^2(t) \sim \tfrac{1}{2} m\omega^2 X^2$$

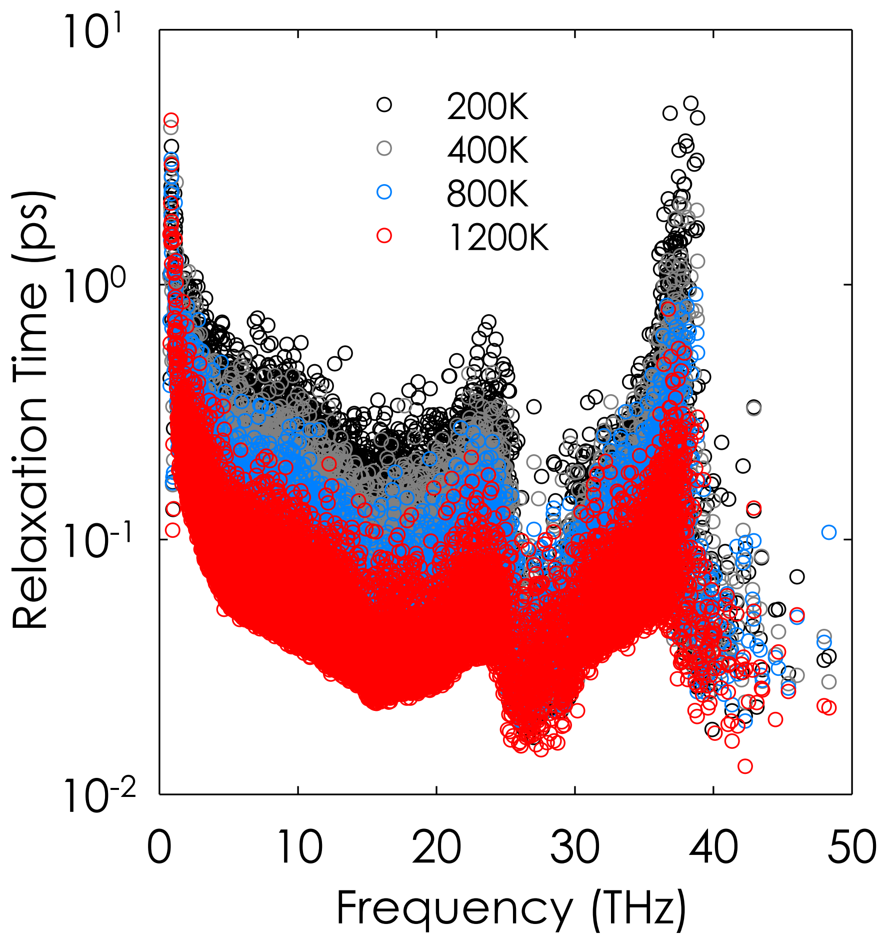
$$E_K = \tfrac{1}{2}\dot{X}_n^2(t) \sim \tfrac{1}{2} m\dot{X}^2$$

$$E_{total} = E_P + E_K \sim \hbar\omega \cdot n(t)$$

$$\delta n(t) \propto \delta E(t) = E_{total} - \langle E_{total} \rangle$$

Time it takes to relax back to equilibrium (average) occupation = correlation time

$$\tau = \int_0^\infty \frac{\langle \delta n(t)\cdot \delta n(t+t')\rangle dt'}{\langle \delta n(t)\cdot \delta n(t)\rangle}$$



Correlation Time → Relaxation Times

Crystalline Silicon
Relaxation Times → Mean Free Paths