

Atomic vibrations

Thermal properties

Outline

- One dimensional chain models
- Three dimensional models
- Experimental techniques
- Amorphous materials: Experiments vs. calculations
- Fractal networks: Fractons
- Low energy excitations
- Thermal properties at low temperatures

Basic equations

- Equation of motion
$$M_n \frac{d^2 \mathbf{u}_n}{dt^2} = - \sum_{n'} \Phi_{nn'} \mathbf{u}_{n'}$$

- Harmonic approximation

- Displacement of atom n: $\mathbf{u}_n = \mathbf{A}_n (M_n)^{-1/2} \exp(-i\omega t)$

- Force acting on n due to displacement of n': Force constant $\Phi_{nn'}$

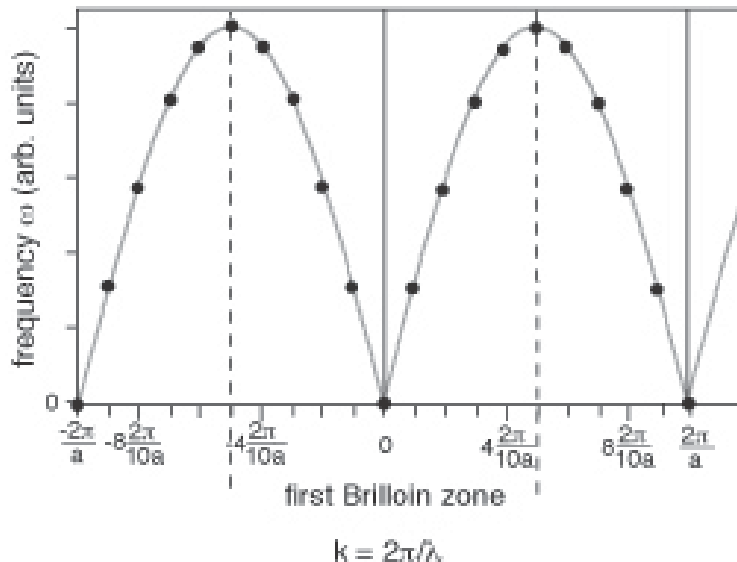
$$\omega^2 \mathbf{A}_n = \sum_{n'} (\Phi_{nn'} / \sqrt{M_n M_{n'}}) \mathbf{A}_{n'} = \sum_{n'} \mathbf{D}_{nn'} \mathbf{A}_{n'}$$

- 3n eigenvalues ω_j^2 – normal modes – phonons

- Diagonalize matrix on RHS to find the eigenvalues

Atomic vibrations

- Crystalline material
- Nearest-neighbor approx.
- Dispersion relation $\omega(k)$ in 1-dim – acoustic branch



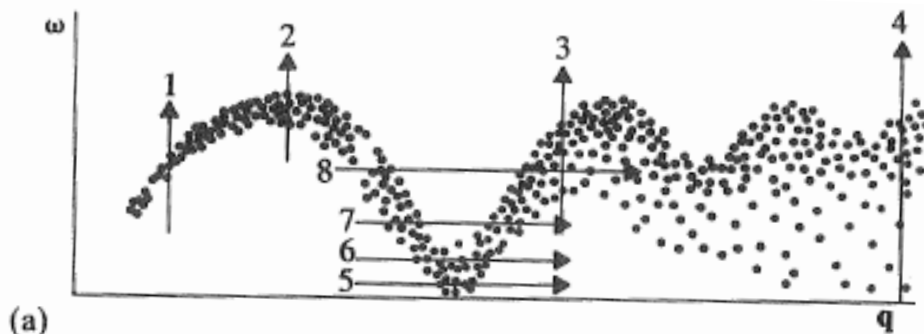
- The translational symmetry of the crystal leads to a periodic $\omega(k)$
- Physical vibrations in first Brillouin zone, $\pi/a < k \leq \pi/a$
- Amorphous material – no periodic structure – no Brillouin Zone – no dispersion relation
- The phonon density of states is still well-defined

Density of states

- "Infinite" unit cell
- Dispersion relation not meaningful
- Scattering vector Q can be measured – inelastic scattering
- Schematic picture of an acoustic branch as a function of Q – well-defined only at long wavelengths
- Vibrational modes are characterized by their density of states (DOS)
- k (i.e. Q) is now only a label of the vibrational states
- General definition of DOS:

$$\rho(\omega) = \sum_k \delta(\omega - \omega_k) = - (1/\pi) \text{Im} \sum_k \lim_{\eta \rightarrow 0} (\omega - \omega_k + i\eta)^{-1}$$

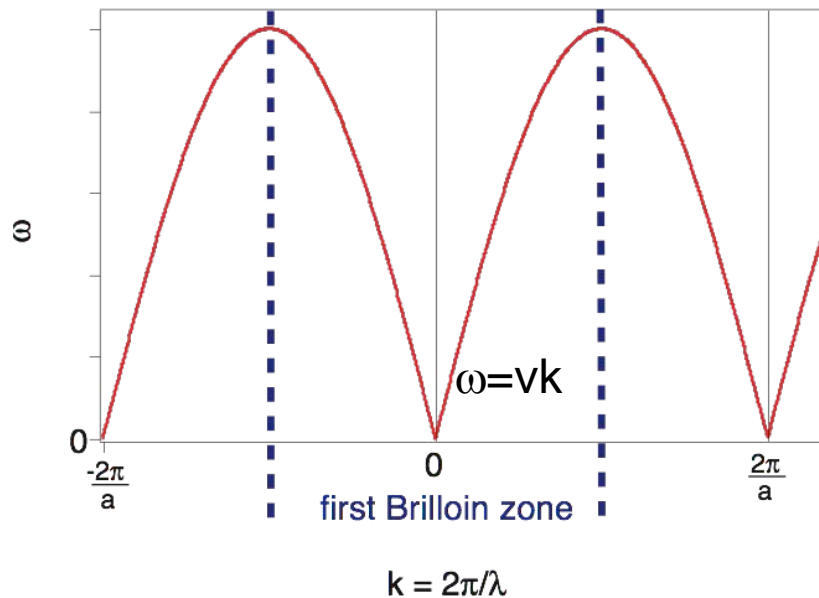
Gives contribution of unity from each vibrational state.



Monatomic one-dim chain

- Crystalline material

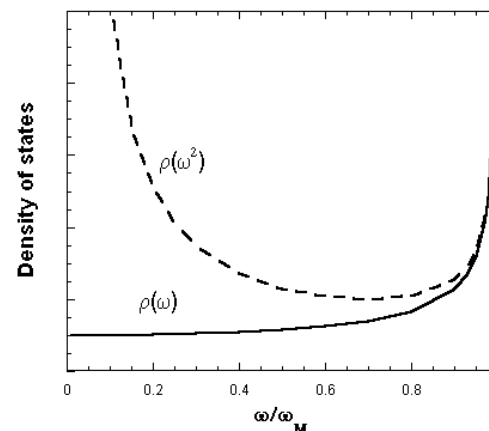
$$\omega(k) = \sqrt{\frac{2\gamma(1 - \cos ka)}{M}} = 2\sqrt{\frac{\gamma}{M}} \left| \sin \frac{ka}{2} \right|$$



- Density of states

$$\rho(\omega) = \frac{2N}{\pi\sqrt{\omega_M^2 - \omega^2}}$$

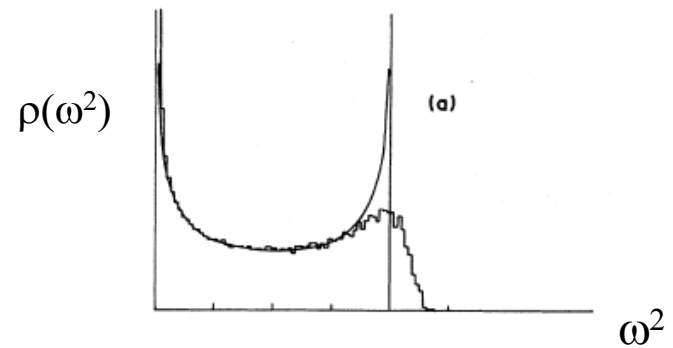
$$\rho(\omega^2) = \frac{N}{\pi\omega\sqrt{\omega_M^2 - \omega^2}}$$



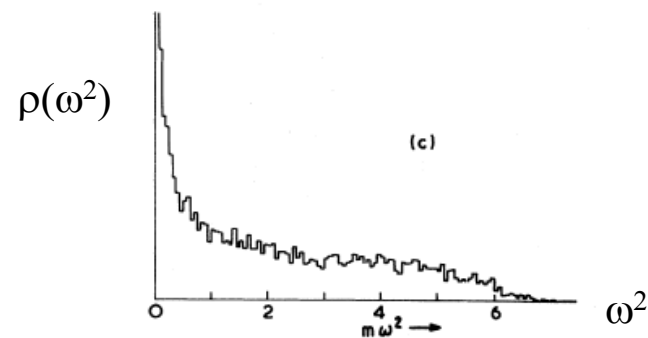
Disordered monatomic chain

- Interactions between nearest neighbour atoms
- Distribution of interatomic distances or force constants
- $P(\Phi) = (\Phi_{\max} - \Phi_{\min})^{-1}$ and zero outside this interval
- Negative eigenvalues of the matrix $\mathbf{D} - \mathbf{I}\omega^2$
- Compare to crystal result

- Narrow distribution

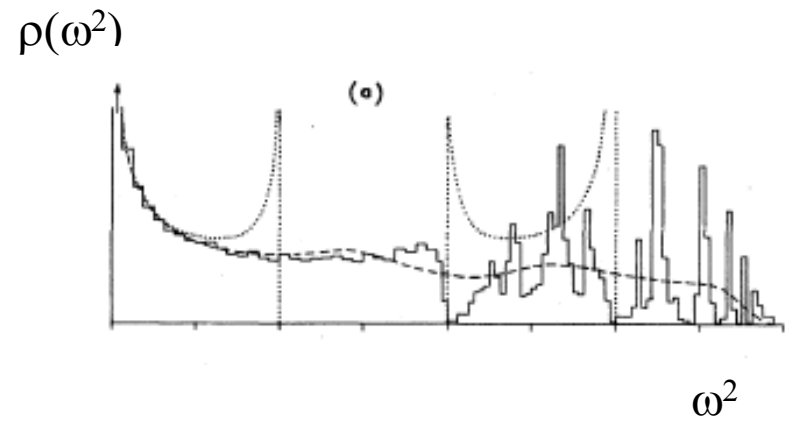
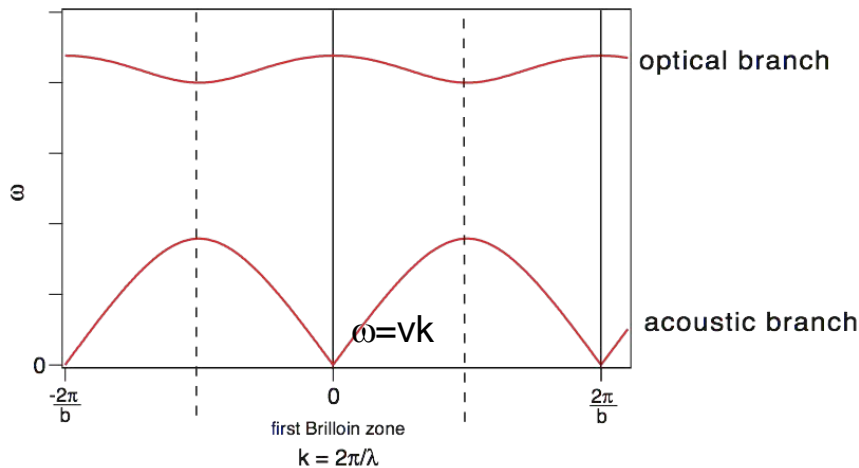


- Broad distribution



Two-atomic chain

- Crystalline material
- Acoustic and optical branches
- Two kinds of atoms A and B with different mass
- Disordered chain with force constants equal
- Mass ratio 2
- Equal conc. of A and B
- Dotted line: Crystalline DOS

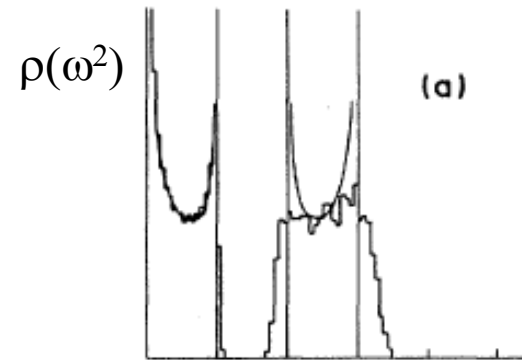


- Source: Dean, Rev. Mod. Phys., 1972

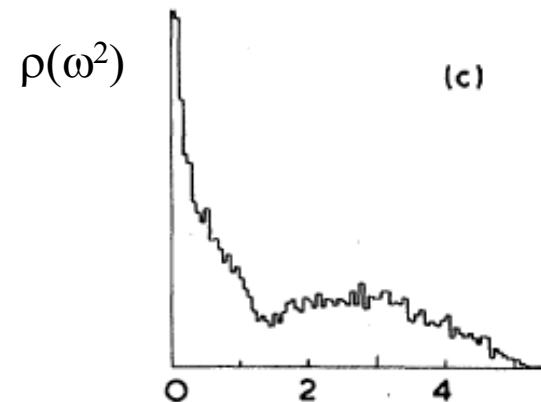
Diatomic alternating chain

- Nearest neighbor interactions
- Different degrees of disorder in force constants
- Mass ratio 2
- Distribution of force constants as for the monatomic case
- Compared to crystalline chain result in (a)

Narrow distribution



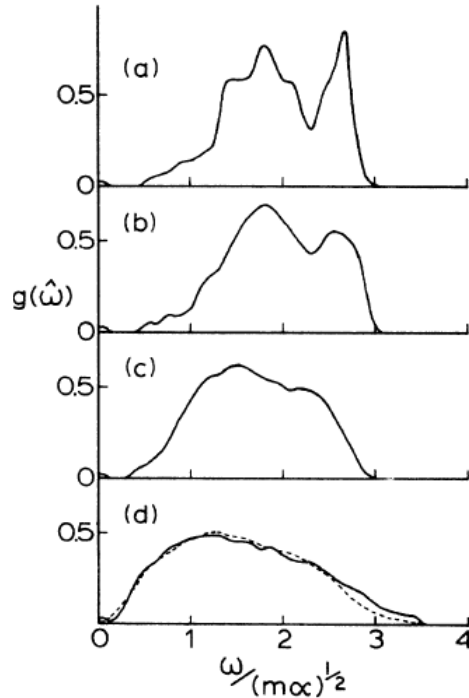
Broad distribution



Source: Dean, Rev. Mod. Phys., 1972

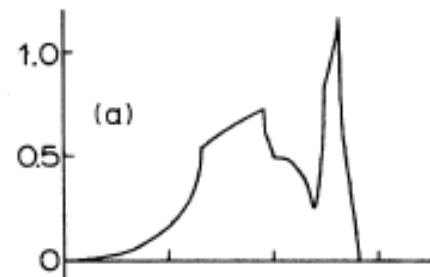
Three-dimensional case: Metal

- Disorder effects on vibrations in fcc lattice



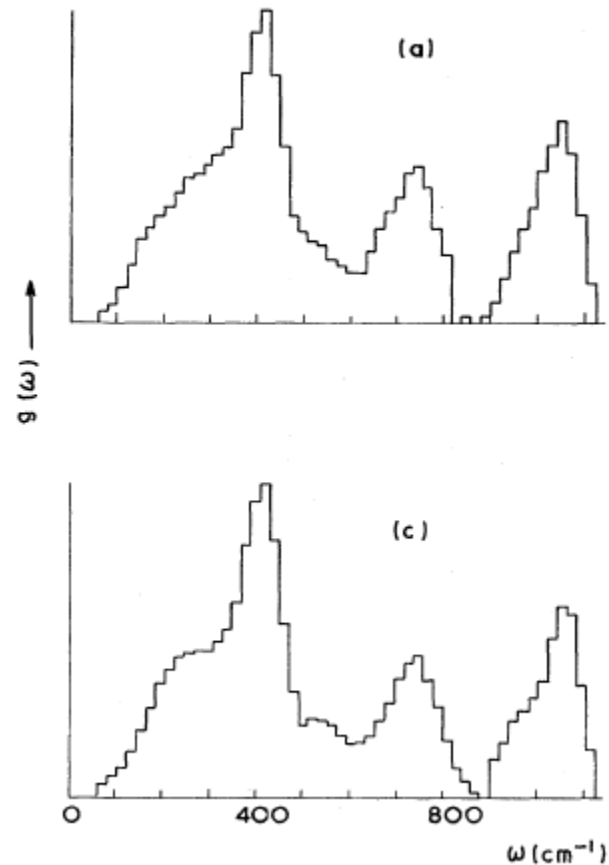
Source: Rehr and Alben, Phys. Rev. B 16 (1977) 2400

- Calculation for a monatomic disordered material
- a) 480 atoms fcc structure
- b) amorphous – force constants equal
- c,d) force constant distributions
- Compare to Cu



Three-dimensional case: SiO_2

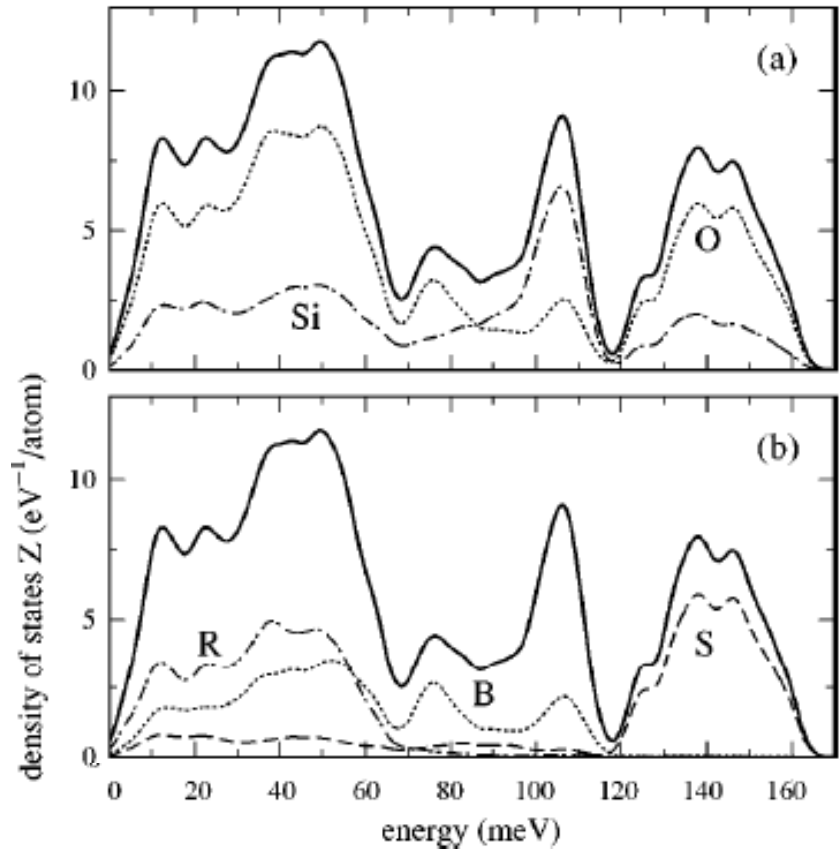
- **Amorphous SiO_2 model**
- Example of early computation: Coordinates from two "toy models"
- Nearest neighbour interactions
- Assume interatomic potential
- Cluster of 500 atoms
- DOS from negative eigenvalues of $\mathbf{D}-\mathbf{I}\omega^2$



Source: Dean, Rev. Mod. Phys., 1972

Amorphous SiO₂

- Modern computation
- Density functional theory to obtain the force constant matrix (second derivative of energy with respect to atomic displacements)
- Cluster of 72 atoms
- DOS from eigenvalues
- Si and O modes
- Stretching, bending and rocking modes



Source: Pasquarello et al, PRB 57 (1998)

Amorphous vs. crystalline

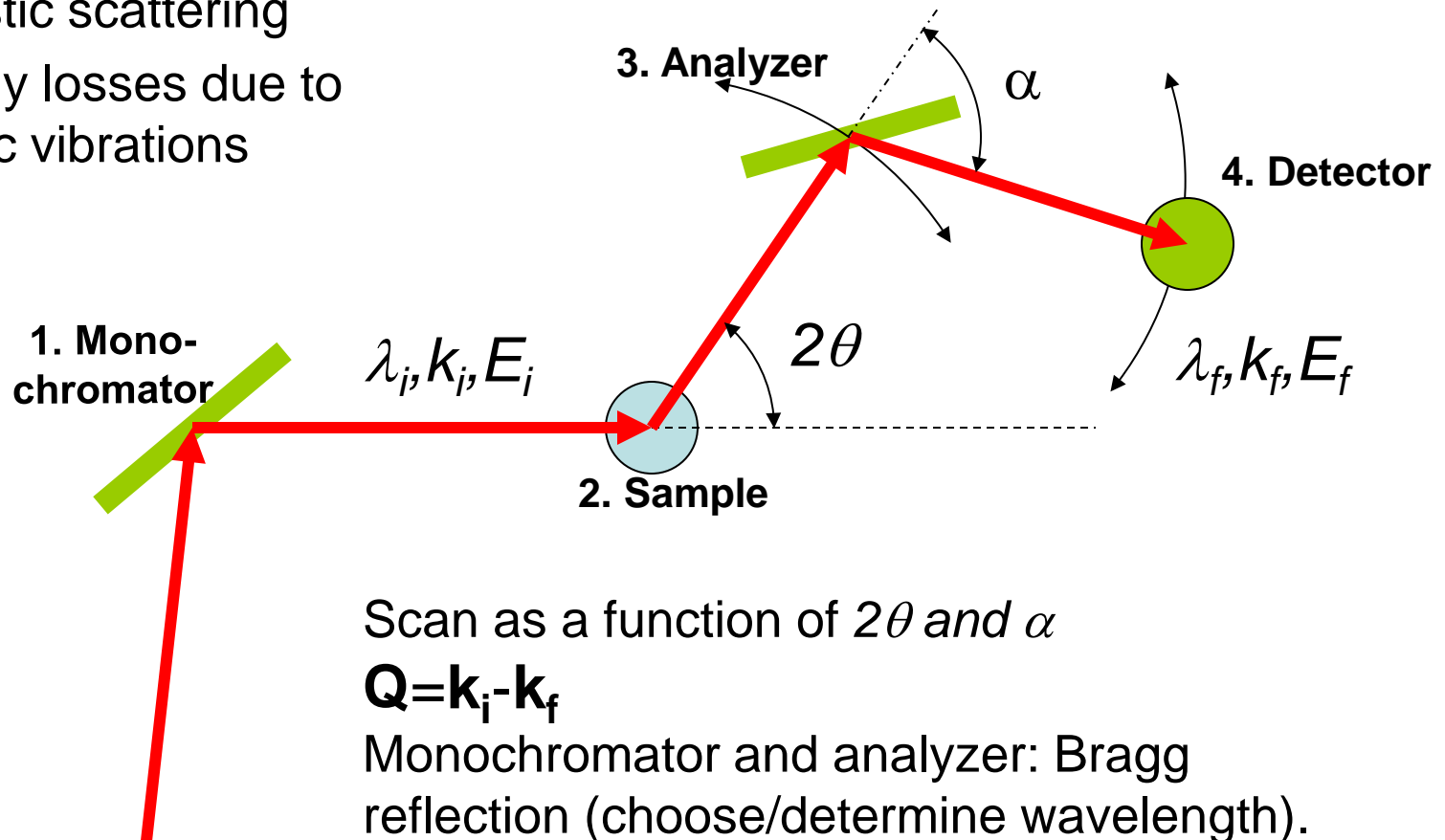
- Short range order determines the main features of the vibrational density of states
- In amorphous materials, discontinuities in slope of $\rho(\omega)$ are washed out
- General broadening of features in DOS
- Not all atoms participate in a given vibrational mode – participation ratio
- Localization of vibration modes occurs in amorphous materials, especially at higher frequencies.

Experimental techniques

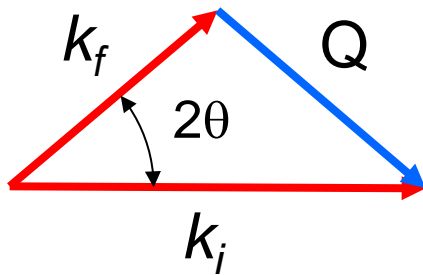
- Inelastic neutron scattering
measures phonon frequency and scattering vector $\omega(\mathbf{Q})$ – density of states
- Infrared spectroscopy
optical phonon modes
- Raman spectroscopy
possible to obtain DOS by modeling
- Brillouin scattering
- Thermal properties

Triple axis neutron spectrometer

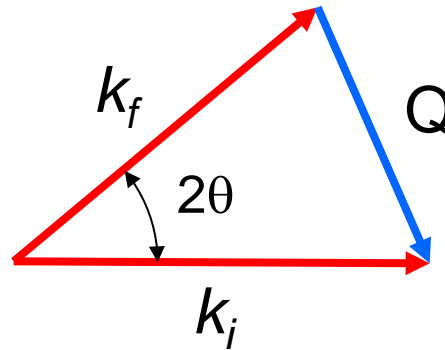
- Inelastic scattering
- Energy losses due to atomic vibrations



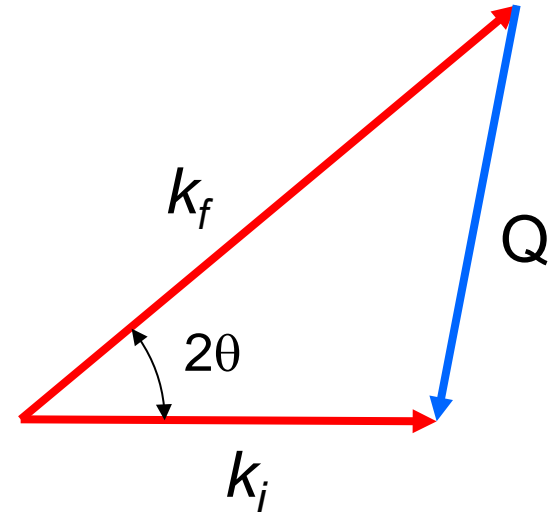
Neutron scattering



Neutron lose energy



Elastic case



Neutron gain energy

$$Q = k_i - k_f \quad \hbar\omega = E_i - E_f$$

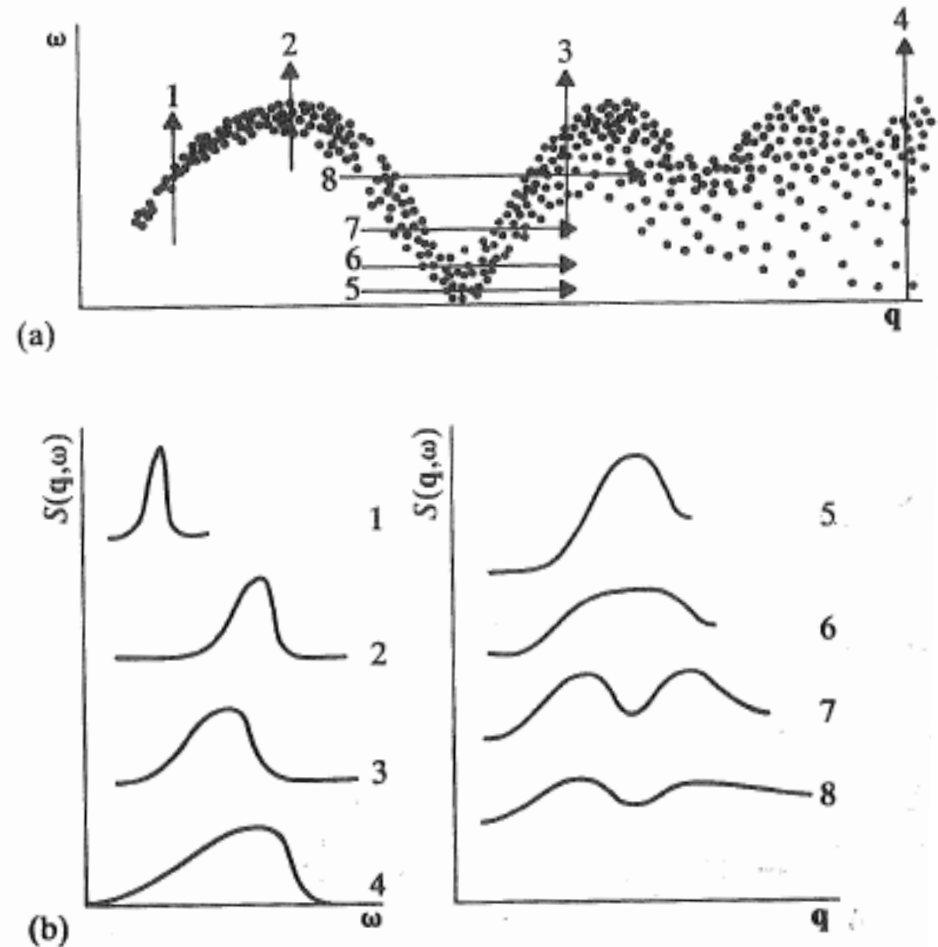
$$\frac{\hbar Q^2}{2m_n} = 2E_i - \hbar\omega - 2\sqrt{E_i(E_i - \hbar\omega)} \cos(2\theta)$$

We measure the scattered neutron intensity I as a function of Q and Energy transfer $\hbar\omega$.

$I(Q, \omega) \propto S(Q, \omega)$, where $S(Q, \omega)$ is the dynamic structure factor.

Dynamic structure factor

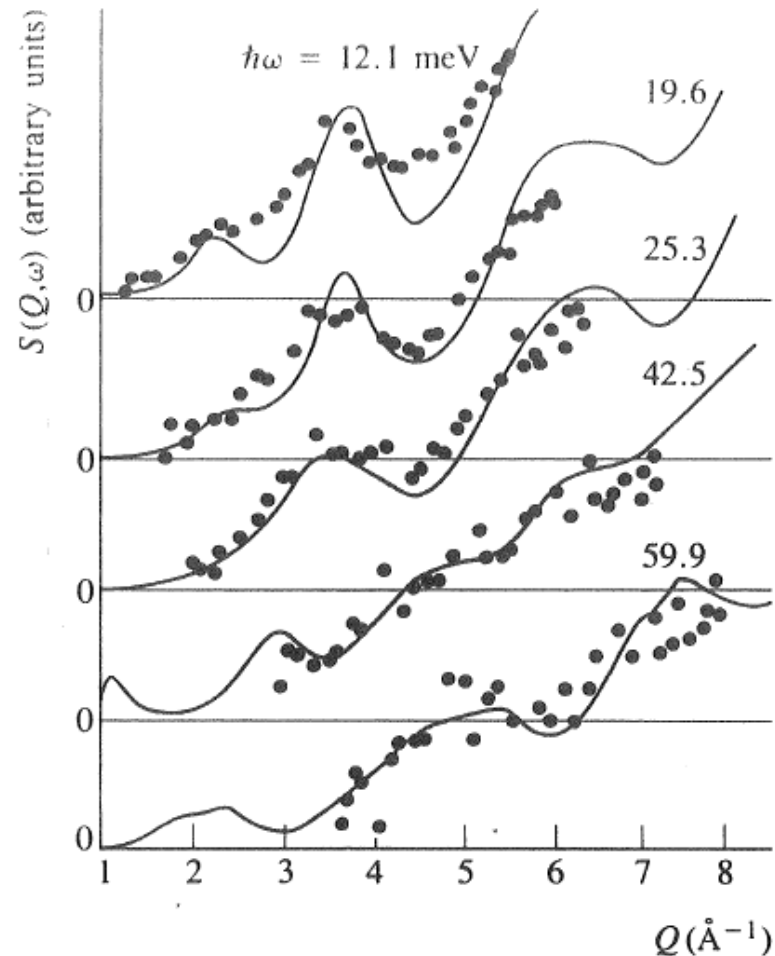
- Schematic picture of vibrational density of states and the dynamic structure factor $S(Q, \omega)$
- Can be obtained from inelastic neutron scattering
- Describes "smearing" of dispersion curves $\omega(Q)$



Source: Elliott, Physics of amorphous materials

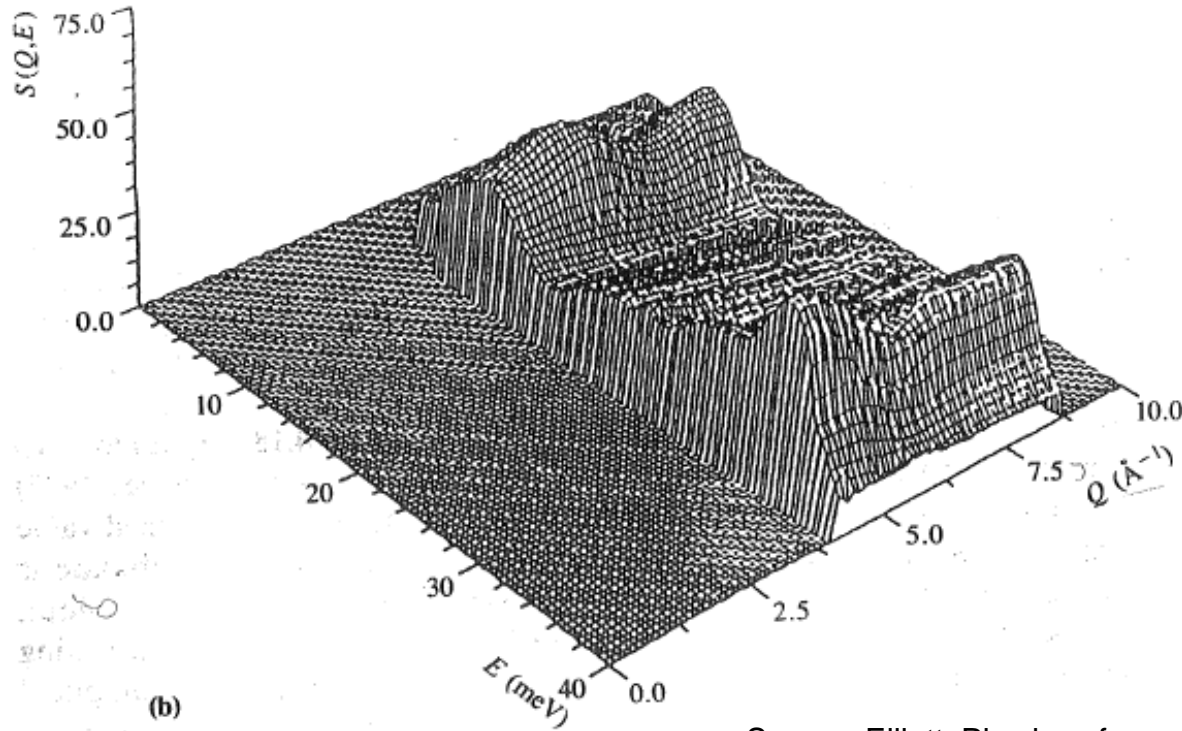
Theory vs. experiment

- Calculations can reproduce well oscillations in $S(Q, \omega)$ seen in experiments
- Example: a-Si
 - good overall agreement



Example 1

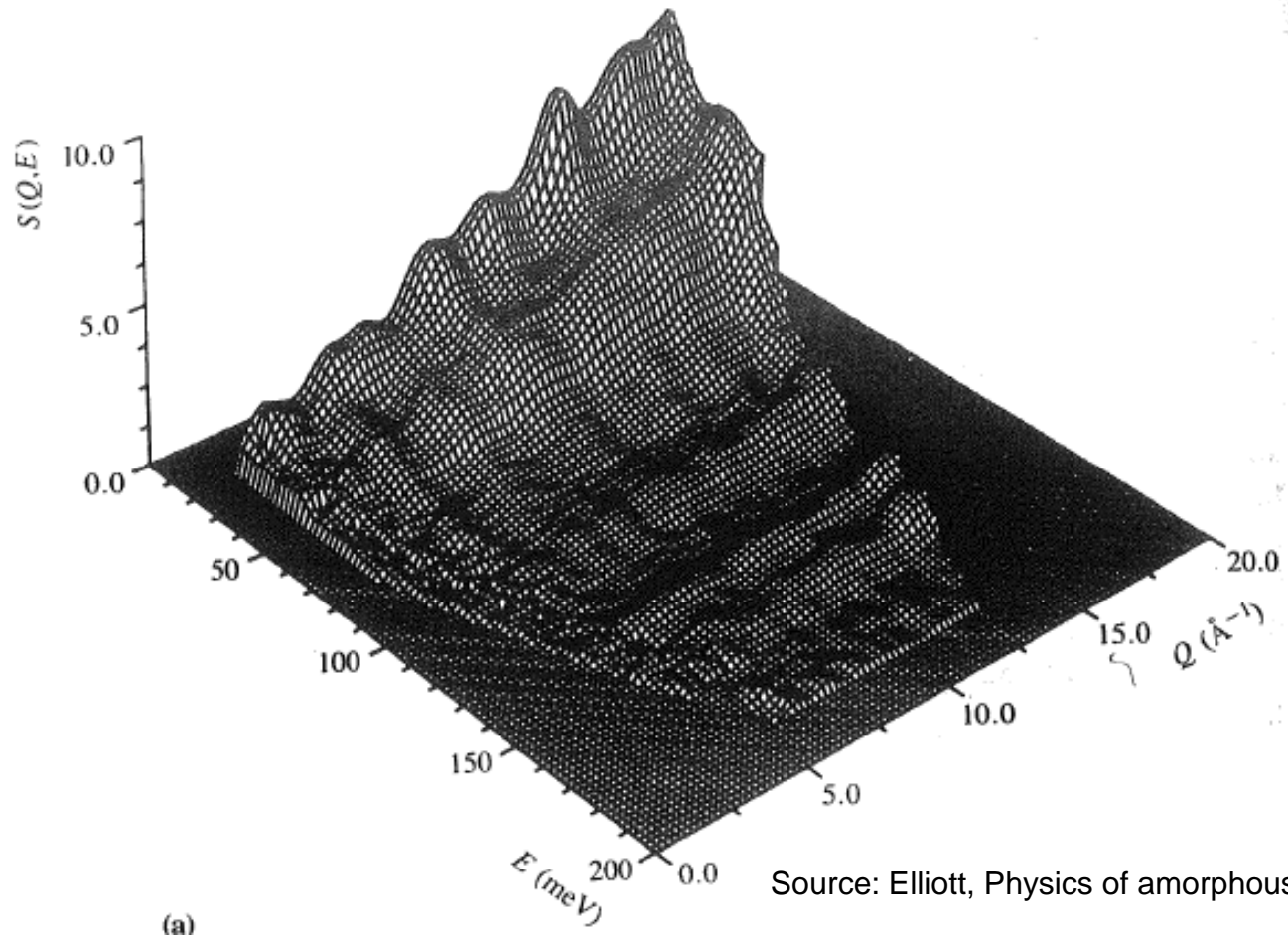
- a-Ge



Source: Elliott, Physics of amorphous materials

Example 2

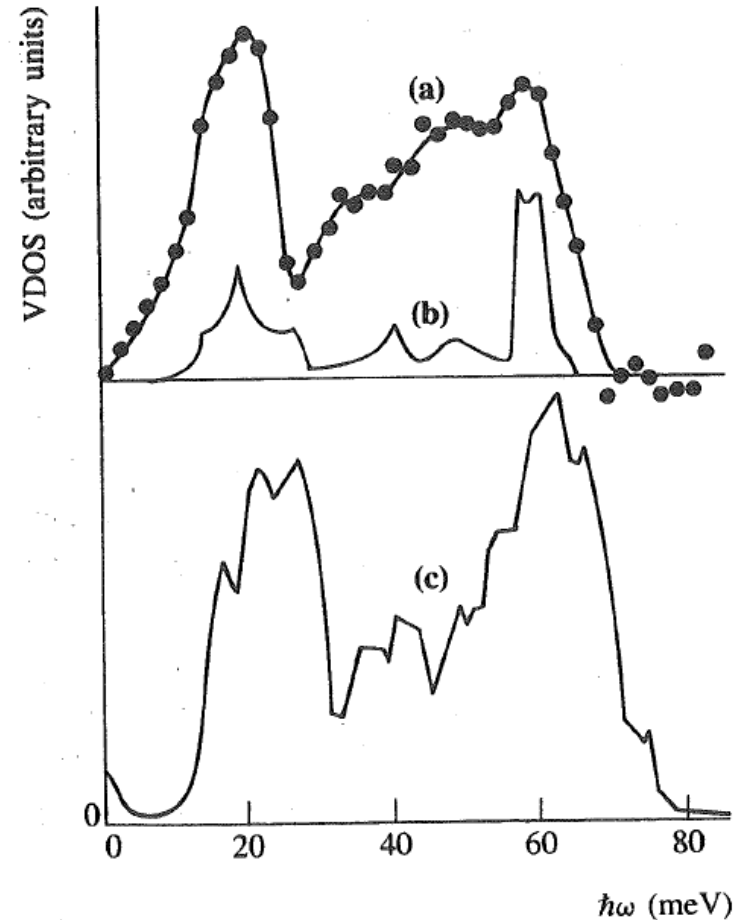
- a-SiO_2



Source: Elliott, Physics of amorphous materials

Amorphous Si

- (a) $\rho(\omega)$ of a-Si from neutron scattering experiment
- (b) calculation for c-Si from model that fits dispersion relations
- TA, LA, LO, TO
- (c) calculation for a-Si 61-atom cluster

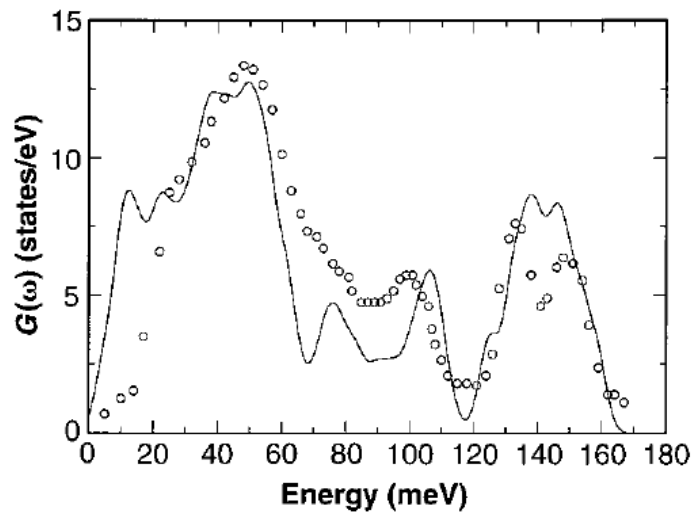


Vibrational spectroscopy

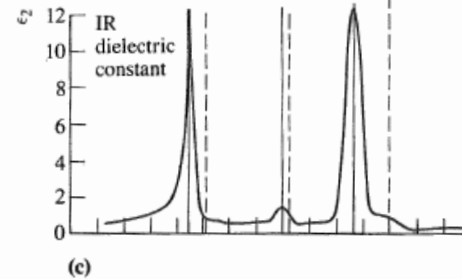
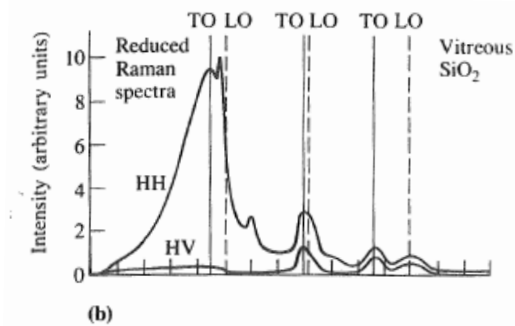
- Infrared spectroscopy
 - Change in dipole moment of vibrational mode
 - Component of ionic bonding
 - Optical transmission and reflection measurements → absorption coefficient
 - Crystal: Absorption from TO modes (LO modes indirectly)
 - Broader spectra for amorphous materials and for example a-Si and a-Ge also exhibit one-phonon IR spectra
- Raman spectroscopy
 - Change in polarizability associated with vibrational mode
 - Polarization H (horizontal) or V (vertical) with respect to scattering plane
 - Crystals: Complementary techniques, IR-inactive modes are Raman active
 - This distinction largely lost for amorphous structures
 - All modes contribute, but not equally to Raman spectra

Infrared and Raman spectroscopy

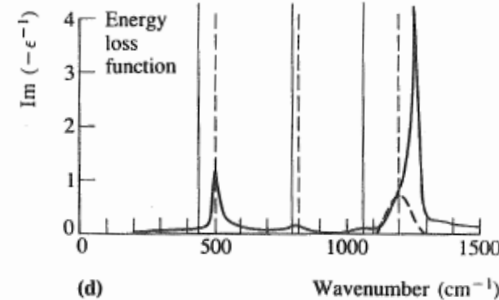
- All modes are weighted differently in infrared and Raman spectra
- Ex: a-SiO₂
- DOS – neutron scattering vs. DFT calculation



Source: Grimsditch et al., JPCM 15 (2003) S2335



From IR absorption



Source: Elliott, Physics of amorphous materials

Composites

- Theoretical models similar for random alloys, mixtures of local coordination polyhedra (Ex: SiO_xN_y tetrahedra) and composites (multiphase mixtures)
- Elaborate "mixing laws" to average over the properties of the constituents
- Details of the nanostructure are also very important
- Coherent Potential Approximation (CPA)
- Effective Medium Theory (EMA)

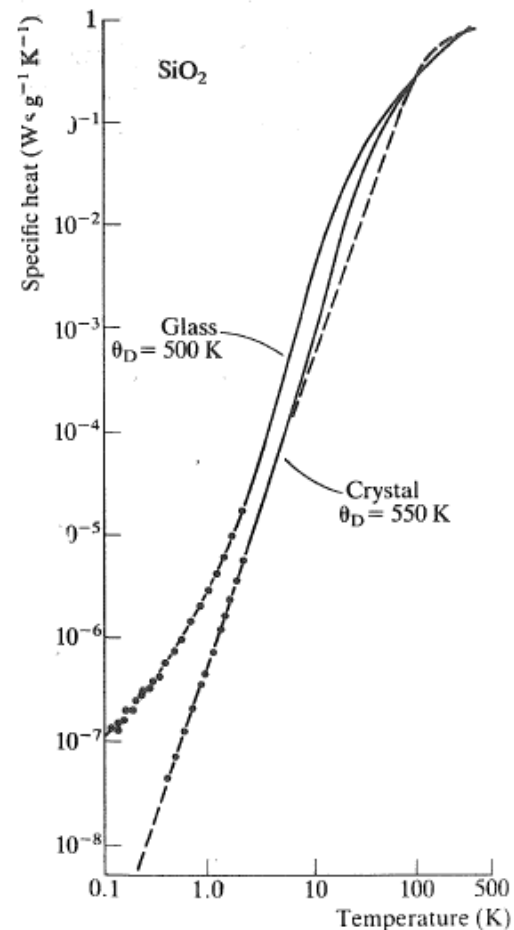
Thermal properties

- Amorphous materials and glasses exhibit unique low temperature thermal properties
- Low energy excitations – new physics?
- No fundamental theory exists
- Phenomenological model – two-level systems

- Excess heat capacity
- Thermal conductivity
- Acoustic and dielectric absorption

Heat capacity

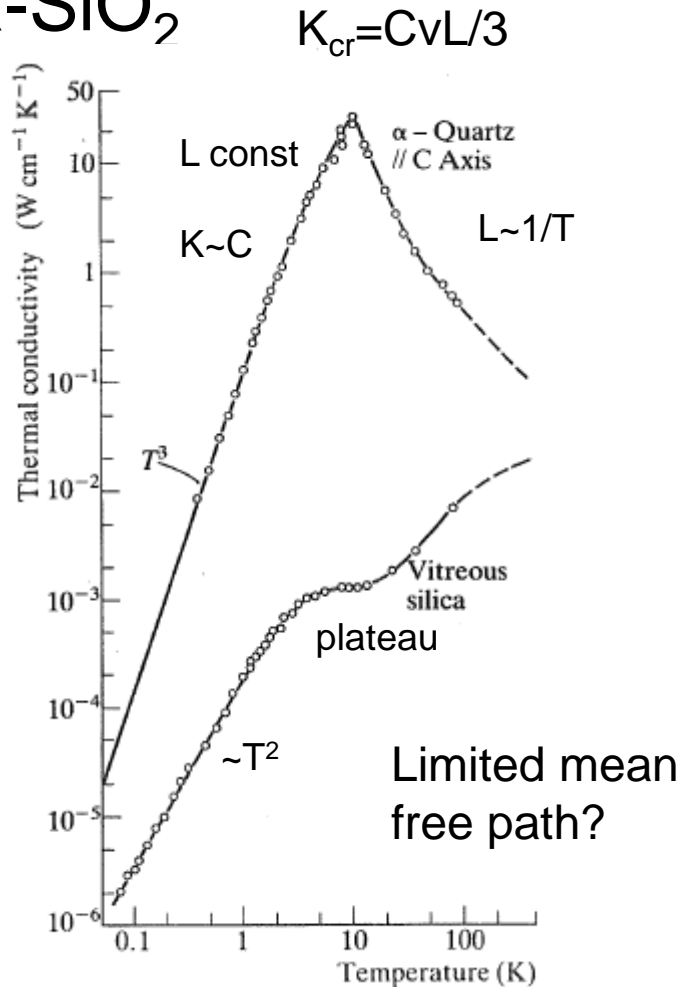
- SiO_2 : Amorphous and crystalline
- Crystal – Debye theory: $C \sim T^3$
- Glass: $C \sim aT + bT^3$
- Excess heat capacity in the glass specially at low temperatures



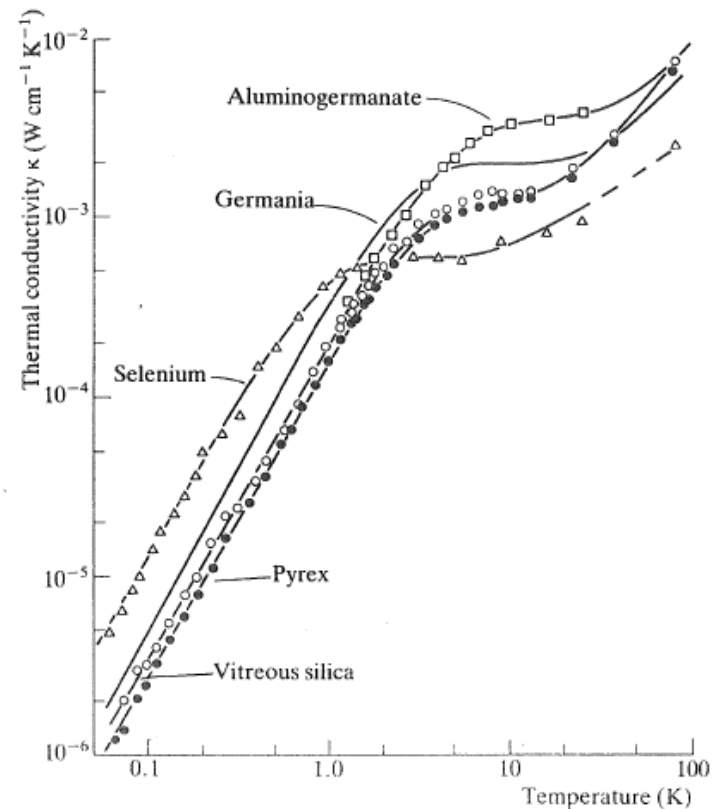
Source: Elliott, Physics of amorphous materials

Thermal conductivity

- a-SiO₂



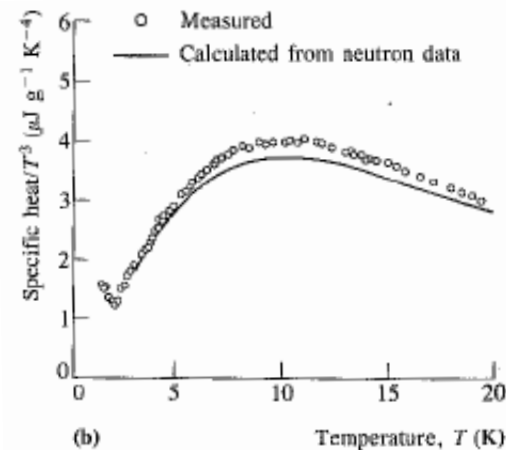
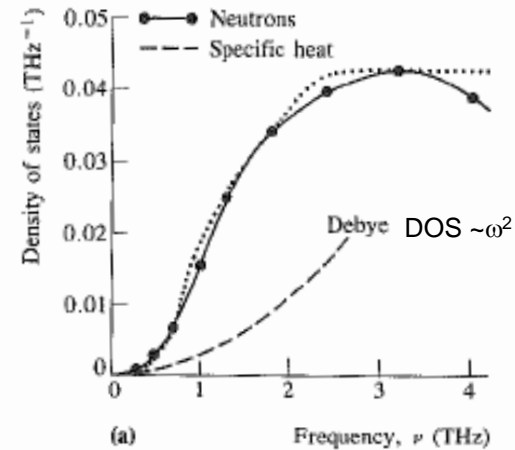
- Different glasses



Source: Elliott, Physics of amorphous materials

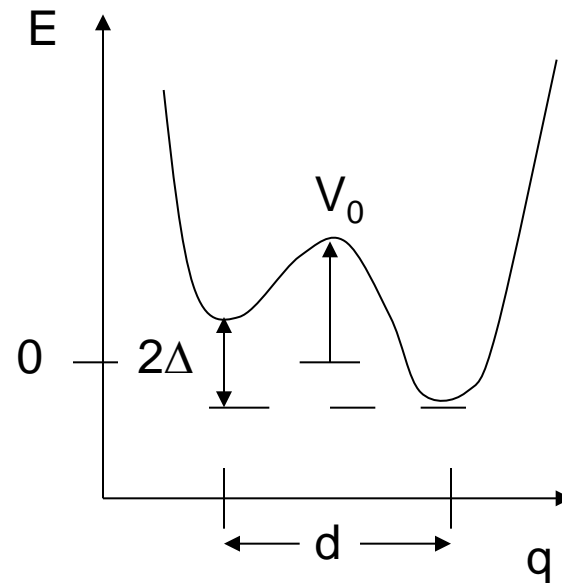
Low energy excitations

- In amorphous materials there is an excess of low frequency vibrational modes
- Broad low ω peak - "boson peak"
- Position and strength depends on material
- Ex: a-SiO₂ (1 THz \sim 4 meV)
- Excess heat capacity at \sim 10K



Model: Two-level systems

- Double potential well
- Two closely spaced energy levels per system
- Tunneling at low temperatures
- 0.1 – 1 K, 0.01 - 0.1 meV
- Wide spectrum of separations, d , or of barrier heights, V_0 .



- q – configurational coordinate

Tunneling

- Choose zero of energy such that the two wells are at energies $\pm \Delta$.
- Tunneling between the wells gives rise to an overlap energy

$$\Delta_0 = \hbar\omega_0 \exp\left[-d(2mV_0/\hbar^2)^{1/2}\right]$$

- Here ω_0 is the frequency of oscillation in a potential well
- The system has a split ground state with energies $\pm E/2$ where

$$E = (\Delta^2 + \Delta_0^2)^{1/2}$$

Heat capacity 1

- Amorphous solid, N two-level systems per unit volume, level splitting E
- Partition function for one system

$$Z = \exp\left(\frac{E}{2k_B T}\right) + \exp\left(-\frac{E}{2k_B T}\right) = 2 \cosh(E / 2k_B T)$$

- Average energy

$$U = \frac{k_B T^2}{Z} \left(\frac{dZ}{dT} \right) = -(E / 2) \tanh(E / 2k_B T)$$

- Heat capacity for one system

$$C = \left(\frac{dU}{dT} \right)_{N,V} = k_B \left(\frac{E}{2k_B T} \right)^2 \operatorname{sech}^2 \left(\frac{E}{2k_B T} \right)$$

$$\operatorname{sech} x = (\cosh x)^{-1}$$

Heat capacity 2

- Distribution of E, $p(E)=p_0$, $0 \leq E \leq E_m$
- Integrate over this distribution

$$C = (p_0 / 4k_B T^2) \int_0^{E_m} E^2 \operatorname{sech}^2(E / 2k_B T) dE = 2k_B^2 T p_0 \int_0^{E_m / 2k_B T} x^2 \operatorname{sech}^2 x dx$$

- When $k_B T \ll E_m$, the $\operatorname{sech}^2 x$ term is small for $x > 1$ and ~ 1 for $x \ll 1$.
- Approx: Integrate over x^2 from 0 to 1

$$C = 2k_B^2 p_0 T / 3 = 2Nk_B^2 T / 3E_m$$

- What happens to this term at higher temperatures?

Thermal conductivity

- The model can also qualitatively explain the low temperature thermal conductivity
- The idea is that phonons are scattered by the two-level systems
- The phonon mean free path is limited by this process
- A slightly different $p(E) \sim E^m$ can qualitatively explain small discrepancies from $C \sim T$ and $K \sim T^2$ often observed

What are the two-level systems?

- No good explanation of their microscopic origin
- Similar for most amorphous materials – explanation must be general
- Connection to excess vibrational DOS seen in neutron scattering at higher energies?
- Small motions of large structural units?
- Estimate: $N \sim 6 \cdot 10^{26} \text{ m}^{-3}$ (1 state per 100 atoms or so) and $d \leq 0.8 \text{ \AA}$

Fractons

- Vibrational excitations in fractal networks
- Described by fracton dimension, d_s
- Connection to the fractal dimension of a random walk on a fractal structure, d_w and to the fractal dimension of the structure, d_f
- Vibrations are localized if $d_s < 2$
- Scaling theory
- Numerical simulations

Scaling theory 1

- Length of a random walk on a fractal

$$\langle L^2(t) \rangle \sim t^{2/d_w}$$

- Vibrational problem: Replace t by $1/\omega^2$

$$L(\omega) \sim \omega^{-2/d_w}$$

- Vibrational density of states

$$\rho(\omega) \sim \omega^{d_s-1}, \quad d_s = 2d_f / d_w$$

- Dispersion relation

$$\omega \sim L^{-d_f/d_s}$$

Scaling theory 2

- Percolation clusters: $d_s \sim 1.3$
- Wavelength larger than the correlation length – $\lambda > \xi$ – homogeneous structure – ordinary phonons - $\rho(\omega) \sim \omega^{E-1} \sim \omega^2$ (Debye)
- Wavelengths between particle size and correlation length – $R < \lambda < \xi$ – fractons
- Wavelength inversely proportional to frequency
- Crossover at $\lambda(\omega_\xi) \sim \xi$
- Different fractons due to bond bending and bond stretching – with different fracton dimensions

Summary of results

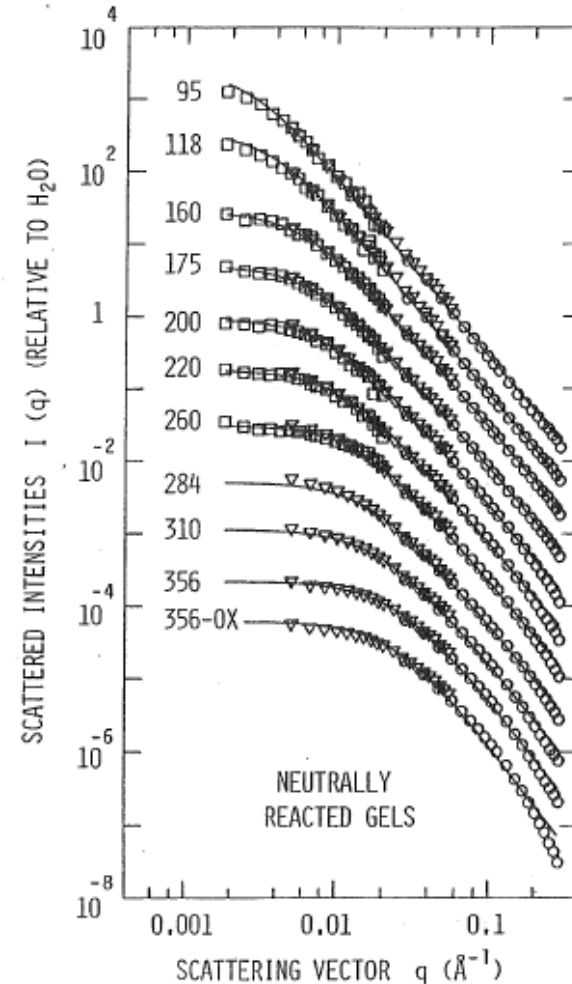
- Phonons: $\omega < \omega_{\xi}$
 - Bending fractons: $\omega_{\xi} < \omega < \omega_e$
 - Stretching fractons: $\omega_e < \omega < \omega_0$
 - Particle vibration modes: $\omega > \omega_0$
-
- The frequencies correspond to different length scales
 - Simulations and experiments confirm this picture

Aerogels

- Extremely porous materials, up to 99%
- Low thermal conductivity
- Optical transparency
- Application as transparent insulation
- Can be made of different materials, but SiO_2 aerogels most studied
- Cluster-cluster aggregation in solution – supercritical drying preserves the porous structure

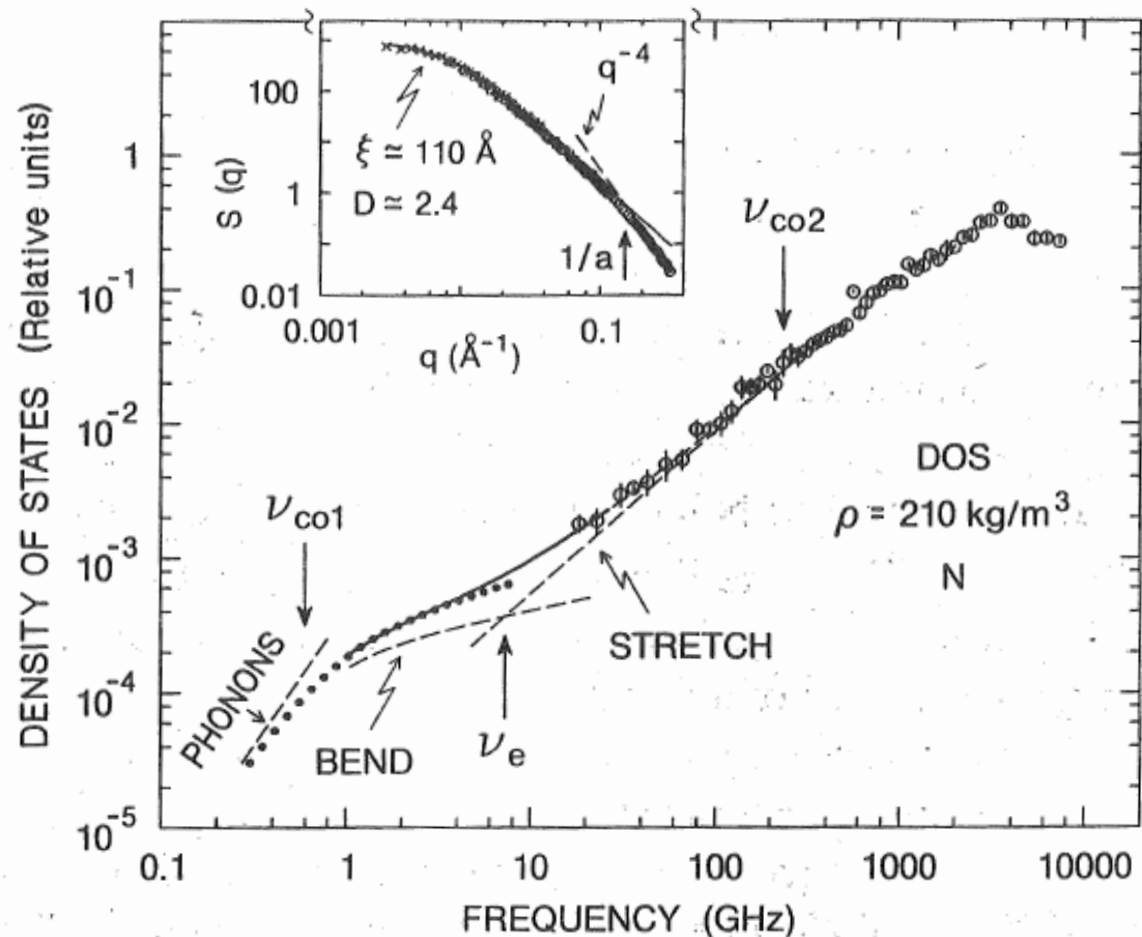
Small-angle scattering

- Aerogel: Fractal structure
- Samples labeled by density in kg/m^3
- Neutrally reacted, $d_f = 2.40 \pm 0.03$
- $\xi \sim \rho^{1/(d_f-3)} \sim \rho^{-1.67}$
- Other method (base catalyzed) gives $d_f \sim 1.8$



DOS by inelastic neutron scattering

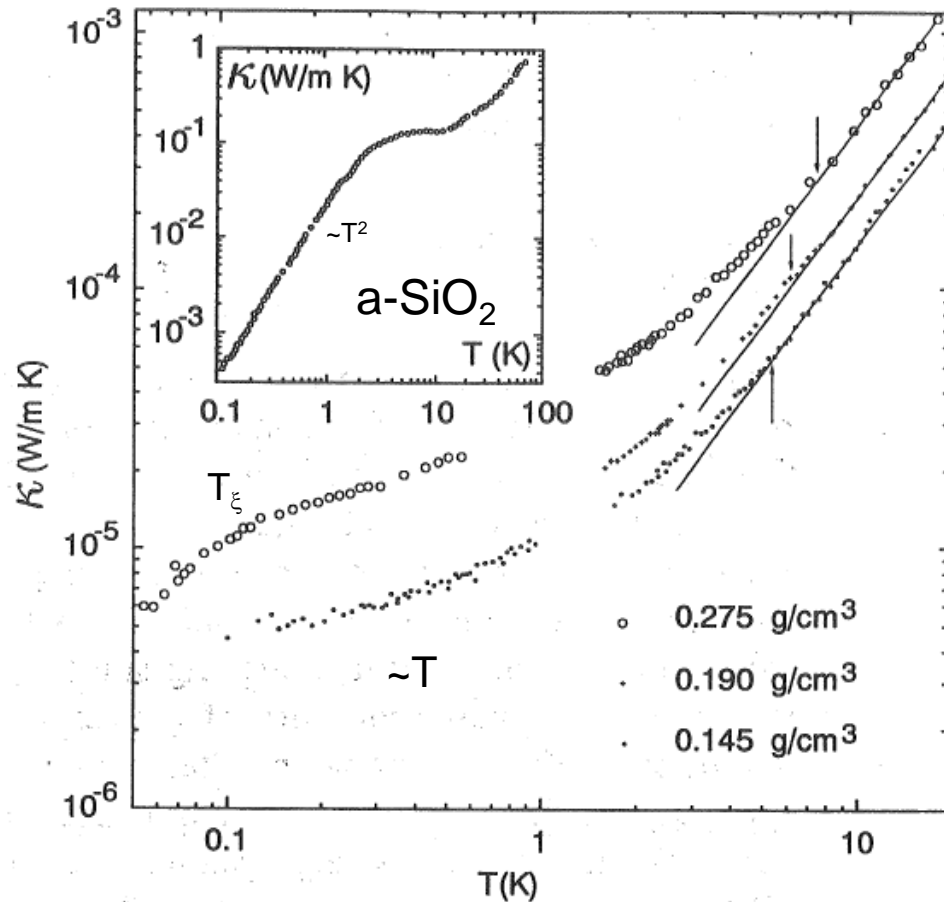
- Bending
 $d_s \sim 1.3$
- Stretching
 $d_s \sim 2.2$



Source: Nakayama et al., Rev. Mod. Phys. 66 (1994)

Thermal conductivity

- Phonons – low T, $T < 0.1$ K
- Phonon assisted fracton hopping, $0.1 \text{ K} < T < 2 \text{ K}$
 $K = K_{\text{ph}} + K_{\text{hop}} = A + BT$
- Contribution from particle modes at $T > 2$ K
- Different from amorphous materials



Source: Nakayama et al., Rev. Mod. Phys. 66 (1994)