Lecture 3

Basics of Crystal Binding, Vibrations, and Neutron Scattering

3.1 Classification of Solids : Ionic; Covalent; Metallic; Molecular and Hydrogen bonded

3.2 Analysis of Elastic Strains: The Strain and Stress Tensors; Stress-strain relationship; Strain energy density; Applications of elasticity theory

3.3 Vibrations of crystals with monatomic basis

3.4 Two atoms per primitive basis

3.5 Quantization of elastic waves

3.6 Phonon momentum

3.7 Inelastic neutron scattering for phonons

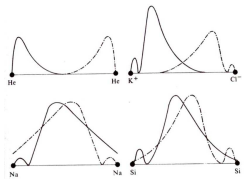
References:
1) Kittel, Chapter 3-4; 2) Marder, Chapter 11-13; 3) Ashcroft, Chapters 22, 24; 4) Burns, Chapters 12; 5) Ziman, Chapter 2; 6) Ibach, Chapter 6

3.1 Classification of Solids

Cohesive energy – energy to dissociate the solid into separate atoms

Solids divide into 5 rough classes for purposes of studying cohesion

- Ionic
- Covalent
- Metallic
- Molecular
- Hydrogen bonded



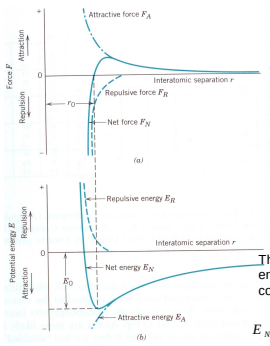
Goal is to obtain conceptual and semi-quantitative estimates of cohesive energies

Cohesive energy has **nothing** to do with the strength of solids. It allows one to decide what the ground state structure ought to be.

Examples and characteristics of 5 types of bonds

Bond type	Examples	Typical energies, eV/atom	Distinct characteristics
Ionic	**LiF, NaCl, CsCl**	**5 - 10**	**Nondirected bonding, giving structures of high coordination; no electrical conductivity at low temperature**
Covalent	**Diamond, Si, Ge, graphite**	**3 - 8**	**Spatially directed bonds, structures with low coordination; low conductivity at low temperature for pure crystals**
Metallic	**Li, Na, Cu, Ta**	**0.7 - 1.6**	**Nondirected bond, structures of very high coordination and density; high electrical conductivity; ductility**
Fluctuating or permanent dipole	Ne, Ar, Kr, Xe, $CHCl_3$	0.05-0.2	Low melting and boiling points
Hydrogen	H_2O, HF	0.25-0.6	Increase in bonding energy over similar molecules without hydrogen bonds

3.1.1 Ionic bonding: Force and Energy Diagram



$$F_{net} = F_{attactive} + F_{repulvise}$$

$$F_{ATTR} = -\frac{(Z_1 e)(Z_2 e)}{4\pi\varepsilon_o a^2}$$

$$F_{REP} = -\frac{nb}{a^{n+1}}$$

n and b are constants; $n = 7-9$

$$F_{NET} = 0 = -\frac{Z_1 Z_2 e^2}{4\pi\varepsilon_o a^2} = \frac{bn}{a^{n+1}}$$

$$n = 9; \quad -\frac{Z_1 Z_2 e^2}{4\pi\varepsilon_o a^2} = \frac{9b}{a^{10}};$$

$$b = -\frac{Z_1 Z_2 e^2 a^8}{4\pi\varepsilon_o \times 9} = -\frac{1}{36}\frac{Z_1 Z_2 e^2 a^8}{\pi\varepsilon_o}$$

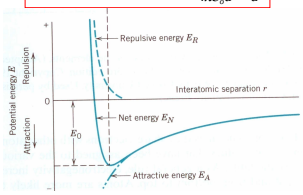
The **interionic energy** can be defined as the energy needed to rip a compound into its components placed ∞ far apart ($E_{NET}(\infty) = 0$)

$$E_{NET} = E_{attractive} + E_{repulsive} = +\frac{Z_1 Z_2 e^2}{4\pi\varepsilon_o a} + \frac{b}{a^n}$$

Interionic Energies

- the energy needed to rip a compound into its components placed ∞ far apart ($E_{net}(\infty) = 0$

$$E_{net} = E_{attraction} + E_{repulsion} = +\frac{Z_1 Z_2 e^2}{4\pi\varepsilon_o a} + \frac{b}{a^n}$$



Electrostatic or Madelung Energy

- Typically large lattice energies: 600-3000 kJ/mol
- High melting temperatures: 801ºC for NaCl

For NaCl: E_{Na+Cl-} = - 7.42 × 10^{-19}J = 4.63eV (2.315 per ion)
Compare to 3.3eV (elsewhere): big difference…!

• Ionic radii of selected ions are listed in the table

Cation	Ionic radius (nm)	Anion	Ionic radius (nm)
Li^+	0.060	F^-	0.136
Na^+	0.095	Cl^-	0.181
K^+	0.133	Br^-	0.195
Rb^+	0.148	I^-	0.216
Cs^+	0.169		

Coordination and neutrality in ionic crystals

Geometrical arrangements (coordination) and neutrality is maintained

CsCl:

8 Cl^- ions can pack around Cs^+

$R(Cs^+)/R(Cl^-)$=

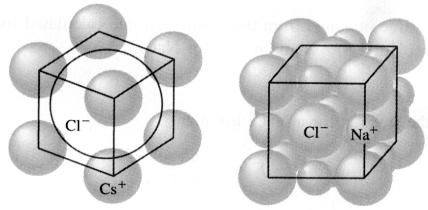
= 0.169 / 0.181 = 0.934

NaCl:

6 Cl^- ions can pack around Na^+

$R(Na^+)/R(Cl^-)$=

= 0.095 / 0.181 = 0.525



Evaluation of the Madelung Constant

1. Consider a cube of 8 ions
2. Consider a line of alternating in sign ions, with distance R between ions
3. Consider a lattice: lattice sum calculation can be used to estimate **Madelung constant**, α

$$\alpha = \sum_j \frac{\pm}{R_{ij}}$$

Structure	α
NaCl	1.7475
CsCl	1.7626
ZnS	1.6381

3.1.2 Covalent bonding

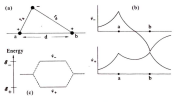


Fig. 8-1 (a) The hydrogen molecular ion. (b) The bonding, ψ_+, and antibonding orbitals, ψ_-, for H_2^+. (c) The energy level diagram for H_2^+

- Takes place between elements with small difference in electronegativity
  - F, O, N, Cl, H, C, Si…
- *s, p, d* electrons are commonly shared to attain noble-gas electron configuration
- Multiple bonds can be formed by one atom; hybridization

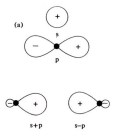


Fig. 8-4 (a) sp hybridization. (b) sp^2 hybridization.

																	H 2.1
Li 1.0	Be 1.5											B 2.0	C 2.5	N 3.1	O 3.5	F 4.1	
Na 1.0	Mg 1.3											Al 1.5	Si 1.8	P 2.1	S 2.4	Cl 2.9	
K 0.9	Ca 1.1	Sc 1.2	Ti 1.3	V 1.5	Cr 1.6	Mn 1.6	Fe 1.7	Co 1.7	Ni 1.8	Cu 1.8	Zn 1.7	Ga 1.8	Ge 2.0	As 2.2	Se 2.5	Br 2.8	
Rb 0.9	Sr 1.0	Y 1.1	Zr 1.2	Nb 1.3	Mo 1.3	Tc 1.4	Ru 1.4	Rh 1.5	Pd 1.4	Ag 1.4	Cd 1.5	In 1.5	Sn 1.7	Sb 1.8	Te 2.0	I 2.2	
Cs 0.9	Ba 0.9	La 1.1	Hf 1.2	Ta 1.4	W 1.4	Re 1.5	Os 1.5	Ir 1.6	Pt 1.5	Au 1.4	Hg 1.5	Tl 1.5	Pb 1.6	Bi 1.7	Po 1.8	At 2.0	
Fr 0.9	Ra 0.9	Ac 1.0	Lanthanides: 1.0–1.2 Actinides: 1.0–1.2														

3.1.3 Nonlocalized electrons in metals

Three contributions to the cohesive energy in metals

1. Electron must interact with the ion cores and itself according to the potential

$$\frac{\mathcal{E}_{el}}{N} = -\frac{\alpha}{2}\frac{e^2}{r_s}$$

Madelung constants for metals

bcc	fcc	hcp	sc	Diamond
1.791 86	1.791 75	1.791 68	1.760 12	1.670 85

2. Add in the kinetic energy of the electrons

$$\frac{\mathcal{E}_{kin}}{N} = \frac{3}{5}\frac{\hbar^2 k_F^2}{2m} = \frac{3}{5}\frac{\hbar^2}{2m}\left(\frac{9\pi}{4}\right)^{2/3}\frac{1}{r_s^2}$$

3. Include exchange energy for electrons in a uniform positive background

$$\frac{\mathcal{E}_{ex}}{N} = -\frac{3}{4\pi}e^2 k_F = -\frac{3}{4\pi}e^2\left(\frac{9\pi}{4}\right)^{1/3}\frac{1}{r_s}$$

Summing:

$$\frac{\mathcal{E}}{N} = \left[-\frac{24.35}{(r_s/a_0)} + \frac{30.1}{(r_s/a_0)^2} - \frac{12.5}{(r_s/a_0)}\right]\mathrm{eV/atom}$$

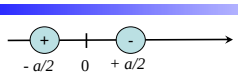
Not satisfactory! Minima at $\frac{r_s}{a_0} = 1.6$ hile typical values are 2-6

Marder, pp.272-274

3.1.4 Molecular or Secondary Bonding

- Fluctuating or permanent dipoles (also called ***physical bonds, or van der Waals bonds or forces)***
- weak relatively to the primary bonding (2-5eV/atom or ion)
  ~ 0.1eV/atom or ~ 10 kJ/mol
- always present, but overwhelmed by other interaction
  most easily observed in inert gases
- dipoles to be considered…

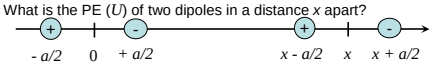
Electric dipole



consider a "+" and "-" charge (e) separated by a distance ***a***

Dipole moment [debye]: $p = e \times a$

What is the PE (U) of two dipoles in a distance x apart?



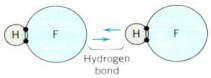
$$U = -\frac{ke^2}{x-a} + 2\frac{ke^2}{x} - \frac{ke^2}{x+a}$$

$$U(x) = -ke^2\left[\frac{1}{x-a} + \frac{1}{x+a} - \frac{2}{x}\right] = -ke^2\left[\frac{x(x+a)+x(x-a)-2(x-a)(x+a)}{x(x-a)(x+a)}\right] =$$

$$= -ke^2\left[\frac{x^2+xa+x^2-xa-2x^2+2a^2}{x^3-xa^2}\right] = -\frac{ke^2 2a^2}{x(x^2-a^2)} \approx -2\frac{ke^2a^2}{x^3} = \boxed{-2\frac{kp^2}{x^3}}$$

- this potential falls off more rapidly than ionic bonds

Permanent Dipoles



• When a covalent molecule has permanent dipole? Depends on geometry of the molecule…

• CO_2 ? CH_3Cl ? H_2O ?

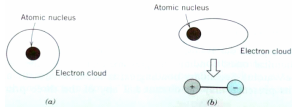
Q.: Calculate the dipole moment associated with the ionic model of the water molecule. The length of the O-H bond is 0.097nm and the angle between the bonds is 104.5º.

• Hydrogen bond: permanent dipole-dipole interaction for the molecules with a hydrogen atoms bonded to a highly electronegative element (F, Cl, O, N)

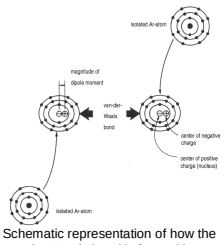
e.g.: H_2O, polymeric materials

Permanent dipole bond: a secondary bond created by the attraction of molecules that have permanent dipoles

Fluctuation Dipole



- Noble-gas elements: s^2p^6
- Stronger effect for larger electron shells → Boiling temperature increases as a function of Z



$$\phi \sim -\frac{\alpha_1 \alpha_2}{r^6}$$

Schematic representation of how the van-der-Waals bond is formed by interaction of induced dipoles.

3.1.5 Hydrogen Bond

The melting and boiling temperature decrease from H_2Te to H_2S

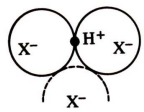
The polarizability ⇓ and the van der Waals attraction ⇓ from Te to S

Abrupt change between H_2S and H_2O ⇒ formation of hydrogen bonding

H^+ ion is just a bare proton, unlike the other alkali metal atoms

Hydrogen has only one electron to form a covalent bond

Extremely small size enables it to bond with only two other atoms



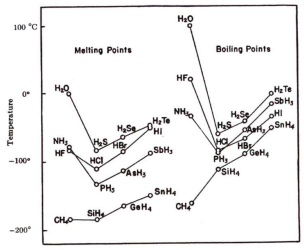
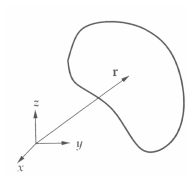


Fig. 6-6 The melting and boiling points of isoelectronic sequences of hydrides. (After Pauling.)

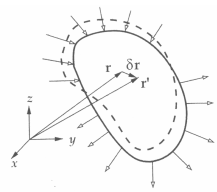
3.2 Analysis of elastic strains

Before deformation



$$\vec{r} = x\hat{x} + y\hat{y} + z\hat{z}$$

After deformation



$$\vec{r} = \vec{r} + \delta\vec{r} = (x+u)\hat{x} + (y+v)\hat{y} + (z+w)\hat{z}$$

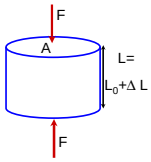
Many ways to derive elasticity…

Could derive from theory of atoms and their interactions. This approach is not accurate, and not fully general

following Kaxiras, Appendix E

Stress (σ) and Strain (ε)

Block of material



Stress (σ)

- defining F is not enough (F and A can vary)
- Stress σ stays constant

$$\sigma = \frac{F}{A}$$

• Units

Force / area = N / m^2 = Pa

usually in MPa or GPa

Strain (ε) – result of stress

• For tension and compression: change in length of a sample divided by the **original** length of sample

$$\varepsilon = \frac{\Delta L}{L}$$

General Theory of Linear Elasticity

Most general approach modeled by Landau:

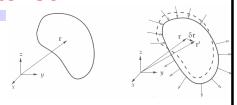
construct free energy simply by considering symmetry and using fact that deformations are small:

- Deformation field vanishes in equilibrium
- Free energy invariant under translation.
- Smallest allowed powers or *u*
- Derivatives of lowest allowed order
- Uniform rotation costs no energy

Unique(?) free energy consistent with these constraints

3.2.1 The strain tensor

$$\vec{r} = \vec{r} + \delta\vec{r} = (x+u)\hat{x} + (y+v)\hat{y} + (z+w)\hat{z}$$



Each of the displacement fields u, v, w is a function of the position in the solid: $u(x, y, z)$, $v(x, y, z)$, $w(x, y, z)$

The normal components of the strain are defined as: $\varepsilon_{xx} = \frac{\partial u}{\partial x}, \varepsilon_{yy} = \frac{\partial v}{\partial y}, \ \varepsilon_{zz} = \frac{\partial w}{\partial z}$

Stretching and shearing are usually coupled; the shear strain components given by:

$$\varepsilon_{xy} = \frac{1}{2}\left(\frac{\partial u}{\partial x} + \frac{\partial v}{\partial y}\right), \varepsilon_{yz} = \frac{1}{2}\left(\frac{\partial v}{\partial y} + \frac{\partial w}{\partial z}\right), \ \varepsilon_{zx} = \frac{1}{2}\left(\frac{\partial w}{\partial z} + \frac{\partial u}{\partial x}\right)$$

it is <u>symmetric</u> (i.e., $\varepsilon_{xy} = \varepsilon_{yx}$)

Strain tensor is a symmetric tensor with diagonal elements ε_{ii} $(i=x, y, z)$ and off-diagonal elements ε_{ij} $(i, j=x, y, z)$

The strain tensor

Rotational tensor is an antisymmetric tensor, $\omega_{ij} = -\omega_{ji}$ $(i, j = x, y, z)$

$$\omega_{xy} = \frac{1}{2}\left(\frac{\partial u}{\partial y} - \frac{\partial v}{\partial x}\right), \omega_{yz} = \frac{1}{2}\left(\frac{\partial v}{\partial z} - \frac{\partial w}{\partial y}\right), \ \omega_{zx} = \frac{1}{2}\left(\frac{\partial w}{\partial x} - \frac{\partial u}{\partial z}\right)$$

If the coordinate axes x and y are rotated around the axis z by an angle θ, the strain components in the new coordinate frame (x', y', z') are given by:

$$\varepsilon_{x'x'} = \frac{1}{2}(\varepsilon_{xx} + \varepsilon_{yy}) + \frac{1}{2}(\varepsilon_{xx} - \varepsilon_{yy})\cos 2\theta + \varepsilon_{xy}\sin 2\theta$$

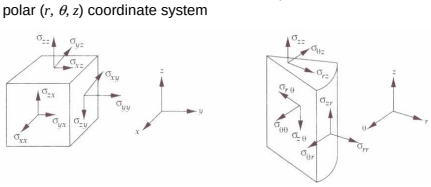
$$\varepsilon_{y'y'} = \frac{1}{2}(\varepsilon_{xx} + \varepsilon_{yy}) - \frac{1}{2}(\varepsilon_{xx} - \varepsilon_{yy})\cos 2\theta - \varepsilon_{xy}\sin 2\theta$$

$$\varepsilon_{x'y'} = \frac{1}{2}(\varepsilon_{yy} - \varepsilon_{xx})\sin 2\theta + \varepsilon_{xy}\cos 2\theta \qquad \Rightarrow \tan 2\theta = \frac{\varepsilon_{xy}}{\varepsilon_{xx} - \varepsilon_{yy}}$$

We can identify the rotation around the z axis which will make the shear components of the strain vanish

3.2.2 The Stress Tensor

Definition of the stress tensor for the cartesian (x, y, z) coordinate system, and the polar (r, θ, z) coordinate system



The forces that act on the these surfaces has arbitrary directions and have F_x, F_y, F_z components

Stress tensor is symmetric tensor with diagonal elements $\sigma_{ii}=F_i/A_i$ $(i=x, y, z)$ and off-diagonal elements $\sigma_{ij}=F_j/A_i$ $(i, j=x, y, z)$

The Stress Tensor

Just as in the analysis of strains, a rotation of the x, y coordinate axes by an angle θ around the z axis

$$\sigma_{x'x'} = \frac{1}{2}(\sigma_{xx} + \sigma_{yy}) + \frac{1}{2}(\sigma_{xx} - \sigma_{yy})\cos 2\theta + \sigma_{xy}\sin 2\theta$$

$$\sigma_{y'y'} = \frac{1}{2}(\sigma_{xx} + \sigma_{yy}) - \frac{1}{2}(\sigma_{xx} - \sigma_{yy})\cos 2\theta - \sigma_{xy}\sin 2\theta$$

$$\sigma_{x'y'} = \frac{1}{2}(\sigma_{yy} - \sigma_{xx})\sin 2\theta + \sigma_{xy}\cos 2\theta$$

On the planes that are perpendicular to the principle stress axes, the shear stress is zero, only the normal component of the stress survives!

We can find the maximum and minimum values of the stress from the equations above:

$$\sigma_{x'x'} = \frac{1}{2}(\sigma_{xx} + \sigma_{yy}) + \left(\frac{1}{4}(\sigma_{xx} - \sigma_{yy})^2 + \sigma_{xy}^2\right)^{1/2}$$

$$\sigma_{y'y'} = \frac{1}{2}(\sigma_{xx} + \sigma_{yy}) - \left(\frac{1}{4}(\sigma_{xx} - \sigma_{yy})^2 + \sigma_{xy}^2\right)^{1/2}$$

3.2.3 Stress-strain relationship

- Stress and strain are properties that don't depend on the dimensions of the material (for small ε), just type of the material

$$\boxed{Y = \frac{\sigma(stress)}{\varepsilon(strain)} \text{ or } \sigma = Y\varepsilon}$$

- Y – Young's Modulus, Pa
- Comes from the linear range in the stress-strain diagram
- many exceptions…

Behavior is related to **atomic bonding between the atoms**

Material	Young's Modulus [GPa]
Metals	20-100
Polypropelene	1.5-2
Rubber	0.01
Hydrogels and live cells	<0.00001

Stress-strain relationship

$$\sigma_{ij} = C_{ijkl}\varepsilon_{kl}$$

Elastic constants of the solid, C_{ijkl}, represented by a tensor of rank 4, or contracted version of this tensor (matrix with only two indices C_{ij})

1 ⇒ xx	$C_{xxxx} \Rightarrow C_{11}$	$\sigma_{xx} = C_{11}\varepsilon_{xx} + C_{12}\varepsilon_{yy} + C_{13}\varepsilon_{zz} + C_{14}\varepsilon_{xy} + C_{15}\varepsilon_{yz} + C_{16}\varepsilon_{zx}$
2 ⇒ yy	$C_{xxyy} \Rightarrow C_{12}$	$\sigma_{yy} = C_{21}\varepsilon_{xx} + C_{22}\varepsilon_{yy} + C_{23}\varepsilon_{zz} + C_{24}\varepsilon_{xy} + C_{25}\varepsilon_{yz} + C_{26}\varepsilon_{zx}$
3 ⇒ zz	$C_{xxzz} \Rightarrow C_{13}$	$\sigma_{zz} = C_{31}\varepsilon_{xx} + C_{32}\varepsilon_{yy} + C_{33}\varepsilon_{zz} + C_{34}\varepsilon_{xy} + C_{35}\varepsilon_{yz} + C_{36}\varepsilon_{zx}$
4 ⇒ yz	$C_{yzxx} \Rightarrow C_{41}$	$\sigma_{yz} = C_{41}\varepsilon_{xx} + C_{42}\varepsilon_{yy} + C_{43}\varepsilon_{zz} + C_{44}\varepsilon_{xy} + C_{45}\varepsilon_{yz} + C_{46}\varepsilon_{zx}$
5 ⇒ zx	$C_{zxxx} \Rightarrow C_{51}$	$\sigma_{zx} = C_{51}\varepsilon_{xx} + C_{52}\varepsilon_{yy} + C_{53}\varepsilon_{zz} + C_{54}\varepsilon_{xy} + C_{55}\varepsilon_{yz} + C_{56}\varepsilon_{zx}$
6 ⇒ xy	$C_{xyxx} \Rightarrow C_{61}$	$\sigma_{xy} = C_{61}\varepsilon_{xx} + C_{62}\varepsilon_{yy} + C_{63}\varepsilon_{zz} + C_{64}\varepsilon_{xy} + C_{65}\varepsilon_{yz} + C_{66}\varepsilon_{zx}$

3.2.4 Strain energy density

Connection between energy, stress and strain

Calculate the energy per unit volume (or strain energy density) in terms of the applied stress and the corresponding strain

$$\frac{dE}{dt} = \boxed{\int_V f_i \frac{\partial u_i}{\partial t} dV} + \boxed{\int_S \sigma_{ij} n_j \frac{\partial u_i}{\partial t} dS}$$

Volume distortions — Surface distortions

Using the divergence theorem: $\frac{dE}{dt} = \int_V \left(f_i \frac{\partial u_i}{\partial t} + \frac{\partial}{\partial x_j}\left(\sigma_{ij} \frac{\partial u_i}{\partial t} \right) \right) dV$

Newton's law of motion $\vec{F} = m \frac{d^2 \vec{r}}{dt^2}$ applied to the volume element takes the form:

$$\boxed{\rho \frac{\partial^2 u_i}{\partial t^2} = f_i + \frac{\partial \sigma_{ij}}{\partial x_j}}$$

Strain energy density

The strain energy density W, defined as the potential energy per unit volume, we can obtain:

$$U = \int_V W dV \Rightarrow \frac{\partial W}{\partial t} = \sigma_{ij} \frac{\partial \varepsilon_{ij}}{\partial t} \Rightarrow \sigma_{ij} = \frac{\partial W}{\partial \varepsilon_{ij}}$$

Using the Taylor expansion for the strain energy density and taking derivatives:

$$W = W_o + \frac{1}{2}\left[\frac{\partial^2 W}{\partial \varepsilon_{ij} \partial \varepsilon_{kl}} \right] \varepsilon_{ij} \varepsilon_{kl} + \ldots$$

$$\sigma_{mn} = \frac{\partial W}{\partial \varepsilon_{mn}} = \frac{1}{2}\left[\frac{\partial^2 W}{\partial \varepsilon_{ij} \partial \varepsilon_{kl}} \right] \left(\delta_{im} \delta_{jn} \varepsilon_{kl} + \delta_{km} \delta_{ln} \varepsilon_{ij} \right) =$$

$$= \frac{1}{2}\left[\frac{\partial^2 W}{\partial \varepsilon_{mn} \partial \varepsilon_{kl}} \right] \varepsilon_{kl} + \frac{1}{2}\left[\frac{\partial^2 W}{\partial \varepsilon_{mn} \partial \varepsilon_{ij}} \right] \varepsilon_{ij} = \frac{1}{2}\left[\frac{\partial^2 W}{\partial \varepsilon_{mn} \partial \varepsilon_{ij}} \right] \varepsilon_{ij}$$

$$C_{ijkl} = \left[\frac{\partial^2 W}{\partial \varepsilon_{ij} \partial \varepsilon_{kl}} \right] \Rightarrow W = W_0 + \frac{1}{2} C_{ijkl} \varepsilon_{ij} \varepsilon_{kl} = W_0 + \frac{1}{2} \sigma_{ij} \varepsilon_{ij}$$

Note: Strain energy density is quadratic in the strain tensor

3.2.5 Applications of elasticity theory

Isotropic elastic solid more definitions…

When normal stress is applied in the x direction, solid can also deform in the y and z directions:

$$\varepsilon_{yy} = \varepsilon_{zz} = -\nu \varepsilon_{xx} = -\nu \frac{\sigma_{xx}}{Y}$$

ν is Poisson's ratio

- the minus sign is there because usually if $\varepsilon_{zz} > 0$, and $\varepsilon_{xx} + \varepsilon_{yy} < 0 \Rightarrow \nu > 0$

If a shear stress σ_{xy} is applied to a solid, the corresponding shear strain is

$$\varepsilon_{xy} = \frac{1}{\mu} \sigma_{xy}$$

where μ is the shear modulus

Lame's constant, λ: $\lambda = \frac{Y\nu}{(1+\nu)(1-2\nu)}$ and bulk modulus, B $B = \frac{Y}{3(1-2\nu)}$

Elastic constants of isotropic solids

Covalent and ionic solids				Metals			
Crystal	μ	λ	ν	Crystal	μ	λ	ν
				W	1.6	2.01	0.278
C	5.36	0.85	0.068	Mo	1.23	1.89	0.305
Si	0.681	0.524	0.218	Cr	1.21	0.778	0.130
Ge	0.564	0.376	0.200	Ni	0.947	1.17	0.276
				Fe	0.860	1.21	0.291
MgO	1.29	0.68	0.173	Cu	0.546	1.006	0.324
LiF	0.515	0.307	0.187	Ag	0.338	0.811	0.354
PbS	0.343	0.393	0.267	Au	0.310	1.46	0.412
NaCl	0.148	0.146	0.248	Al	0.265	0.593	0.347
KCl	0.105	0.104	0.250	Pb	0.101	0.348	0.387
AgBr	0.087	0.345	0.401	Na	0.038	0.025	0.201
				K	0.017	0.029	0.312

Among three elastic constants (Young's modulus, Poisson's ratio and shear modulus) only two are independent:

$$\mu = \frac{Y}{2(1+\nu)}$$

Solid with cubic symmetry

$$W = W_0 + \frac{1}{2} C_{ijkl} \varepsilon_{ij} \varepsilon_{kl}$$

Consider symmetry elements, we can only have the following kinds:

$$\varepsilon_{ii}^2, \varepsilon_{ij}^2, \varepsilon_{ii}\varepsilon_{jj}, \varepsilon_{ii}\varepsilon_{ij}, \varepsilon_{ii}\varepsilon_{jk}, \varepsilon_{ij}\varepsilon_{kl}$$

Same for $\varepsilon_{xx}^2, \varepsilon_{yy}^2, \varepsilon_{zz}^2 \Rightarrow C_{11} = C_{22} = C_{33}$

Same for $\varepsilon_{xy}^2 \Rightarrow C_{12} = C_{13} = C_{21} = C_{23} = C_{31} = C_{32}$

Same for $\varepsilon_{xx}\varepsilon_{zz} \Rightarrow C_{44} = C_{55} = C_{66}$

$C_{14} = C_{15} = C_{16} = C_{41} = C_{51} = C_{61} = 0$

$C_{24} = C_{25} = C_{26} = C_{42} = C_{52} = C_{62} = 0$

$C_{34} = C_{35} = C_{36} = C_{43} = C_{53} = C_{63} = 0$

$C_{45} = C_{46} = C_{54} = C_{64} = C_{56} = C_{65} = 0$

$$W = \frac{1}{2} C_{11}\left(\varepsilon_{xx}^2 + \varepsilon_{yy}^2 + \varepsilon_{zz}^2\right) + \frac{1}{2} C_{44}\left(\varepsilon_{xy}^2 + \varepsilon_{yz}^2 + \varepsilon_{zx}^2\right) + C_{12}\left(\varepsilon_{xx}\varepsilon_{yy} + \varepsilon_{yy}\varepsilon_{zz} + \varepsilon_{zz}\varepsilon_{xx}\right)$$

Solids of Cubic Symmetry

Element	C_{11} (GPa)	C_{44} (GPa)	C_{12} (GPa)	Element	C_{11} (GPa)	C_{44} (GPa)	C_{12} (GPa)
Al	108	28.3	62	Li (195K)	13.4	9.6	11.3
Ar (80 K)	2.77	0.98	1.37	Mo	459	111	168
Ag	123	45.3	92	Na	7.59	4.30	6.33
Au	190	42.3	161	Ne (6 K)	1.62	0.93	0.85
Cs (78 K)	2.47	2.06	1.48	Ni	247	122	153
Ca	16	12	8	Nb	245	28.4	132
Cr	346	100	66	O (54.4 K)	2.60	0.275	2.06
Cu	169	75.3	122	Pd	224	71.6	173
C (diamond)	1040	550	170	Pt	347	76.5	251
Fe	230	117	135	Rb	2.96	1.60	2.44
Ge (undoped)	129	67.1	48	Si (undoped)	165	79.2	64
Ge (n-doped, 10^{19} Sb)	128.8	65.5	47.7	Si (n-doped, 10^{19} As)	162.2	78.7	65.4
Ge (p-doped, 10^{20} Ga)	118.0	65.3	39.0	Sr	14.7	5.74	9.9
He^3 (0.4 K, 24 cm^3/mole)	0.0235	0.01085	0.0197	Ta	262	82.6	156
He^4 (1.6 K, 12 cm^3/mole)	0.0311	0.0217	0.0281	Th	76	46	49
Ir	600	270	260	W	517	157	203
K	3.71	1.88	3.15	V	230	43.2	120
Kr (115 K)	2.85	1.35	1.60	Xe (156 K)	2.98	1.48	1.90
Pb	48.8	14.8	41.4				

Basics of Crystal Binding, Vibrations, and Neutron Scattering

3.1 Classification of Solids : Ionic; Covalent; Metallic; Molecular and Hydrogen bonded

3.2 Analysis of Elastic Strains: The Strain and Stress Tensors; Stress-strain relationship; Strain energy density; Applications of elasticity theory

3.3 Vibrations of crystals with monatomic basis

3.4 Two atoms per primitive basis

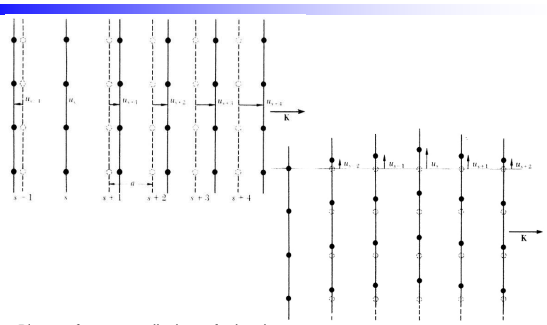
3.5 Quantization of elastic waves

3.6 Phonon momentum

3.7 Inelastic neutron scattering for phonons

References:
1) Kittel, Chapter 3-4; 2) Marder, Chapter 11-13; 3) Ashcroft, Chapters 22, 24; 4) Burns, Chapters 12; 5) Ziman, Chapter 2; 6) Ibach, Chapter 6

3.3 Longitudinal and transverse waves



Planes of atoms as displaces for longitudinal and transverse waves

Continuous Elastic Solid

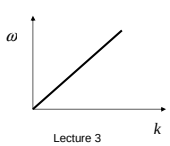
We can describe a propagating vibration of amplitude *u* along a rod of material with Young's modulus Y and density ρ with the wave equation:

$$\frac{\partial^2 u}{\partial t^2} = \frac{Y}{\rho}\frac{\partial^2 u}{\partial x^2}$$ for wave propagation along the x-direction

By comparison to the general form of the 1-D wave equation:

$$\frac{\partial^2 u}{\partial t^2} = v^2 \frac{\partial^2 u}{\partial x^2}$$ we find that $$v = \sqrt{\frac{Y}{\rho}}$$ So the wave speed is independent of wavelength for an elastic medium!

$$\omega = 2\pi f = 2\pi \frac{v}{\lambda} = kv$$



$\omega(k)$ is called the dispersion relation of the solid, and here it is linear (no dispersion!)

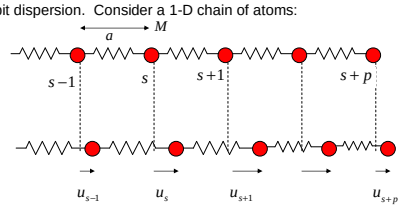
group velocity $$v_g = \frac{d\omega}{dk}$$

3.3 Vibrations of Crystals with Monatomic Basis

By contrast to a continuous solid, a real solid is not uniform on an atomic scale, and thus it will exhibit dispersion. Consider a 1-D chain of atoms:

In equilibrium:

Longitudinal wave:



For atom *s* (*for plane s*) $F_s = \sum_p c_p \left(u_{s+p} - u_s\right)$

p = atom label
p = ± 1 nearest neighbors
p = ± 2 next nearest neighbors
c_p = force constant for atom *p*

The equation of motion of the plane s

Elastic response of the crystal is a linear function of the forces (elastic energy is a quadratic function of the relative displacement)

The total force on plane *s* comes from planes *s ± 1*

$$F_S = C\,(u_{S+1} - u_S) + C\,(u_{S-1} - u_S)$$

C – the force constant between nearest-neighbor planes (different for transverse and longitudinal waves)

Equation of motion of the plane s: $M\dfrac{d^2u_S}{dt^2} = C(u_{S+1} + u_{S-1} - 2u_S)$

Solutions with all displacements having time dependence exp(*-iωt*). Then

$$\frac{d^2u_S}{dt^2} = -\omega^2 u_S$$

$$-M\omega^2 u_s = C(u_{S+1} + u_{S-1} - 2u_S)$$ This is a **difference equation** in the displacements *u*

$$\boxed{u_{S\pm1} = ue^{isKa}e^{\pm iKa}}$$

Equation of Motion for 1D Monatomic Lattice

Applying Newton's second law: $F_s = M\dfrac{\partial^2 u_s}{\partial t^2} = \sum_p c_p\left(u_{s+p} - u_s\right)$

For the expected harmonic traveling waves, we can write $u_s = ue^{i(kx_s - \omega t)}$ $x_s = sa$ position of atom *s*

Thus: $Mu(-i\omega)^2 e^{i(ksa-\omega t)} = \sum_p c_p\left(ue^{i(k(s+p)a-\omega t)} - ue^{i(ksa-\omega t)}\right)$

Or: $-M\omega^2 e^{i(ksa-\omega t)} = e^{i(ksa-\omega t)}\sum_p c_p\left(e^{ikpa} - 1\right)$

So: $-M\omega^2 = \sum_p c_p\left(e^{ikpa} - 1\right)$ Now since $c_{-p} = c_p$ by symmetry,

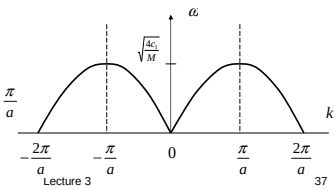
$$-M\omega^2 = \sum_{p>0} c_p\left(e^{ikpa} + e^{-ikpa} - 2\right) = \sum_{p>0} 2c_p\left(\cos(kpa) - 1\right)$$

Dispersion relation of the monatomic 1D lattice

The result is: $\omega^2 = \frac{2}{M}\sum_{p>0} c_p(1-\cos(kpa)) = \frac{4}{M}\sum_{p>0} c_p \sin^2(\tfrac{1}{2}kpa)$

Often it is reasonable to make the nearest-neighbor approximation (p = 1): $\omega^2 \cong \frac{4c_1}{M}\sin^2(\tfrac{1}{2}ka)$

The result is periodic in *k* and the only unique solutions that are physically meaningful correspond to values in the range $-\frac{\pi}{a} \le k \le \frac{\pi}{a}$



Theory vs. Experiment

In a 3-D atomic lattice we expect to observe 3 different branches of the dispersion relation, since there are two mutually perpendicular transverse wave patterns in addition to the longitudinal pattern we have considered

Along different directions in the reciprocal lattice the shape of the dispersion relation is different

Note the resemblance to the simple 1-D result we found

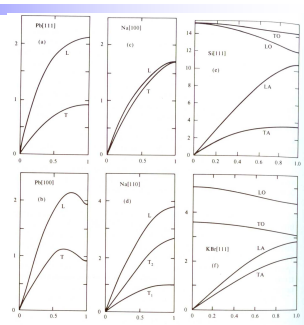


Fig. 12-10 ω vs. k for vibrational modes in different directions in reciprocal space and for different crystals as labeled. The k-values are all given in reduced values, that is, k/k_{max} where k_{max} is the Brillouin zone edge in that particular direction. Thus all the k-values go from 0 to 1. ω is plotted in units of meV (1meV = 10^{-3} eV = 8.03 cm^{-1}). T and L stand for transverse and longitudinal branches, respectively.

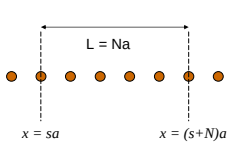
Counting Modes and Finding N(ω)

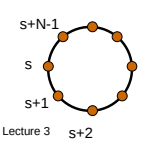
A vibrational mode is a vibration of a given wave vector $\vec{k}$ and thus λ), frequency ω, and energy $E = \hbar\omega$. How many modes are found in the interval between $(\omega, E, \vec{k})$ and $(\omega + d\omega, E + dE, \vec{k} + d\vec{k})$?

modes $dN = N(\omega)d\omega = N(E)dE = N(k)d^3\vec{k}$

We will first find *N(k)* by examining allowed values of *k*. Then we will be able to calculate N(ω)

First step: simplify problem by using periodic boundary conditions for the linear chain of atoms:





We assume atoms s and s+N have the same displacement—the lattice has periodic behavior, where N is very large

Step one: finding N(k)

Since atoms *s* and *s+N* have the same displacement, we can write:

$$u_s = u_{s+N} \qquad ue^{i(ksa-\omega t)} = ue^{i(k(s+N)a-\omega t)} \longrightarrow \boxed{1 = e^{ikNa}}$$

This sets a condition on allowed k values:

$$kNa = 2\pi n \;\rightarrow\; k = \frac{2\pi n}{Na} \qquad n = 1, 2, 3, \ldots$$

So the separation between allowed solutions (k values) is:

$$\Delta k = \frac{2\pi}{Na}\Delta n = \frac{2\pi}{Na}$$

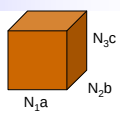
independent of k, so the density of modes in k-space is uniform

Thus, in 1-D:

$$\frac{\#\ of\ modes}{interval\ of\ k-space} = \frac{1}{\Delta k} = \frac{Na}{2\pi} = \frac{L}{2\pi}$$

Next step: finding N(ω)

Now for a 3-D lattice we can apply periodic boundary conditions to a sample of N_1 x N_2 x N_3 atoms:



$$\frac{\#\ of\ modes}{volume\ of\ k-space} = \frac{N_1 a}{2\pi}\frac{N_2 b}{2\pi}\frac{N_3 c}{2\pi} = \frac{V}{8\pi^3} = N(k)$$

Now we know from before that we can write the differential # of modes as:

$$dN = N(\omega)d\omega = N(k)d^3\vec{k} = \frac{V}{8\pi^3}d^3\vec{k}$$

We carry out the integration in k-space by using a "volume" element made up of a constant ω surface with thickness dk:

$$d^3\vec{k} = (surface\ \ area)\ dk = \left[\int dS_\omega\right]dk$$

Finding N(ω)

Rewriting the differential number of modes in an interval:

$$dN = N(\omega)d\omega = \frac{V}{8\pi^3}\int dS_\omega dk$$

We get the result:

$$\boxed{N(\omega) = \frac{V}{8\pi^3}\int dS_\omega \frac{dk}{d\omega} = \frac{V}{8\pi^3}\int dS_\omega \frac{1}{\frac{\partial\omega}{\partial k}}}$$

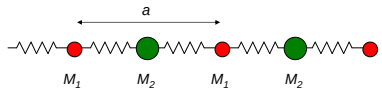
A very similar result holds for N(E) using constant energy surfaces for the density of electron states in a periodic lattice!

<u>This equation gives the prescription for calculating the density of modes N(ω) if we know the dispersion relation ω(k).</u>

3.4 Two Atoms per Primitive Basis

Consider a linear diatomic chain of atoms (1-D model for a crystal like NaCl):

In equilibrium:



$M_1 < M_2$

Applying Newton's second law and the nearest-neighbor approximation to this system gives a dispersion relation with two "branches":

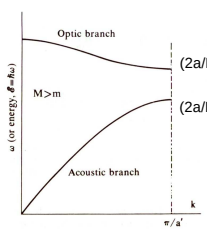
$$\omega^2 = c_1\left(\frac{M_1+M_2}{M_1M_2}\right) \pm \left[c_1^2\left(\frac{M_1+M_2}{M_1M_2}\right)^2 - \frac{4c_1^2}{M_1M_2}\sin^2\left(\tfrac{1}{2}ka\right)\right]^{1/2}$$

$\omega_-(k)$ $\omega \rightarrow 0$ as $k \rightarrow 0$ <u>acoustic modes</u> (M_1 and M_2 move in phase)

$\omega_+(k)$ $\omega \rightarrow \omega_{max}$ as $k \rightarrow 0$ <u>optical modes</u> (M_1 and M_2 move out of phase)

Optical and acoustical branches

Two branches may be presented as follows:



$M_1 < M_2$

$(2a/M_1)^{1/2}$

gap in allowed frequencies

$(2a/M_2)^{1/2}$

Fig. 12-6 The ω vs. k (optic and acoustic branches) for a linear diatomic chain.

If there are *p* atoms in the primitive cell, there are 3p branches to the dispersion relation: 3 acoustical branches and 3p-3 optical branches

Optical and acoustical branches

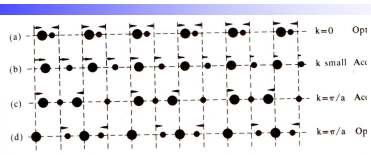
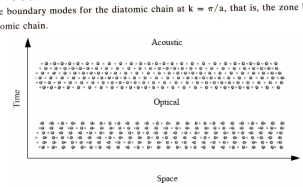


Fig. 12-7 A schematic diagram showing the atomic displacements for (a) k = 0 branch; (b) acoustic branch for small but certainly not zero k; (c) and (d) show zone boundary modes for the diatomic chain at k = π/a, that is, the zone boundar diatomic chain.

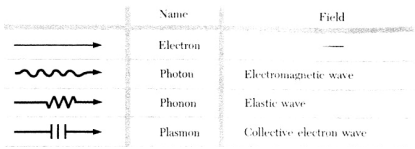


3.5 Quantization of Elastic Waves

The energy of a lattice vibrations is **quantized**

The quantum of energy is called a **phonon** (analogy with the photon of the electromagnetic wave)

Energy content of a vibrational mode of frequency ω is an integral number of energy quanta $\hbar\omega$. We call these quanta "phonons".
While a photon is a quantized unit of electromagnetic energy, a phonon is a quantized unit of vibrational (elastic) energy.



	Name	Field
	Electron	—
	Photon	Electromagnetic wave
	Phonon	Elastic wave
	Plasmon	Collective electron wave

3.6 Phonon Momentum

Associated with each mode of frequency ω is a wavevector $\vec{k}$, which leads to the definition of a "crystal momentum": $\hbar\vec{k}$

Crystal momentum is analogous to but not equivalent to linear momentum. No net mass transport occurs in a propagating lattice vibration, so a phonon **does not carry physical momentum**

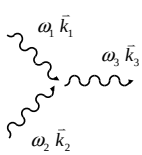
But phonons interacting with each other or with electrons or photons obey a conservation law similar to the conservation of linear momentum for interacting particles

Conservation Laws

Lattice vibrations (phonons) of many different frequencies can interact in a solid. In all interactions involving phonons, energy must be conserved and crystal momentum must be conserved to within a reciprocal lattice vector:

$$\hbar\omega_1 + \hbar\omega_2 = \hbar\omega_3$$
$$\hbar\vec{k}_1 + \hbar\vec{k}_2 = \hbar\vec{k}_3 + \hbar\vec{G}$$

Schematically:



Compare this to the special case of elastic scattering of x-rays with a crystal lattice: $\vec{k}' = \vec{k} + \vec{G}$

Just a special case of the general conservation law!

Photon wave vectors

Brilloiun Zone in 3D

Brilloiun Zone in 3D: Wigner-Seitz cell of the reciprocal lattice

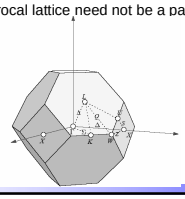
Recall: reciprocal lattice vector $\vec{G} = 2\pi\, n_1\vec{b}_1 + 2\pi\, n_2\vec{b}_2 + 2\pi\, n_3\vec{b}_3,$

where $\vec{b}_1, \vec{b}_2, \vec{b}_3$ are basic vectors such that $\vec{b}_1 = \frac{\vec{a}_2 \times \vec{a}_3}{\vec{a}_1 \cdot \vec{a}_2 \times \vec{a}_3}$; $\vec{b}_2 = \frac{\vec{a}_3 \times \vec{a}_1}{\vec{a}_1 \cdot \vec{a}_2 \times \vec{a}_3}$; $\vec{b}_3 = \frac{\vec{a}_1 \times \vec{a}_2}{\vec{a}_1 \cdot \vec{a}_2 \times \vec{a}_3}$;

Some properties of reciprocal lattice:

The direct lattice is the reciprocal of its own reciprocal lattice

The unit cell of the reciprocal lattice need not be a paralellopiped, e.g., Wigner-Seitz cell



first Brilloin Zone (BZ) of the *fcc* lattice

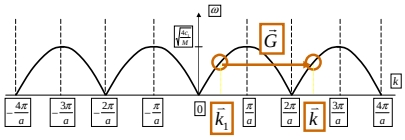
Back to Brillouin Zones

The 1st BZ is the region in reciprocal space containing all information about the lattice vibrations of the solid

Only the $\vec{k}$ values in the 1st BZ correspond to unique vibrational modes. Any $\vec{k}$ outside this zone is mathematically equivalent to a value $\vec{k}_1$ inside the 1st BZ

This is expressed in terms of a general translation vector of the reciprocal lattice:

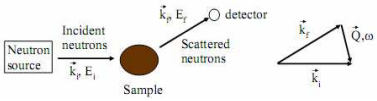
$$\vec{k} = \vec{k}_1 + \vec{G}$$



3.7 Neutron scattering measurements

What is a neutron scattering measurement?

- neutron source sends neutron to sample
- some neutrons scatter from sample
- scattered neutrons are detected



Conservation of energy: $\frac{\hbar^2 k_i^2}{2M} = \frac{\hbar^2 k_f^2}{2M} \pm \Delta E$

When a phonon of wavelength |*K*| is created by the inelastic scattering of a photon or neutron, the wavevector selection rule:

$$\vec{k}_f + \vec{K} = \vec{k}_i + \vec{G} \quad \text{creation of a phonon}$$

$$\vec{k}_f = \vec{k}_i + \vec{K} + \vec{G} \quad \text{annihilation of a phonon}$$

Why neutrons?

Wavelength: $\lambda = \frac{9.044}{\sqrt{E}}$

- At 10 meV, λ=2.86Å ⇒ similar length scales as structures of interest

Energy:
- thermal sources: 5-100meV
- cold sources: 1-10meV
- spallation sources: thermal and epithermal neutrons (>100meV)

can cover range of typical excitation energies in solids and liquids!

http://www.ncnr.nist.gov/summerschool/ss05/Vajklecture.pdf

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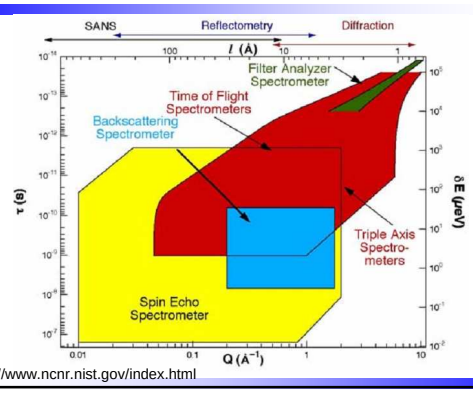
Energy and Length Scale



http://www.ncnr.nist.gov/index.html

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Effective Cross Section

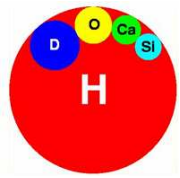
Cross Section, σ: an effective area which represents probability that a neutron will interact with a nucleus

σ varies from element to element and even isotope to isotope

Typical σ ~ 10^{-24} cm^2 for a single nucleus

One unit of cross section is a **1 barn=** 10^{-24} cm^2

… as in "it can't hit the size of the barn"



Total nuclear cross section for several isotopes

http://www.ncnr.nist.gov/index.html Lecture 3

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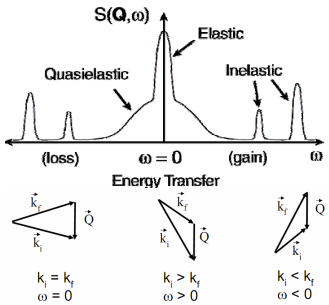
Neutron Scattering

Number of scattered neutrons is proportional to scattering function, S (**G**, ω)

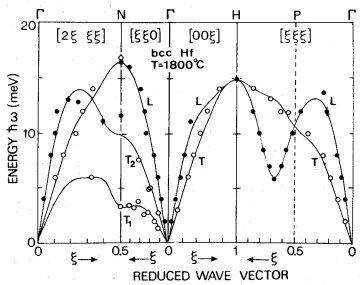
Scattering:
elastic;
quasielastic;
Inelastic

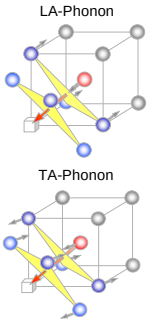
Neutrons are sensitive to components of motion parallel to the momentum transfer Q

Angular width of the scattered neutron beam gives information on the lifetime of phonons



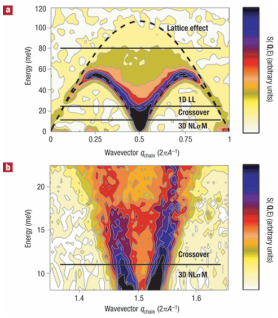
Phonon dispersion of bcc-Hf





Trampenau *et al. (1991)*

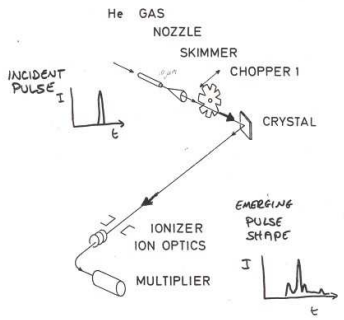
Inelastic neutron scattering data for $KCuF_3$ measured



Bella Lake, D. Alan Tennant, Chris D. Frost and Stephen E. Nagler *Nature Materials* 4, 329 - 334 (2005)

2D: Inelastic Scattering on the Surfaces

Thermal Energy Helium Atom Scattering



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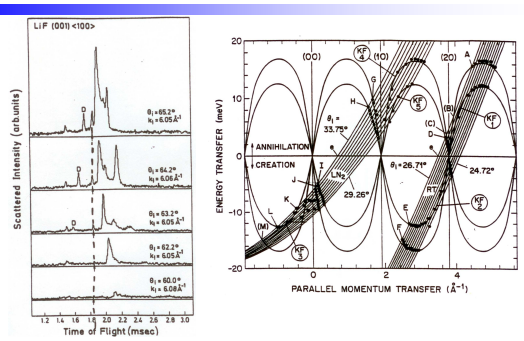
Time-of-Flight Spectra and Dispersion Curves



Time-of-flight spectrum for He atoms scattering from an LiF(001) surface along the [100] azimuth. The sharp peaks are due to single surface phonon interactions (From Brusdeylins et al, 1980)

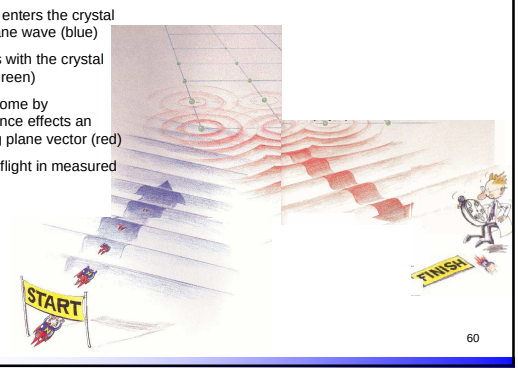
Neutron Scattering

Neutron enters the crystal as a plane wave (blue)

Interacts with the crystal lattice (green)

And become by interference effects an outgoing plane vector (red)

Time-of-flight in measured



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