Lattice Dynamics

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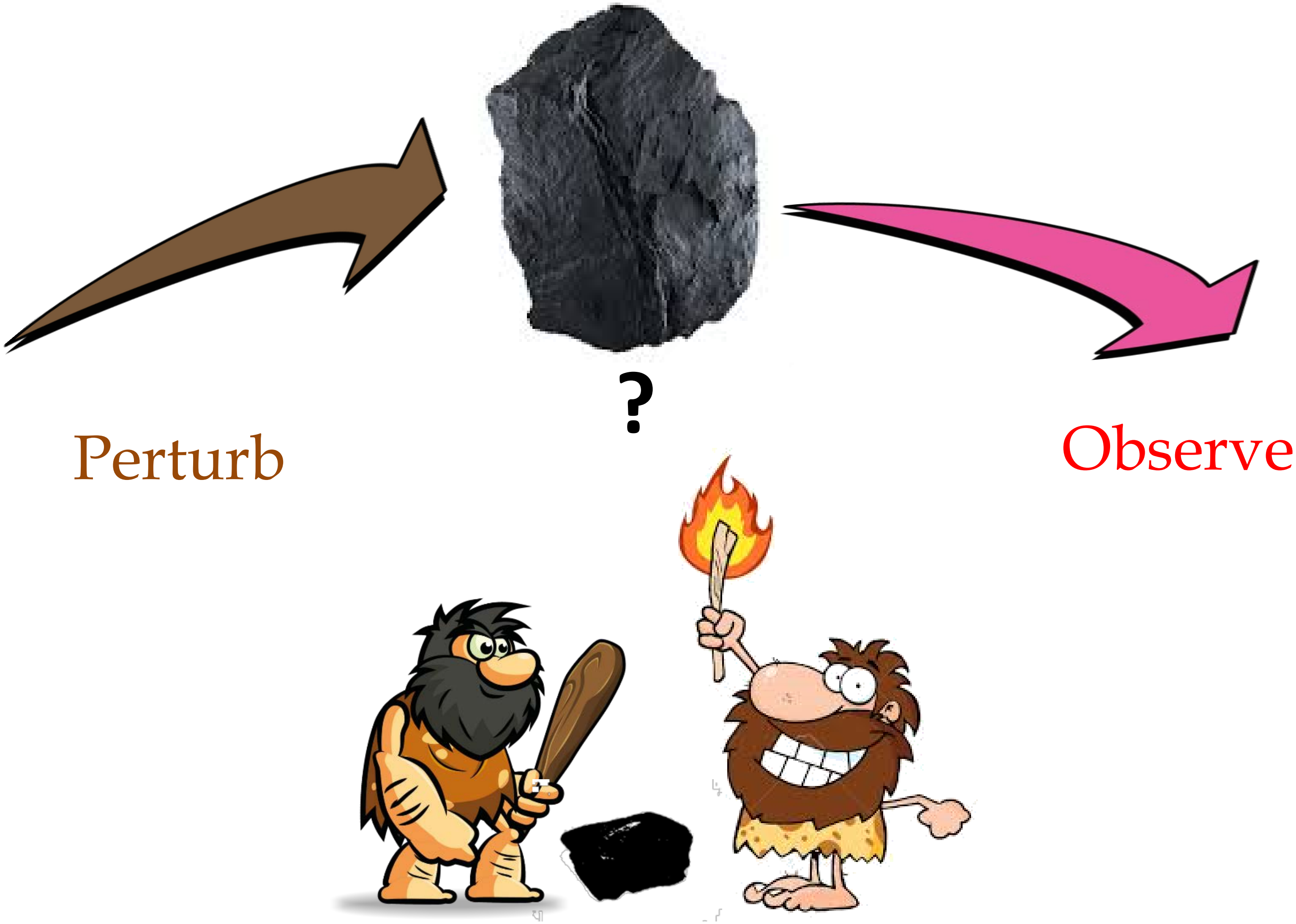
?


?
Perturb
Observe


?
Perturb
Observe

?

Perturb

- Knock
- Burn
- Smash

Observe

- Sound
- Heat
- Inside

?

Perturb
(Pump)

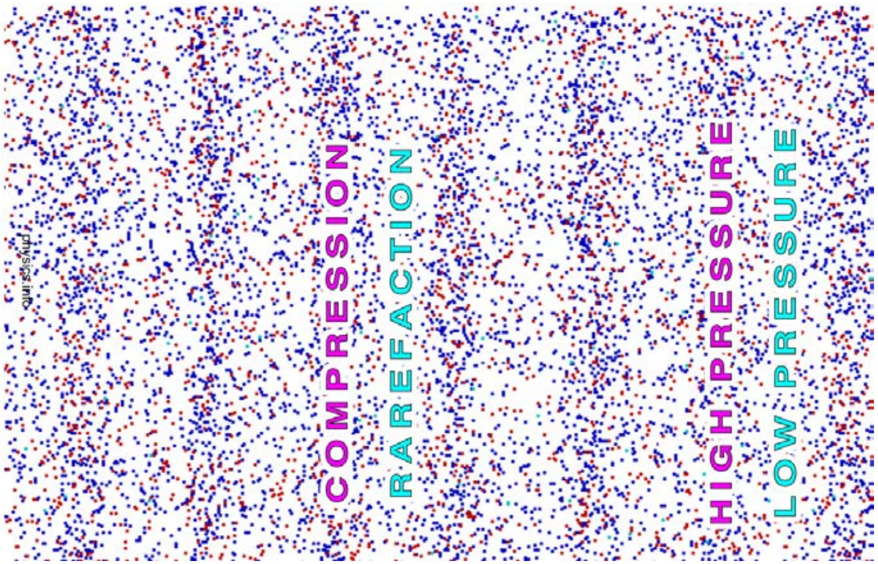
- Knock
- Burn
- Smash

Observe
(Probe)

- Sound
- Heat
- Inside

Inelastic Scattering !!!!

The **pitch** of a note **depends** on the frequency of the source of the **sound**.



solids	v (m/s)	liquids	v (m/s)
aluminum	6420	alcohol, ethyl	1207
glass, pyrex	5640	argon	319
wood, maple	4110	water, distilled	1497

The acoustic velocity is related to the change in pressure and density of the substance

$$v_s = \sqrt{\frac{dP}{d\rho}} = \sqrt{\frac{E}{\rho}} \quad \text{(Hooke's law)}$$

Heat capacity is a measure of the amount of heat a material can **store** when the temperature is changed

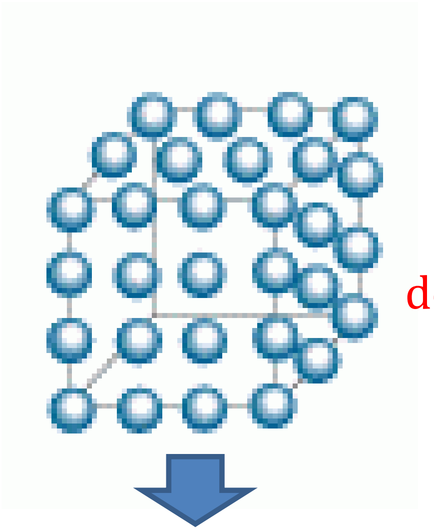
	C_p (J/mol.K)
Al	24.3
Fe	25.7
Ni	26.8
Cu	24.4
Pb	26.9
Ag	25.5
C	10.9
Water	75.3

$$C_p = \frac{dU}{dT}$$

Dulong–Petit law (1819) states that the gram-atomic heat capacity (specific heat times atomic weight) of an element is a constant; that is, it is the same for all solid elements.

Dynamics

related to movement of atoms about their equilibrium positions

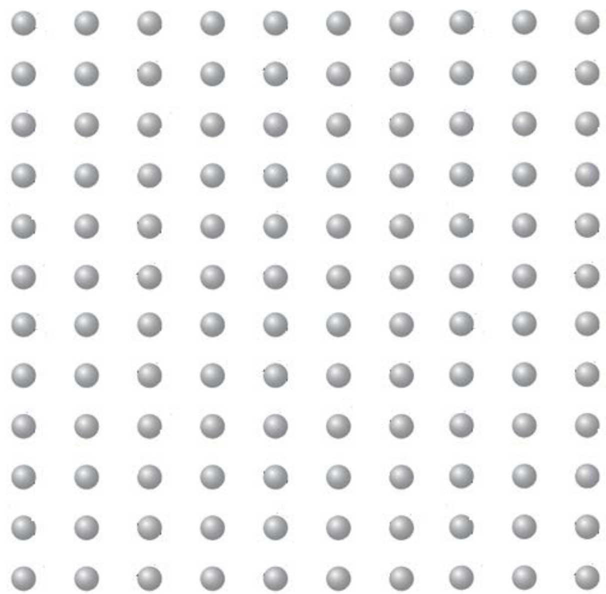


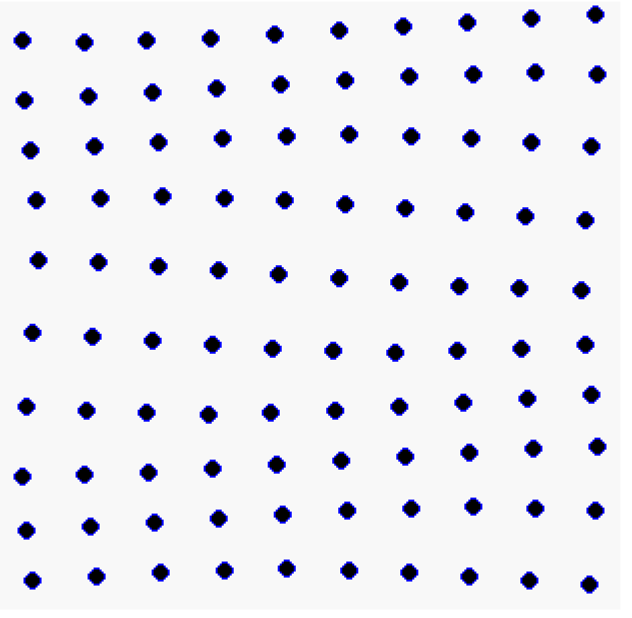
Structure

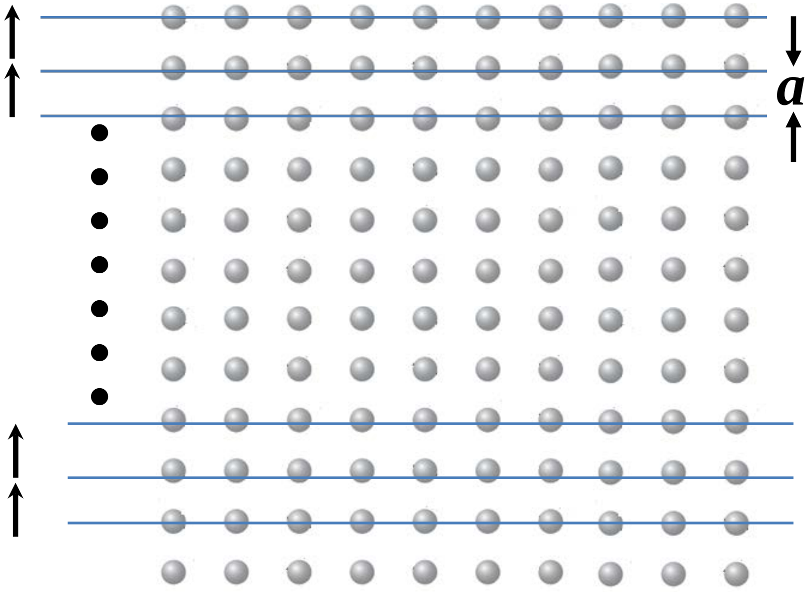
determined by electronic structure

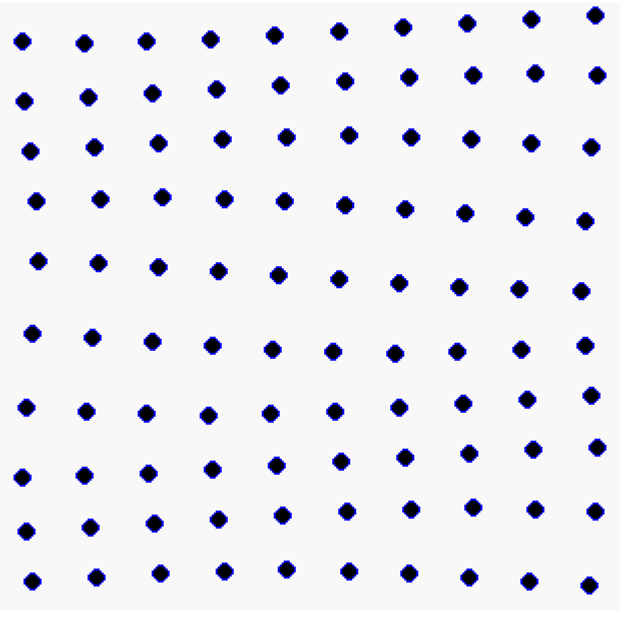
Electronic and Physical properties

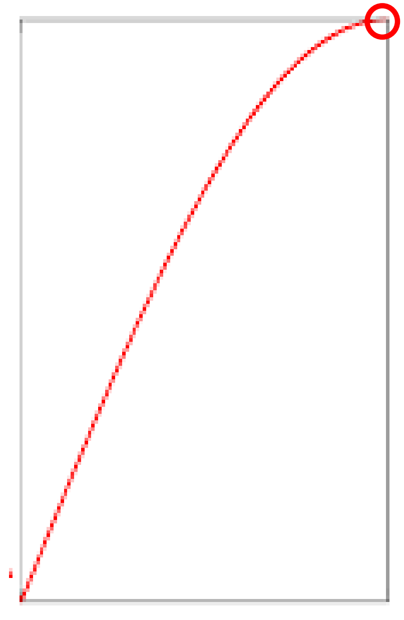
- Sound velocity
- Thermal properties: -specific heat
  -thermal expansion
  -thermal conductivity
- Hardness of perfect single crystals
- Vibrations






a

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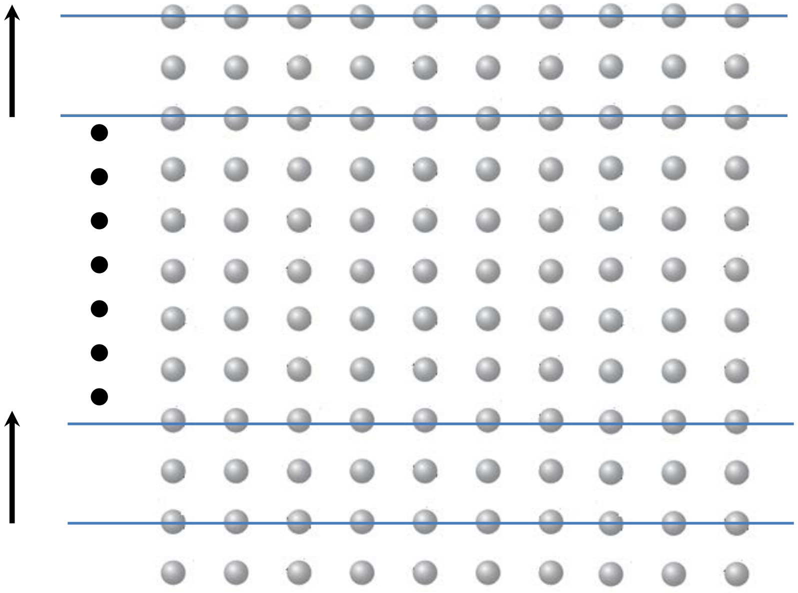
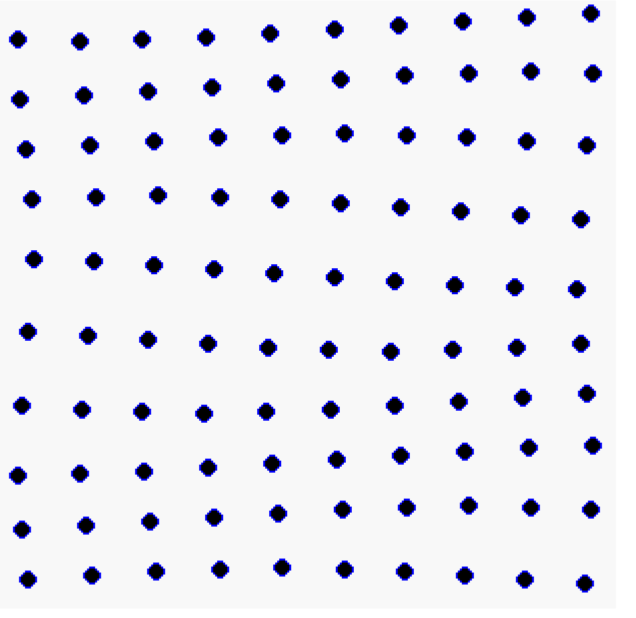
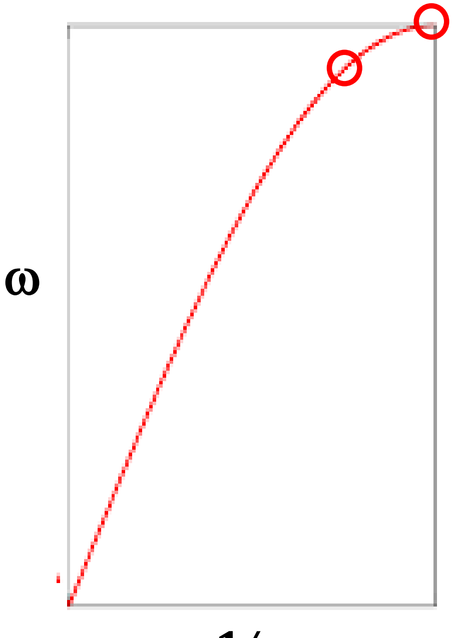
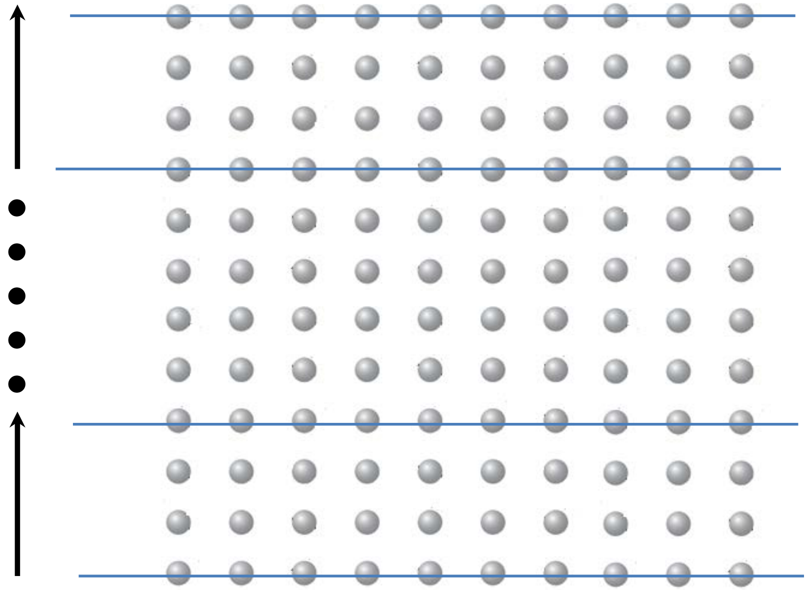
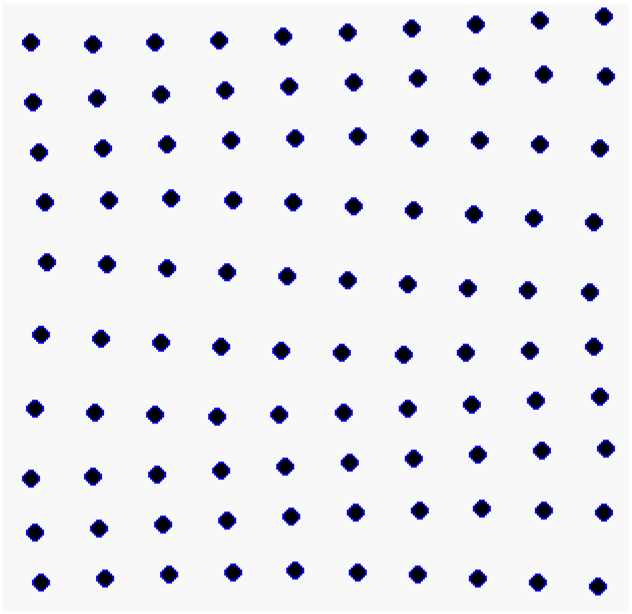
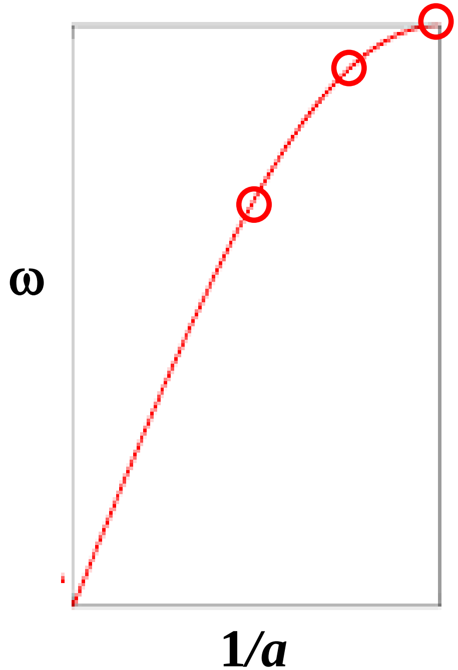


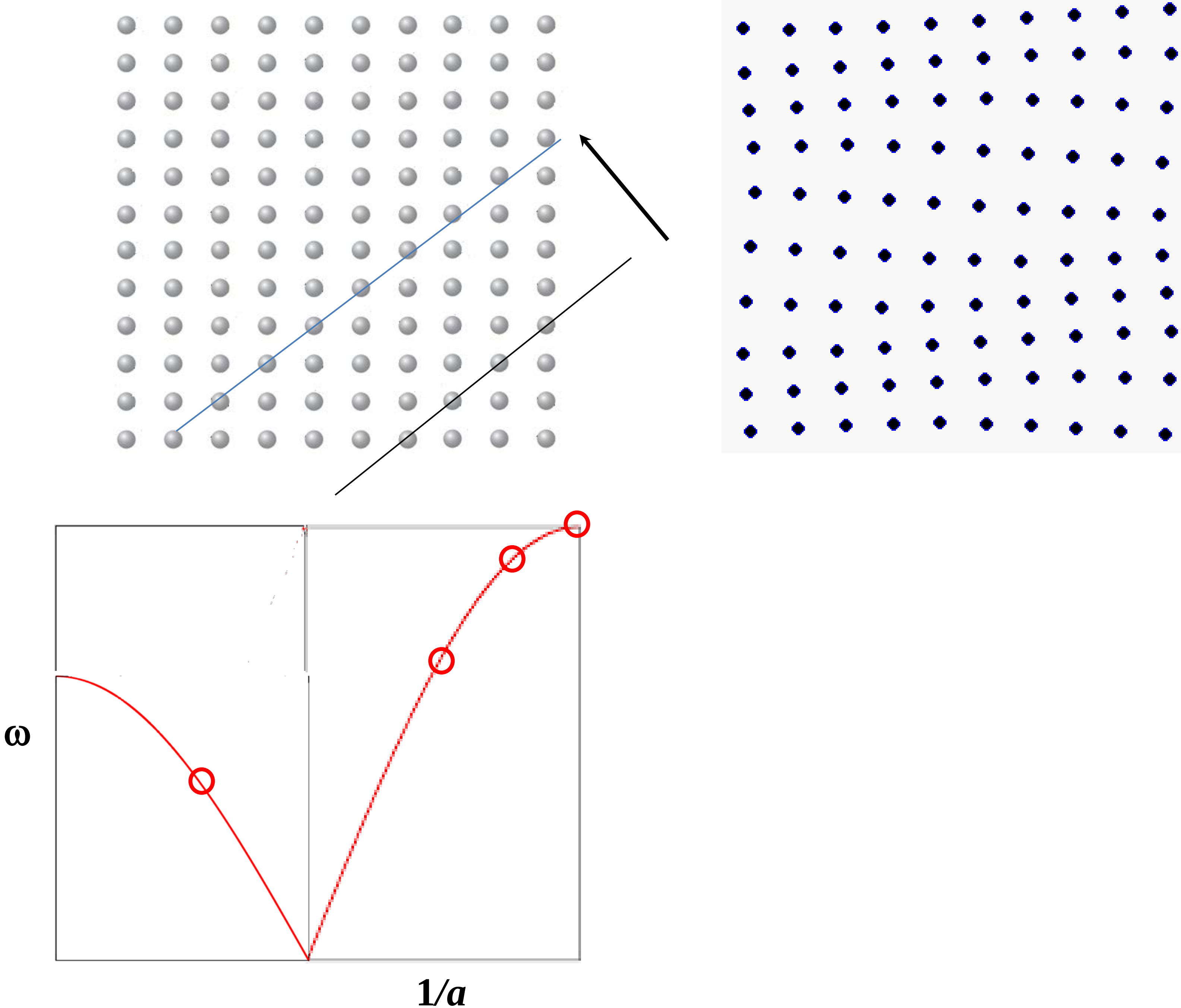



ω
1/a






ω
1/a


ω
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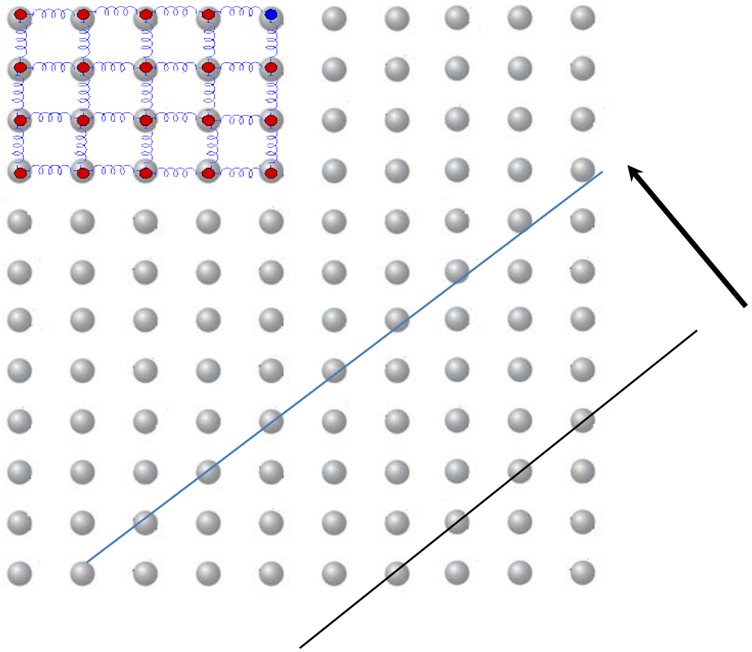
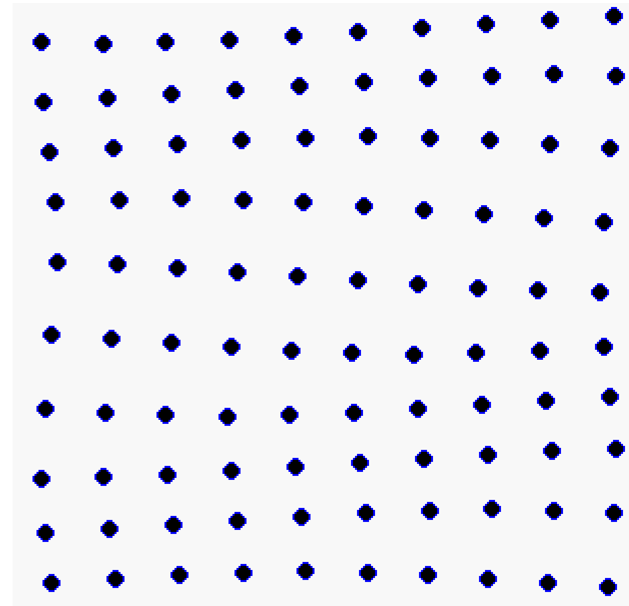
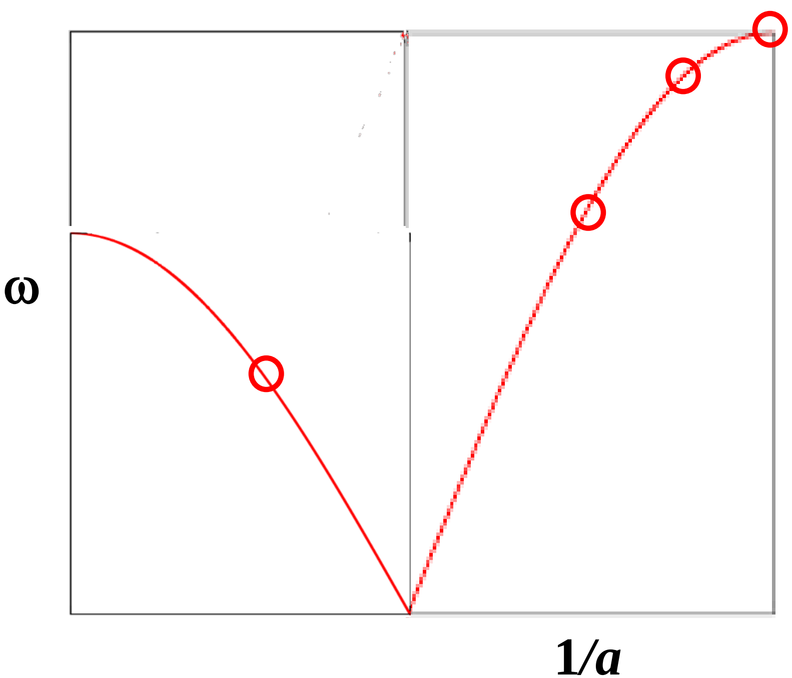
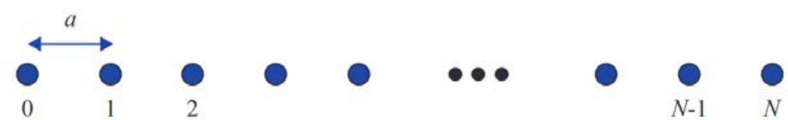
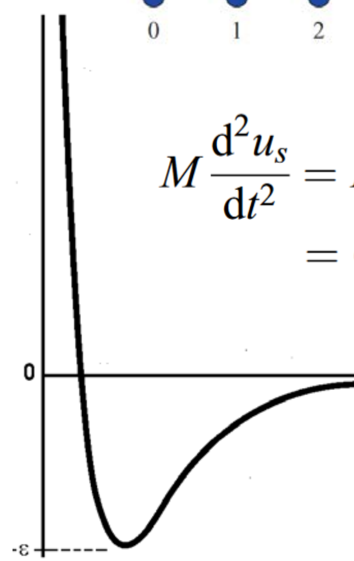








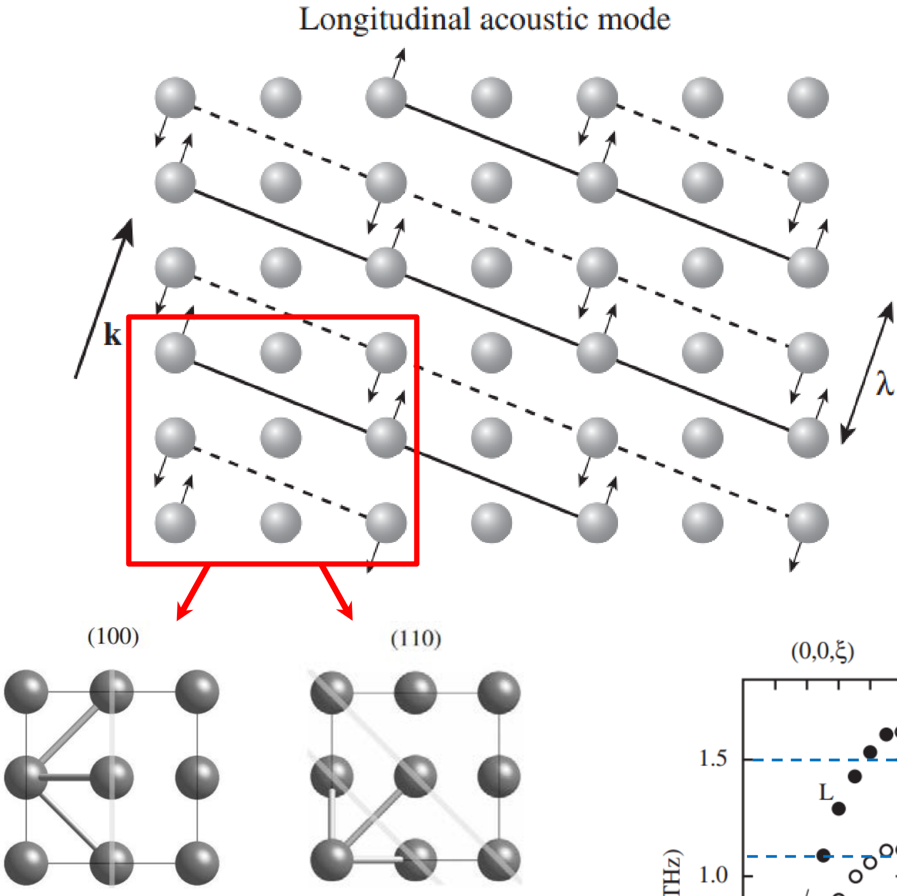


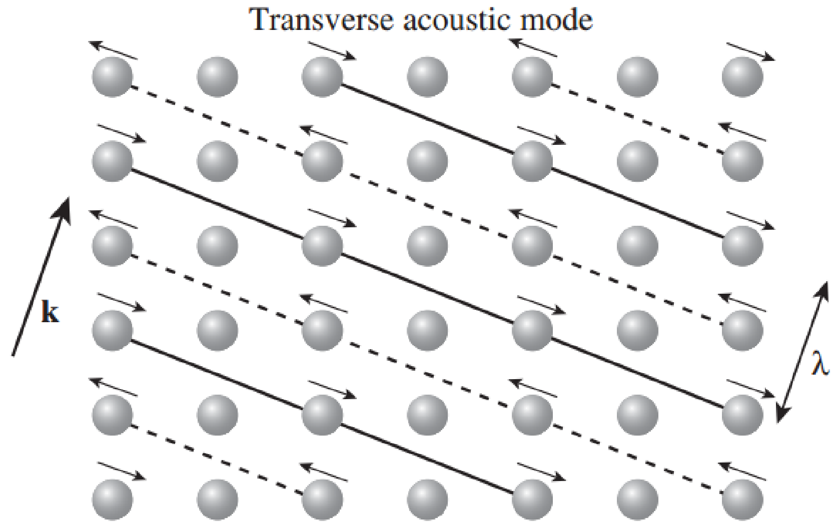
$$M\frac{\mathrm{d}^2u_s}{\mathrm{d}t^2} = F_s$$
$$= C(u_{s+1} - U_s) + C(u_{s-1} - U_s)$$

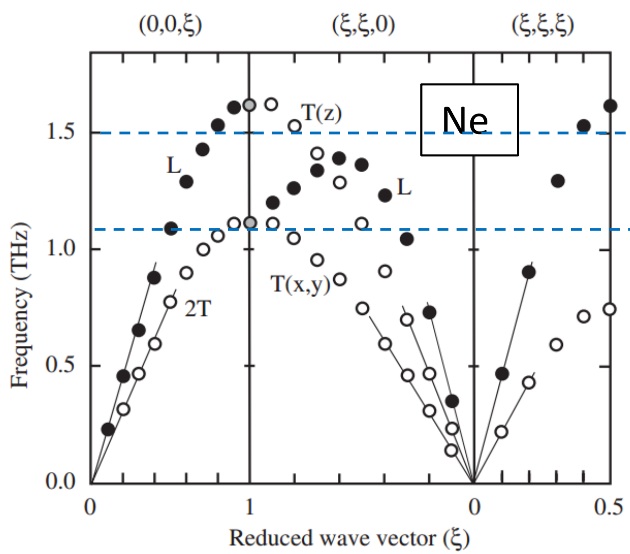
$$u_s \sim \mathrm{e}^{\mathrm{i}(qx-\omega t)}$$

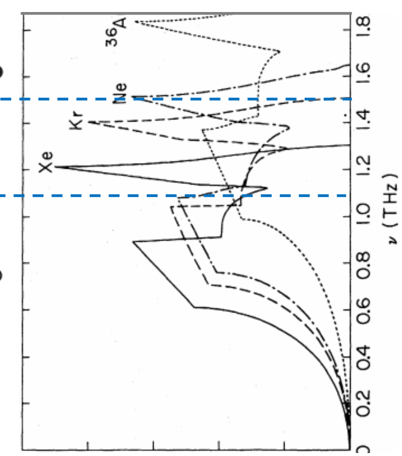
$$\omega^2 = \frac{4C}{M}\sin^2\left(\frac{qa}{2}\right)$$

Phonon band structure



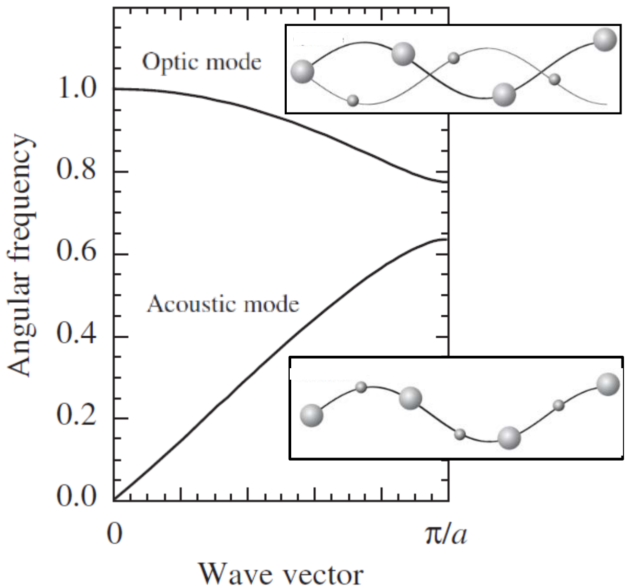


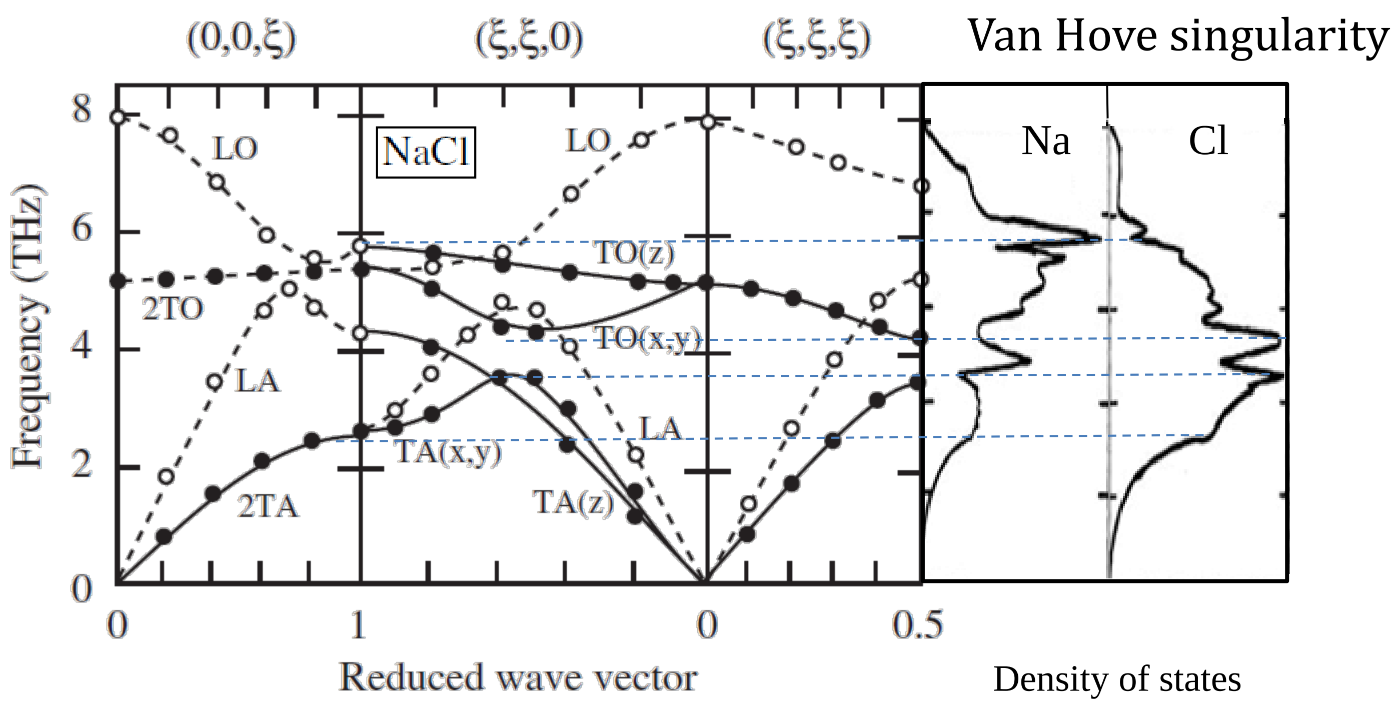




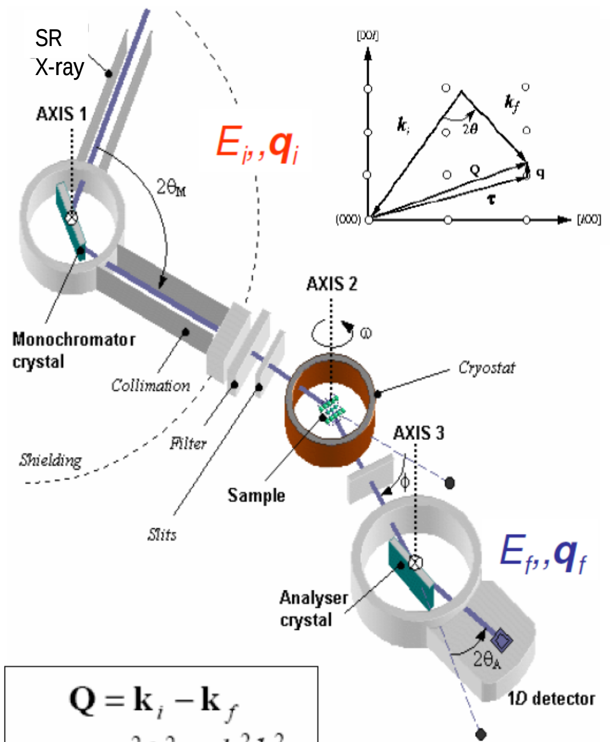
Density of states, $g(\omega) = \mathrm{d}n/\mathrm{d}E$
$= 1/(\mathrm{d}E/\mathrm{d}n)$

Phonon band structure of polyatomic systems



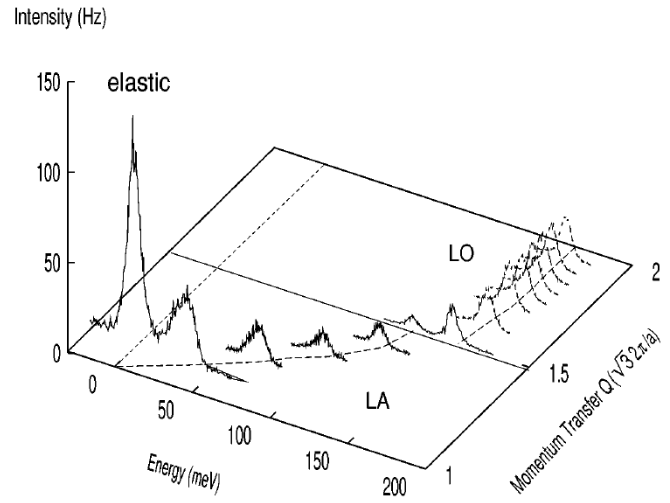


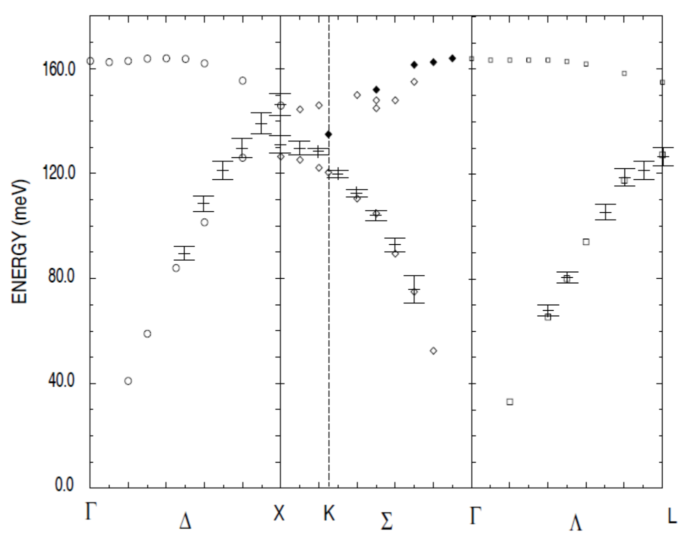
Phonon Dispersion of Diamond Measured by Inelastic X-Ray Scattering - Single crystal



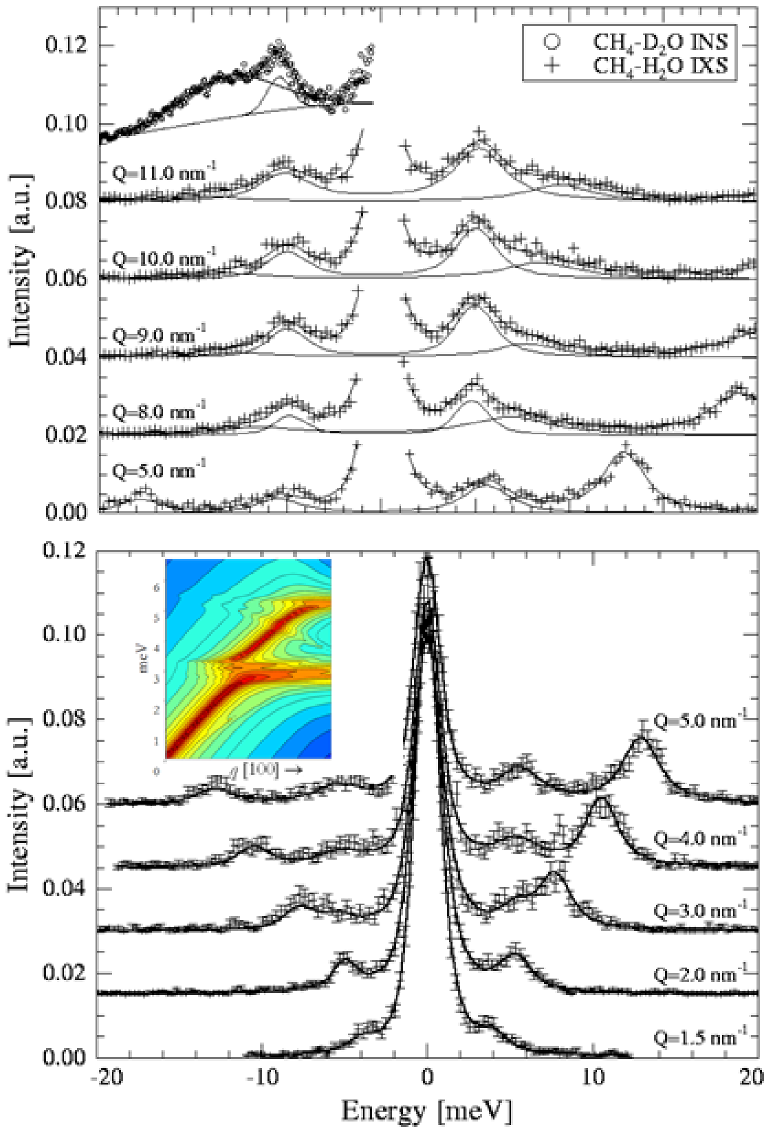
$$\mathbf{Q} = \mathbf{k}_i - \mathbf{k}_f$$

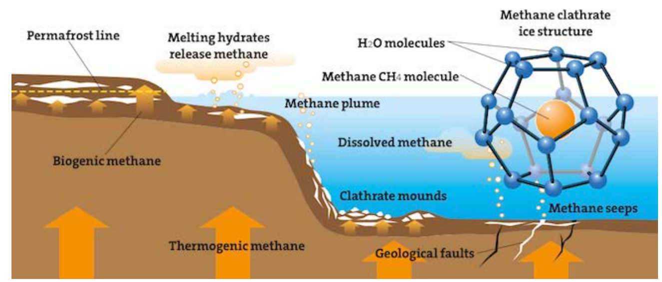
$$\Delta E = \frac{\hbar^2 k_i^2}{2m} - \frac{\hbar^2 k_f^2}{2m}$$

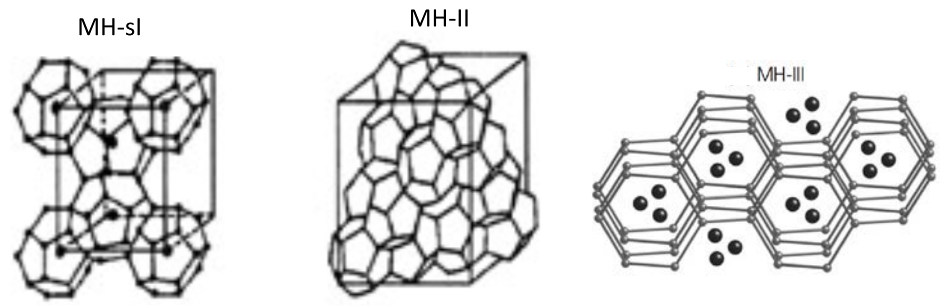




Phonon dispersion of polycrystals





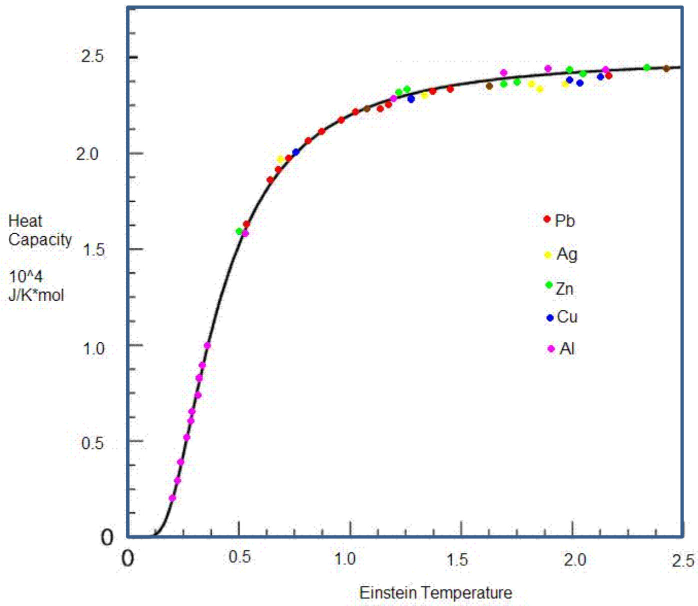


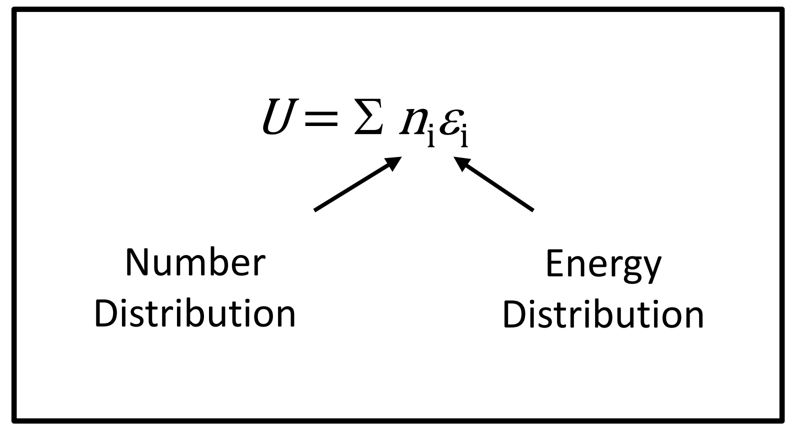
Hydrate pressure	MH-II 17 kbar	MH-III 21 kbar	MH-sI 0.2 kbar
ρ (g/cm^3)	1.07 (Ref. 4)	1.16 (Ref. 4)	0.90
B (GPa)	14.4 (Ref. 18)	23.5 (Ref. 4)	8.0
v_p (km/s)	4.2±0.1	4.6±0.1	3.7
C (GPa)	18.9±0.8	24.5±1.0	12.3
G (GPa)	3.4±0.6	0.8±0.7	3.3
v_s (km/s)	1.8±0.15	0.8±0.4	1.9

J. Baumert, C. Gutt, V. P. Shpakov, J. S. Tse, M. Krisch, M. Müller, H. Requardt, D. D. Klug, S. Janssen, and W. Press, *Phys. Rev.* B 68, 174301 (2003)

J. Baumert, C. Gutt, M. Krisch, H. Requardt,4 M. Müller, J. S. Tse, D. D. Klug, and W. Press, Phys. Rev., B 72, 054302 (2005)

Heat Capacity – Einstein model





There is a temperature dependence (*i.e.* distribution) of the oscillators!
Introduce Bose-Einstein distribution,

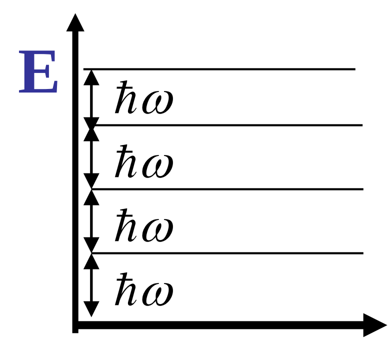
$$\bar{n} = \frac{1}{e^{\hbar\omega/k_B T} - 1}$$

the total internal energy of the solid $U = 3N\hbar\omega\left(\bar{n} + \frac{1}{2}\right)$

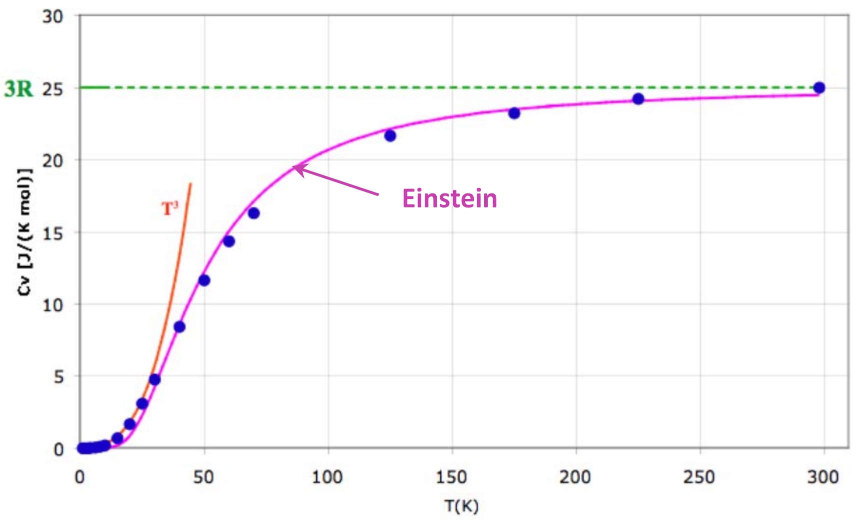
$$C_v = \left(\frac{\partial U}{\partial T}\right)_v = 3Nk_B F_E\left(\frac{\hbar\omega}{k_B T}\right)$$

$$F_E(x) = \frac{x^2}{(e^x - 1)(1 - e^{-x})}$$

Energy levels are equally spaced!



Heat Capacity – Einstein/Debye model



Einstein Approximation: all modes (oscillators) have the same frequency $\Rightarrow \omega_E$

Debye approximation: In the low temperature limit acoustic modes dominate.
i.e. there is distribution of vibration modes !

Therefore the total internal energy should be,

$$U = \int_0^\infty \frac{\hbar\omega}{\exp(\hbar\omega/kT)-1} g(\omega)d\omega$$

No. of phonons in $d\omega$ at ω

Einstein statistic

Debye model – vibrational density of states

Debye assumed a dispersion relationship (phonon in a box)

$$\omega_j(k) = ck$$

and a phonon distribution function

$$g(\omega)d\omega \propto 4\pi k^2 dr$$

therefore,

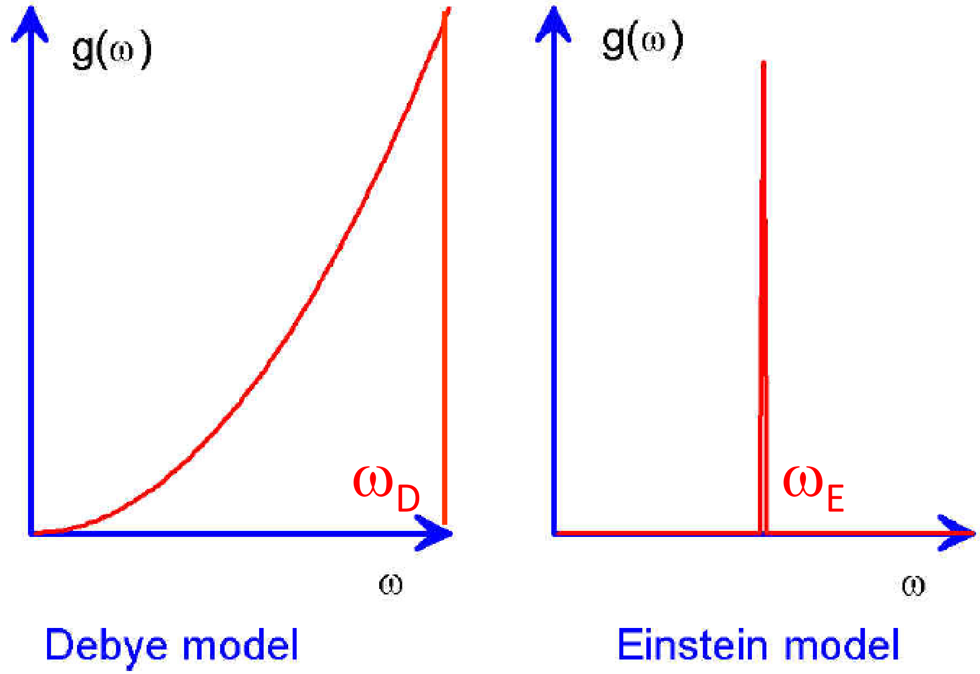
$$g(\omega) = D\omega^2$$

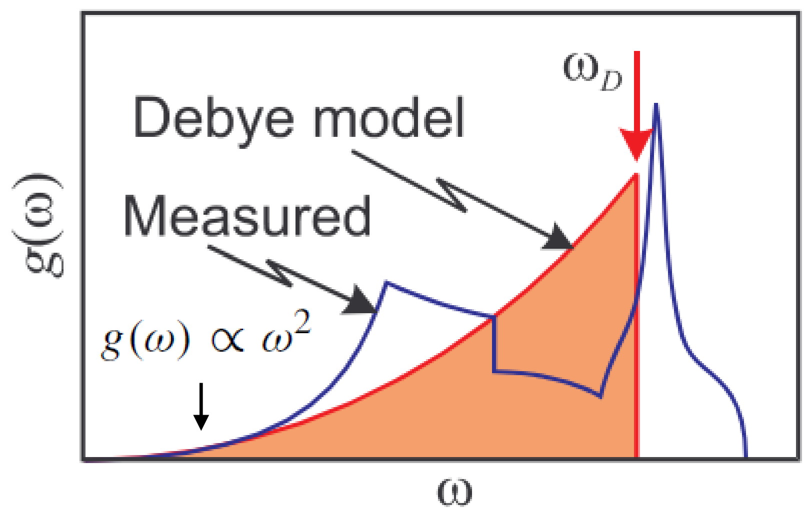
with a cutoff frequency, ω_D

$$g(\omega) = \frac{V}{2\pi^2}\left(\frac{1}{v_l^3} + \frac{2}{v_t^3}\right)\omega^2 = \frac{3V}{2\pi^2}\frac{\omega^2}{v_a^3}$$

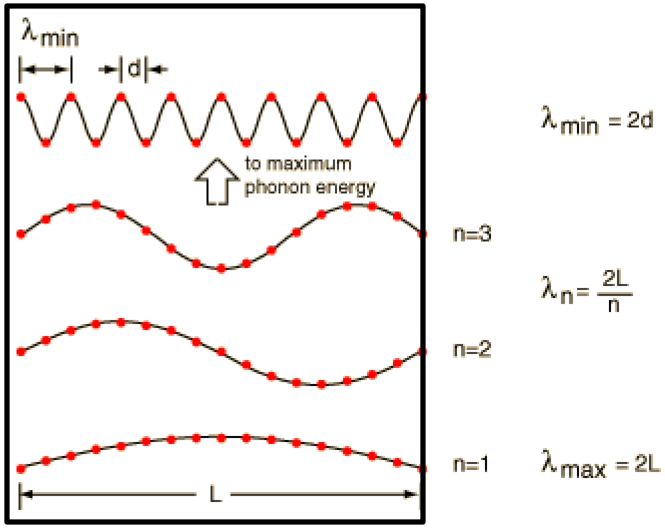
$$U = \frac{3V\hbar}{2\pi^2 v_s^3}\int_0^{\omega_D} \omega^3 \frac{1}{\exp(\hbar\omega/kT)-1} d\omega$$

$$c_V = \int_0^{\omega_D} \frac{3V\omega^2}{2\pi^2 c^3}\hbar\omega\frac{\partial n}{\partial T}\, d\omega$$



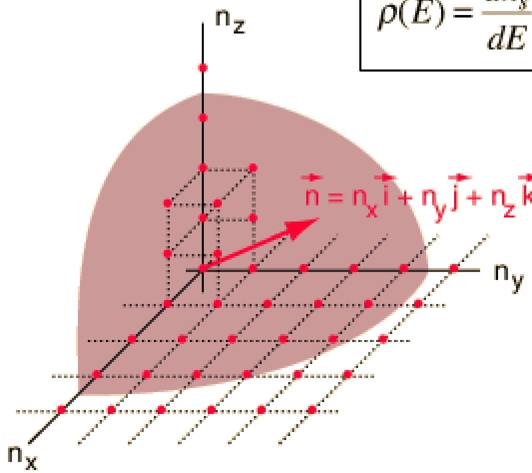


Phonon in a box



$$h\upsilon = \frac{h v_s}{\lambda} = \frac{h v_s n}{2L}$$

$$\rho(E) = \frac{dn_s}{dE} = \frac{8\pi}{(hc)^3}E^2$$



$$E = \frac{h^2 k^2}{2m}$$

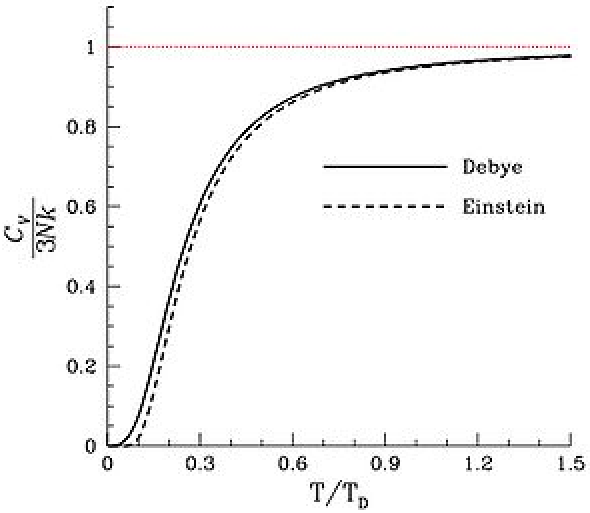
$$\rho(E) \propto k^2$$

the total energy in the lattice vibrations is of the form $U = 3\int_0^{E_{\max}} \frac{E}{e^{E/kT}-1}dE$

expressed in terms of the phonon modes by expressing the integral in terms of the mode number n. $U = \frac{3\pi}{2}\int_0^{n_{\max}} \frac{h v_s n}{2L}\frac{n^2}{e^{h v_s n/2LkT}-1}dn$

let $x_{\max} = \frac{h v_s n_{\max}}{2LkT} = \frac{h v_s}{2kT}\left(\frac{6N}{\pi V}\right)^{1/3} = \frac{T_D}{T}$ the integral takes the form $U = \frac{9NkT^4}{T_D^3}\int_0^{T_D/T}\frac{x^3}{e^x-1}dx$

What can we learn from Debye temperature?



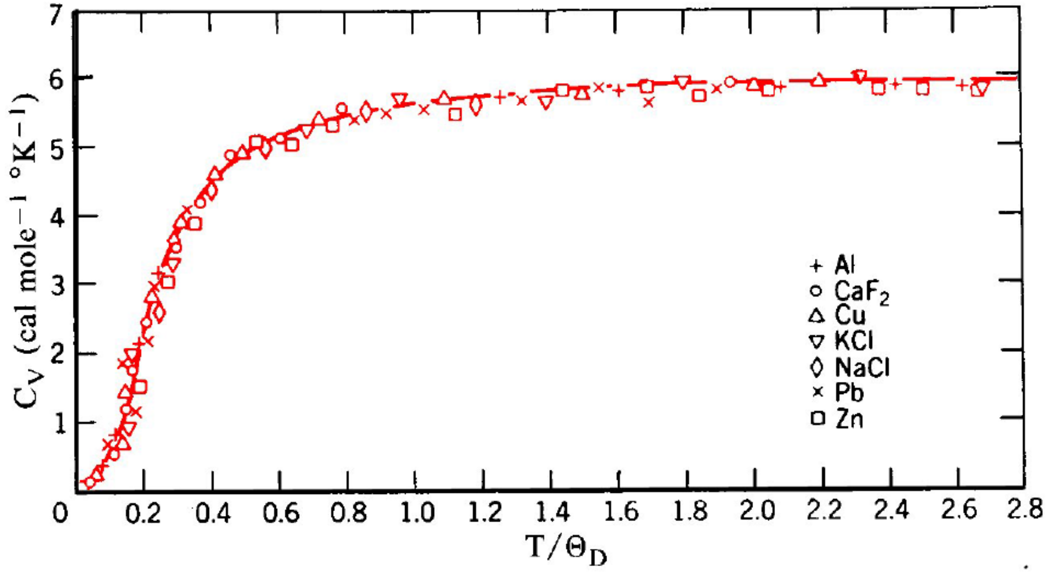


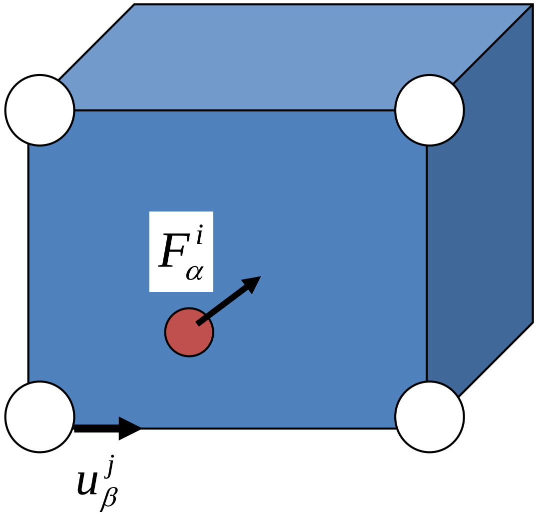
Table 4.5 Debye temperatures T_D, heat capacities, and thermal conductivities of selected elements

	Crystal							
	Ag	**Be**	**Cu**	**Diamond**	**Ge**	**Hg**	**Si**	**W**
T_D (K)*	215	1000	315	1860	360	100	625	310
C_m (J K^{-1} mol^{-1})†	25.6	16.46	24.5	6.48	23.38	27.68	19.74	24.45
c_s (J K^{-1} g^{-1})†	0.237	1.825	0.385	0.540	0.322	0.138	0.703	0.133
κ (W m^{-1} K^{-1})†	429	183	385	1000	60	8.65	148	173

Theoretical lattice dynamics
Harmonic approximation

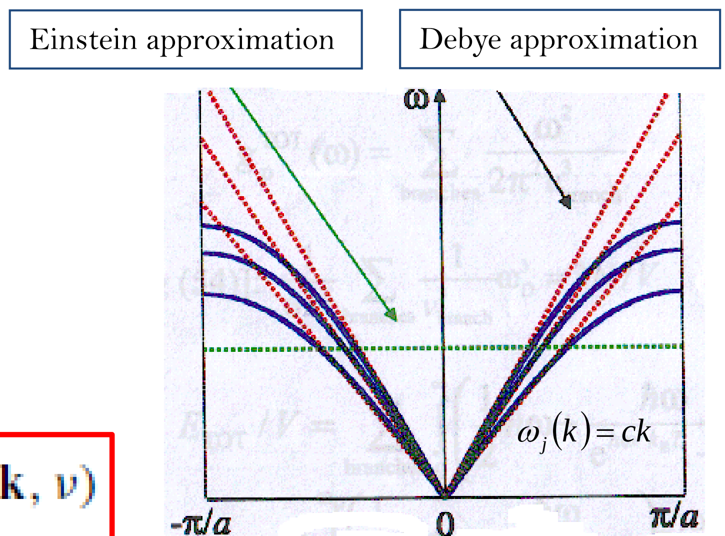
Force constant, Hooke's Law

$$\Phi_{\alpha\beta}^{ij} = \frac{\partial^2 E_{tot}}{\partial u_\alpha^i \partial u_\beta^j} = -\frac{\partial F_\alpha^i}{\partial u_\beta^j} \approx -\frac{F_\alpha^i}{u_\beta^j} \qquad i, j = 1, N \qquad \alpha, \beta = x, y, z$$



Dynamic matrix is the Fourier transformation of force constants

$$D_{\alpha\beta}^{ij}(q) = \frac{1}{\sqrt{M_i M_j}} \sum_L \Phi_{\alpha\beta}^{i,j+L} e^{-iq\cdot(R^{j+L}-R^i)}$$



Diagonalize Dynamic matrix to get phonon dispersions, and DOS

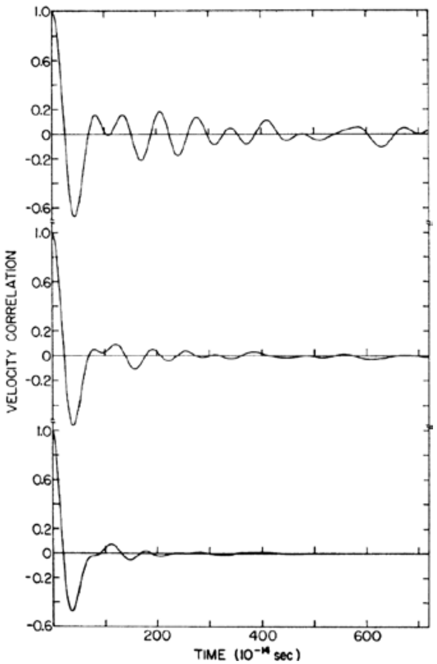
$$\mathbf{u}(jl) = \frac{1}{\sqrt{N m_j}} \sum_{\mathbf{k},\nu} \boxed{\mathbf{e}(j,\mathbf{k},\nu)\exp(i\mathbf{k}\cdot\mathbf{r}(jl))Q(\mathbf{k},\nu)}$$

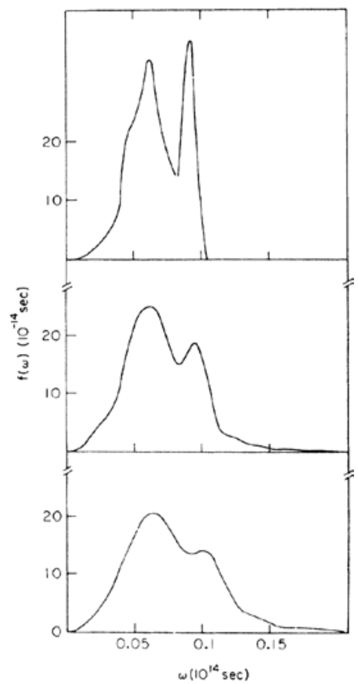
Theoretical molecular dynamics
Beyond harmonic approximation

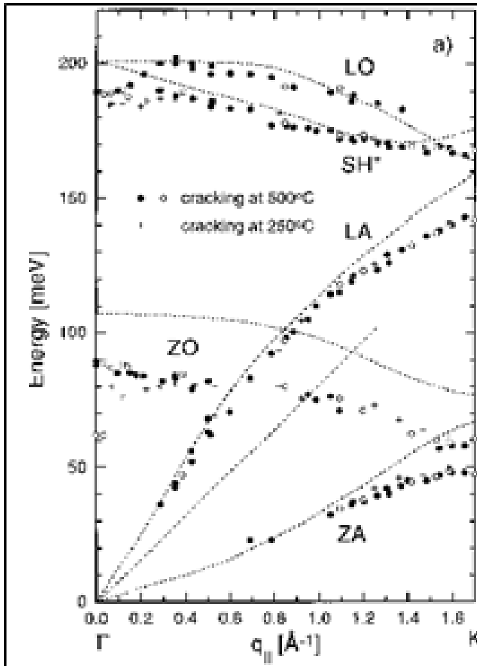
Time correlation function formalism

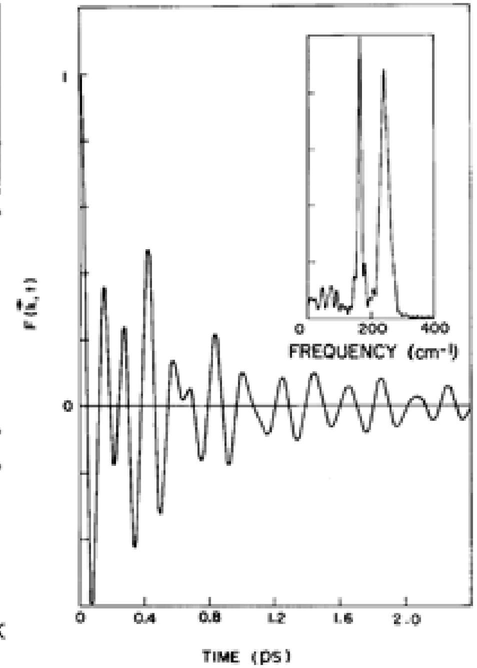
$$P(\omega) = m \int \langle \dot{\mathbf{r}}(\tau)\dot{\mathbf{r}}(t+\tau)\rangle_\tau e^{-i\omega t} dt$$

$$\langle \dot{\mathbf{r}}(\tau)\dot{\mathbf{r}}(t+\tau)\rangle_\tau \Rightarrow P(\omega)$$









$$S(\mathbf{k},\omega) = \int_0^\infty dt \exp(i\omega t) F(\mathbf{k},t),$$

where

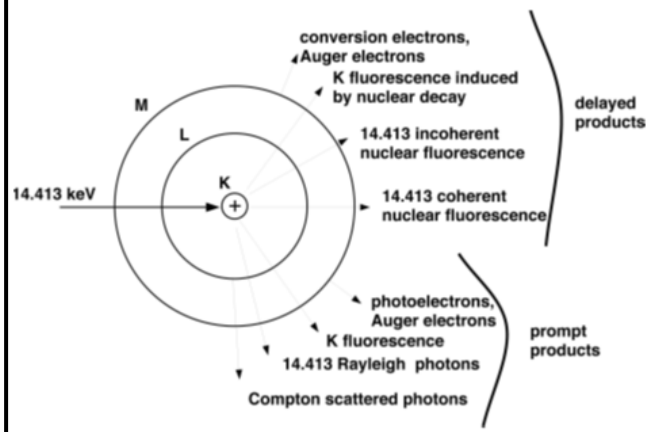
$$F(\mathbf{k},t) = \left\langle \sum_i b_i \exp - [i\mathbf{k}\cdot\mathbf{R}_i(t)] \sum_j b_j \exp[i\mathbf{k}\cdot\mathbf{R}_j(0)] \right\rangle$$

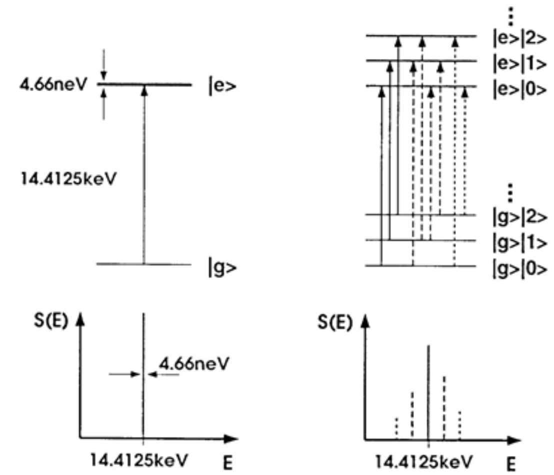
J. M. Dickey and A. Paskein, *Phys. Rev*. 188, 1407 (1969)

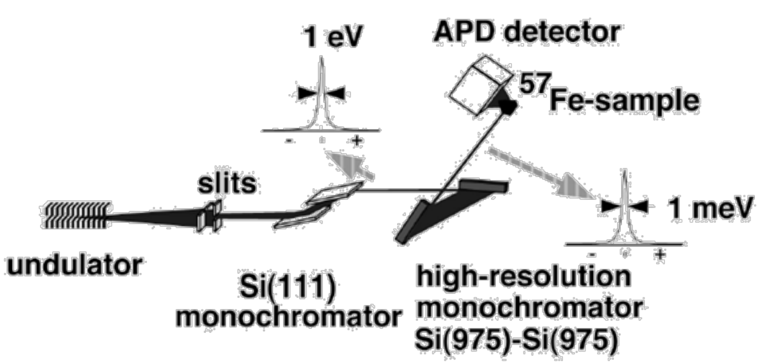
J.S. Tse and M.L. Klein *and* I.R. McDonald, *J. Chem. Phys*,. 81, 6124 (1984)

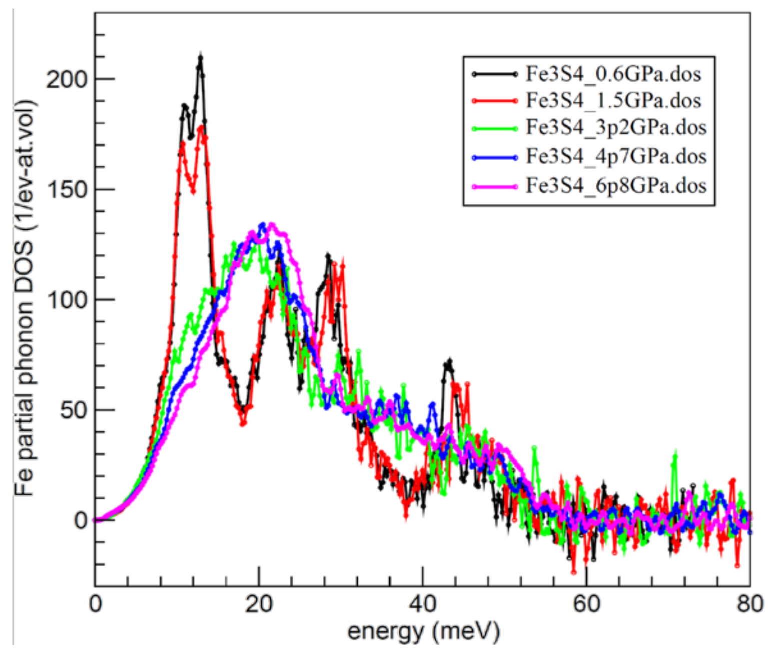
Recoilless Nuclear Resonance Absorption of Gamma Radiation

The Mossbauer effect involves the emission and absorption of gamma rays from the excited states of a nucleus. When an excited nucleus emits a gamma ray, it must recoil in order to conserve momentum since the gamma ray photon has momentum. **Mossbauer discovered that by placing emitting and absorbing nuclei in a crystal, one could use the crystal lattice for recoil**, lessening the recoil energy loss to the point that these extremely sharp emission and absorption lines would overlap so that absorption was observed.

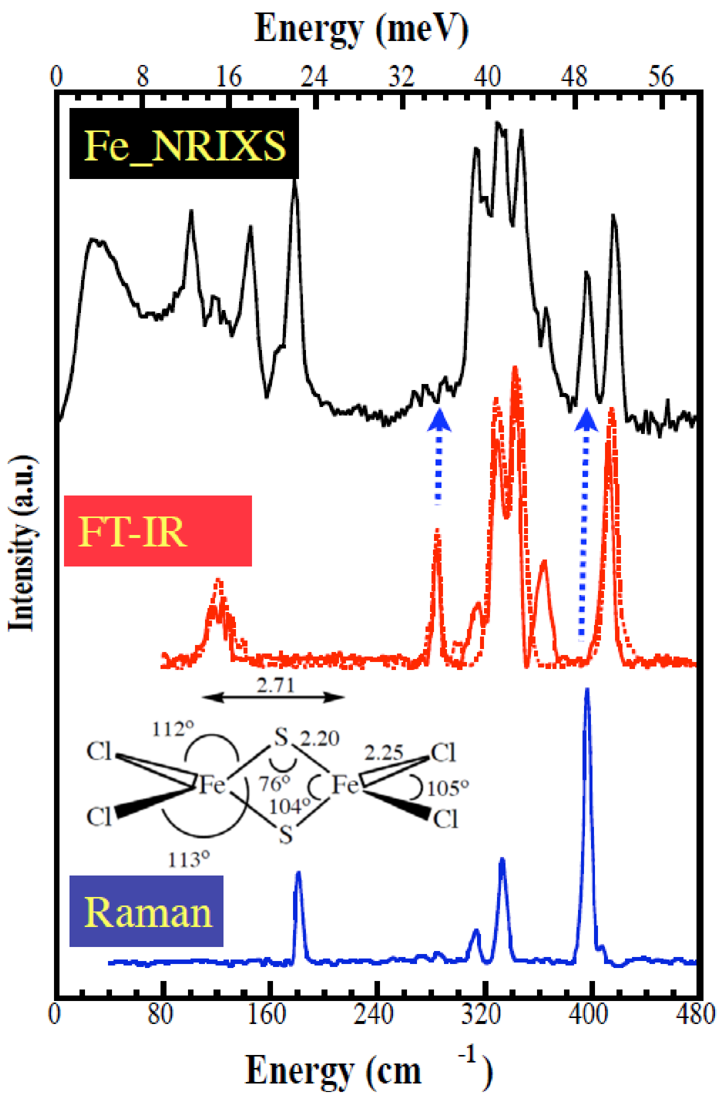








Advantage of VDOS – no selection rules



Selection rules:

- Infrared
  Only "*u*" modes are active
  $I \propto |\partial\mu/\partial q|^2$

- Raman
  Only "*g*" modes are active
  $I \propto |\partial\alpha/\partial q|^2$

- NRVS
  All modes are active
  $I \propto$ VDOS

Matt Smith, et al, Inorganic Chemistry, 2005, 44,5562

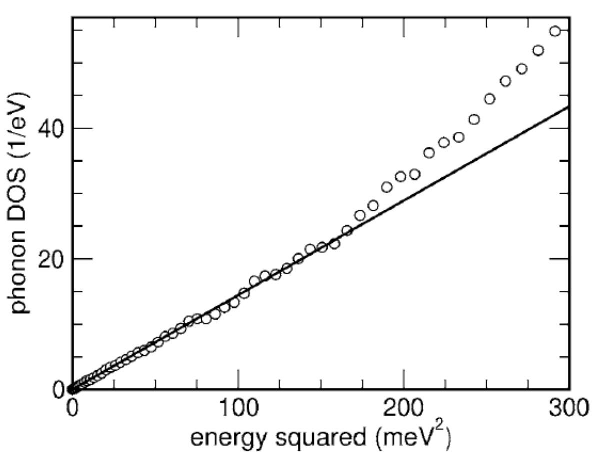
Extraction of sound velocity

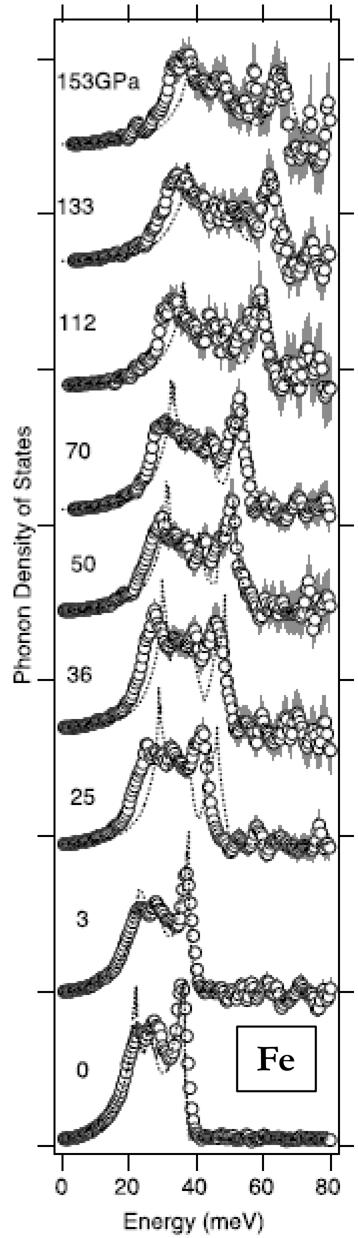
$$g(\omega) = \frac{V\omega^2}{2\pi^2}\frac{1}{v_s^3} \Rightarrow g(\omega) = \frac{V\omega^2}{2\pi^2}\left(\frac{1}{v_L^3} + \frac{2}{v_T^3}\right)$$

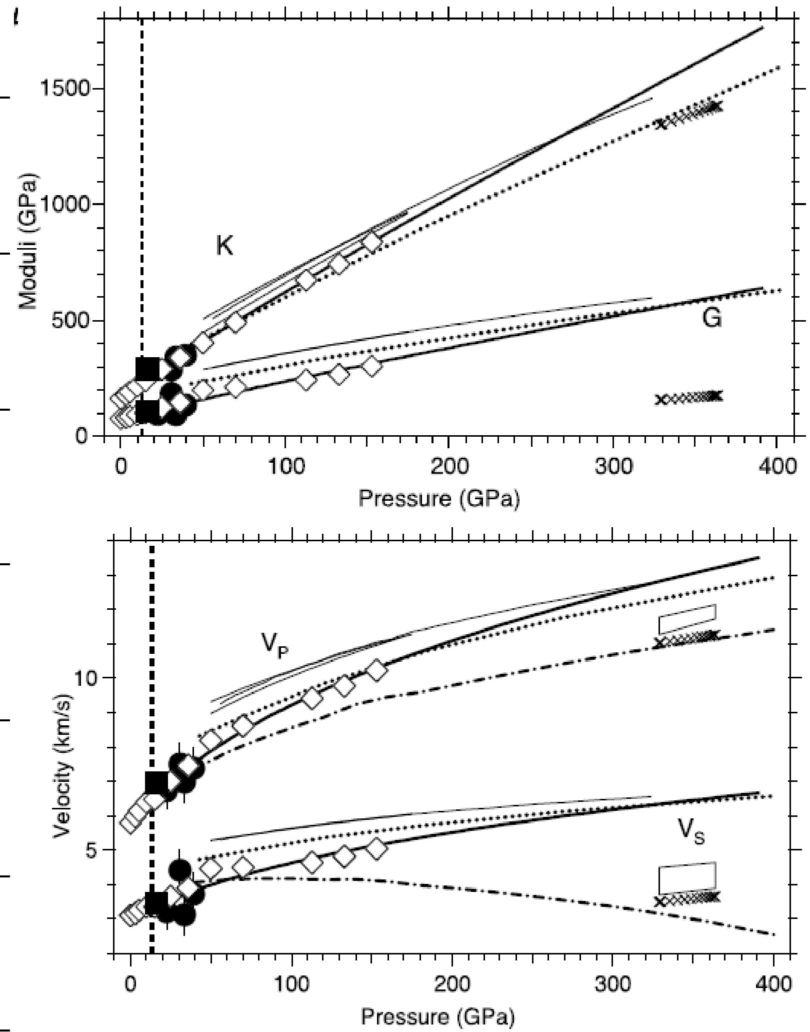
$$\frac{3}{V_D^3} = \frac{1}{V_P^3} + \frac{2}{V_S^3}$$

$$\frac{K}{\rho} = V_P^2 - \frac{4}{3}V_S^2$$

$$\frac{G}{\rho} = V_S^2$$







H.K. Mao, et.al., Science **292**, 914 (2001)

Properties derived from vibrational density of states

The partition function for the harmonic lattice is given by

$$\ln Z^N = -3N \int \ln\left(2\sinh\frac{\beta E}{2}\right) g(E)\,\mathrm{d}E$$

the vibrational energy per atom

$$U = -\frac{\partial \ln Z}{\partial \beta} = \frac{3}{2}\int E\coth\frac{\beta E}{2}\, g(E)\,\mathrm{d}E$$

vibrational entropy per atom S

$$S = k_{\mathrm{B}}\beta U + k_{\mathrm{B}}\ln Z$$

the free energy per atom F

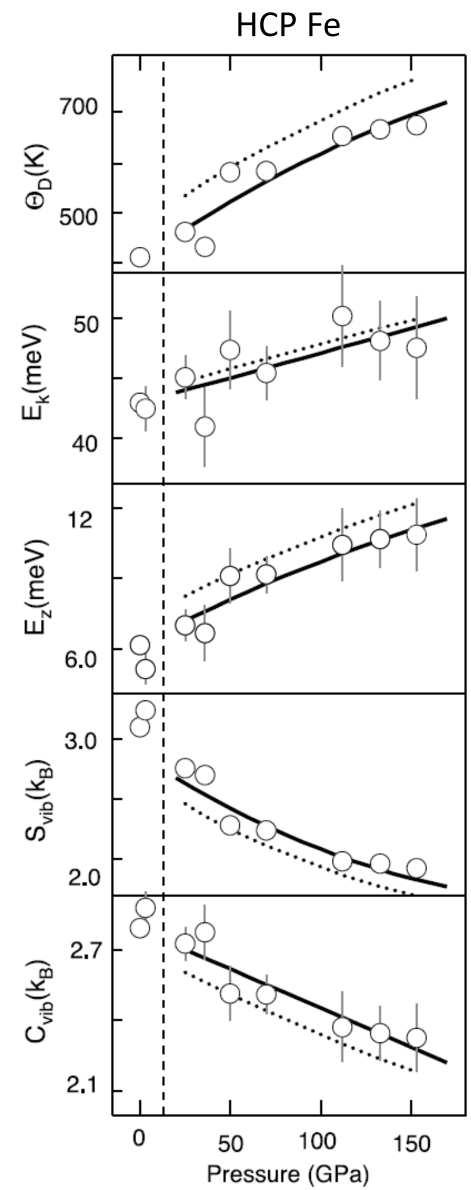
$$F = -\frac{1}{\beta}\ln Z$$

the specific heat per atom at constant volume

$$c_V = \frac{\partial U}{\partial T} = k_{\mathrm{B}}\beta^2\frac{\partial^2 \ln Z}{\partial \beta^2} = 3k_{\mathrm{B}}\int\left(\frac{\beta E}{2\sinh(\beta E/2)}\right)^2 g(E)\,\mathrm{d}E$$

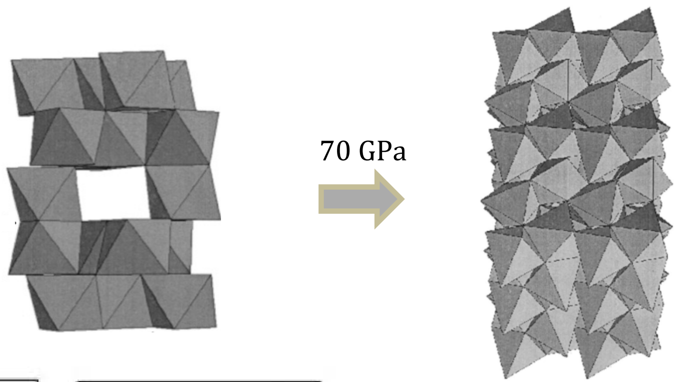
mean force constant

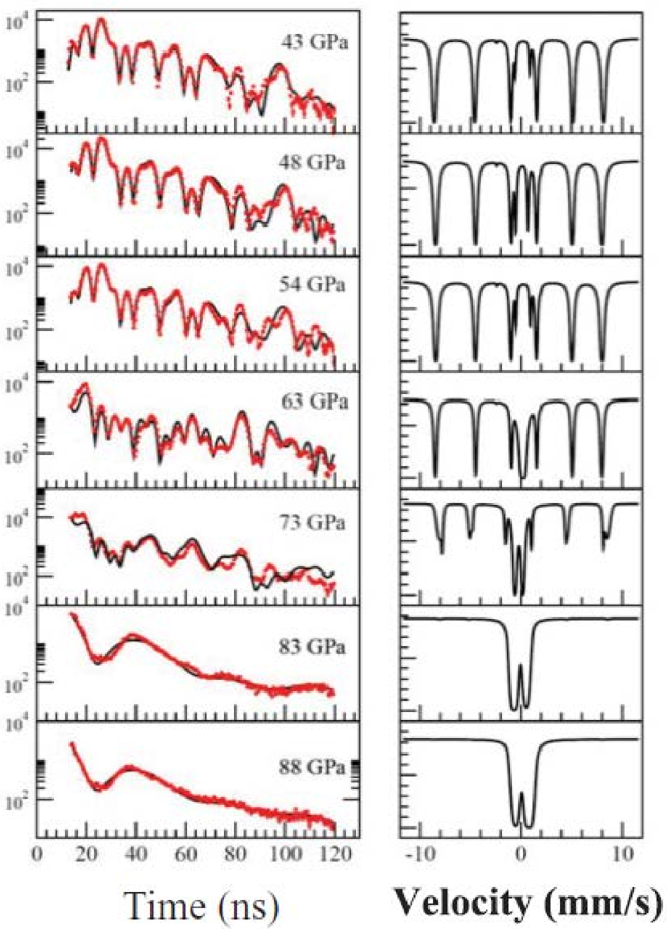
$$F_m = \frac{9}{10}\frac{k^2}{E_r} k_{\mathrm{B}}^2 \theta_{\mathrm{D}}^2$$

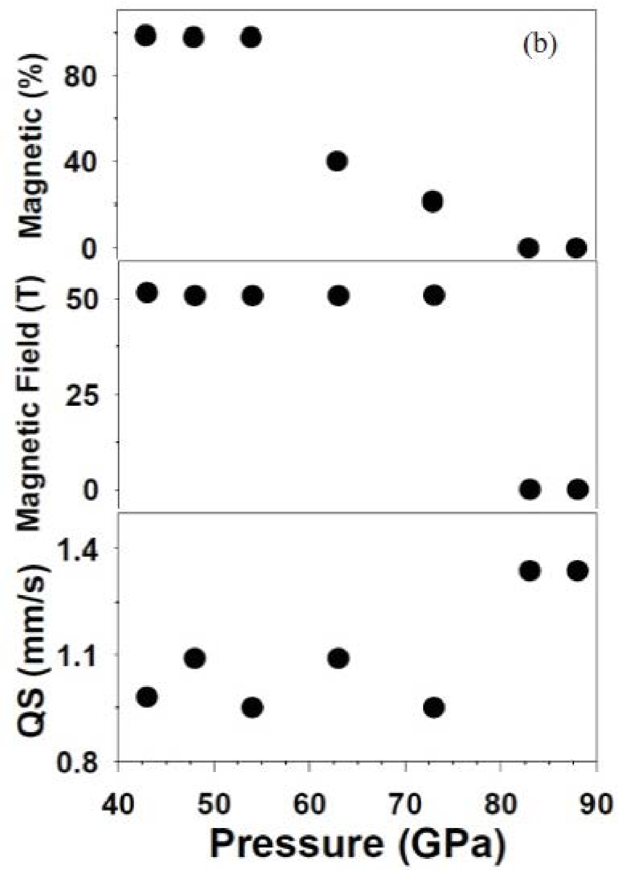


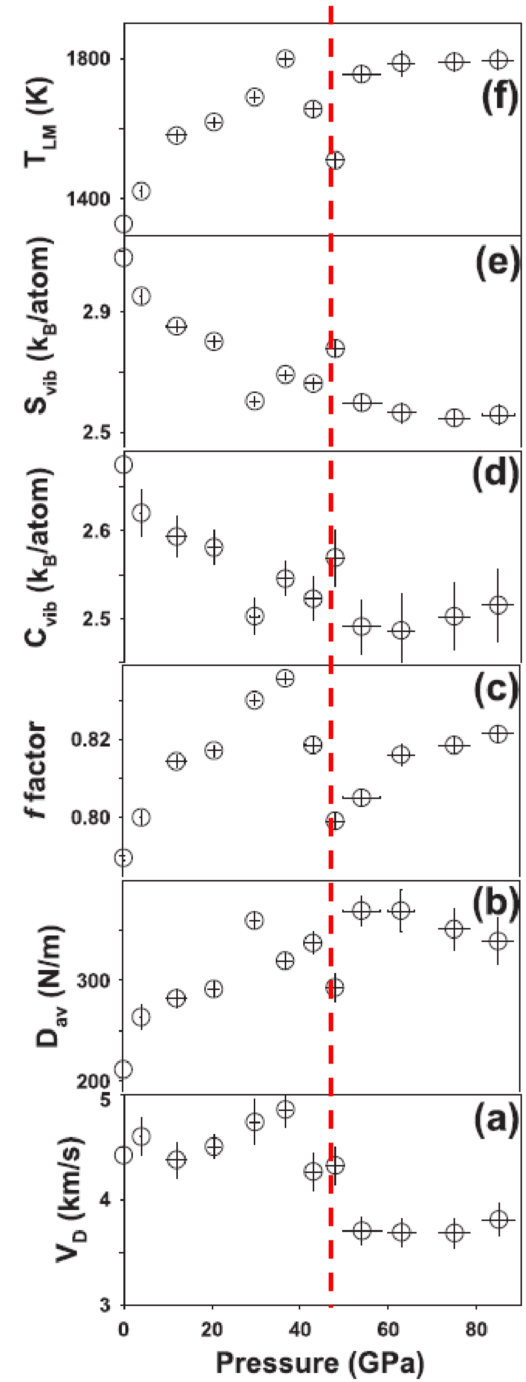
H.K. Mao, et.al., Science **292**, 914 (2001)

Hematite Fe_2O_3



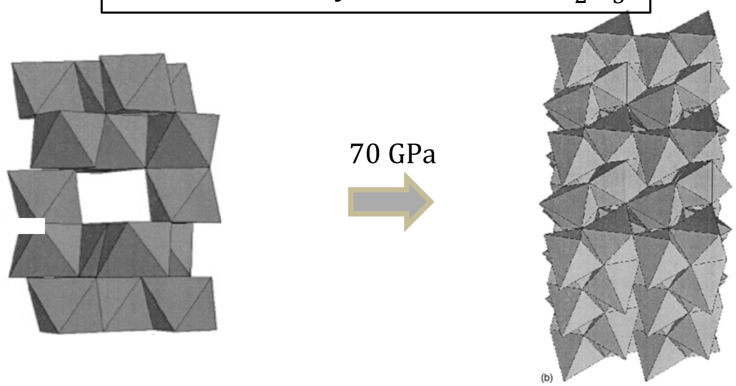


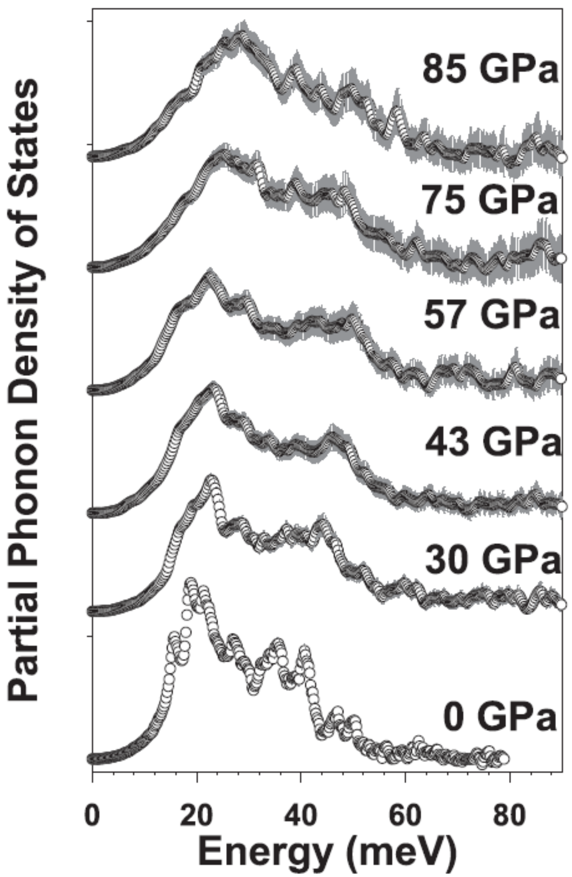


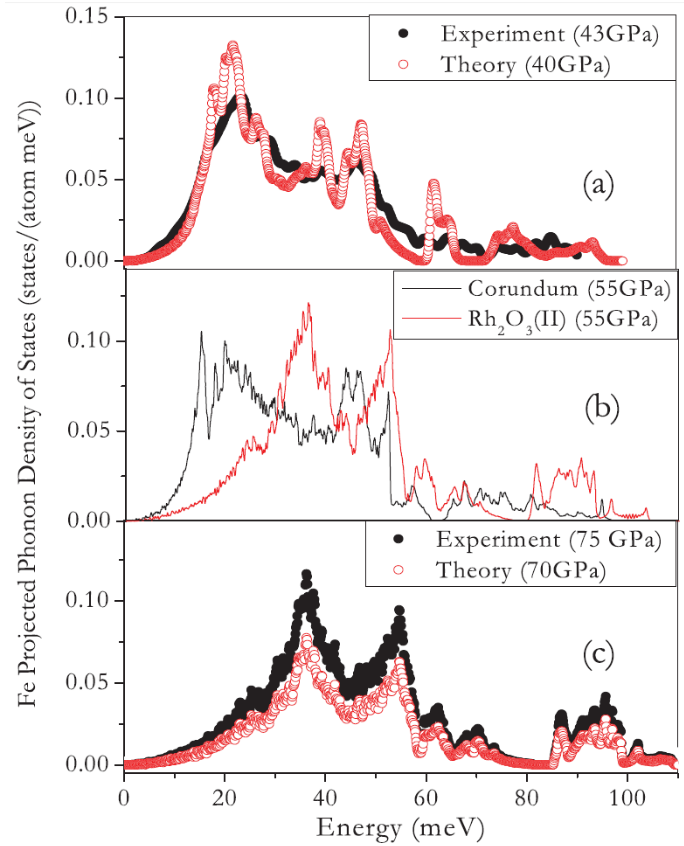


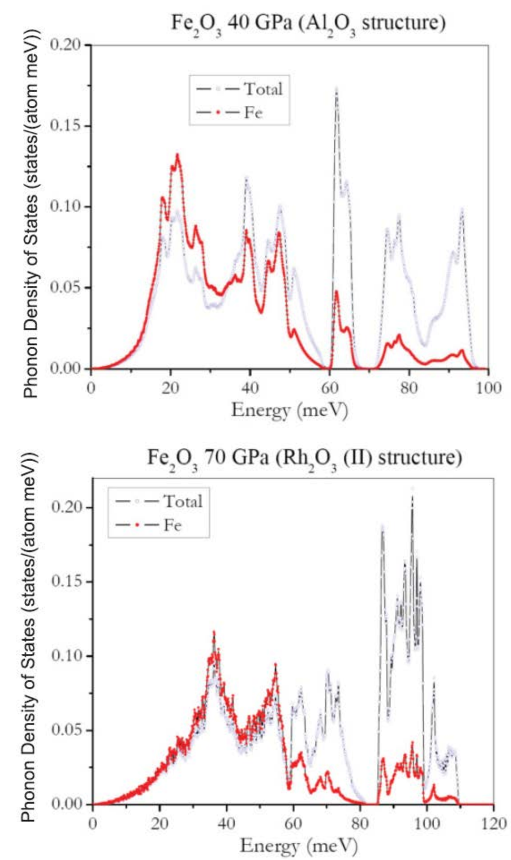
J.F. Lin, J.S. Tse, et.al., *Phys. Rev*. B **84**, 064424 (2011).

Phase stability - Hematite Fe_2O_3



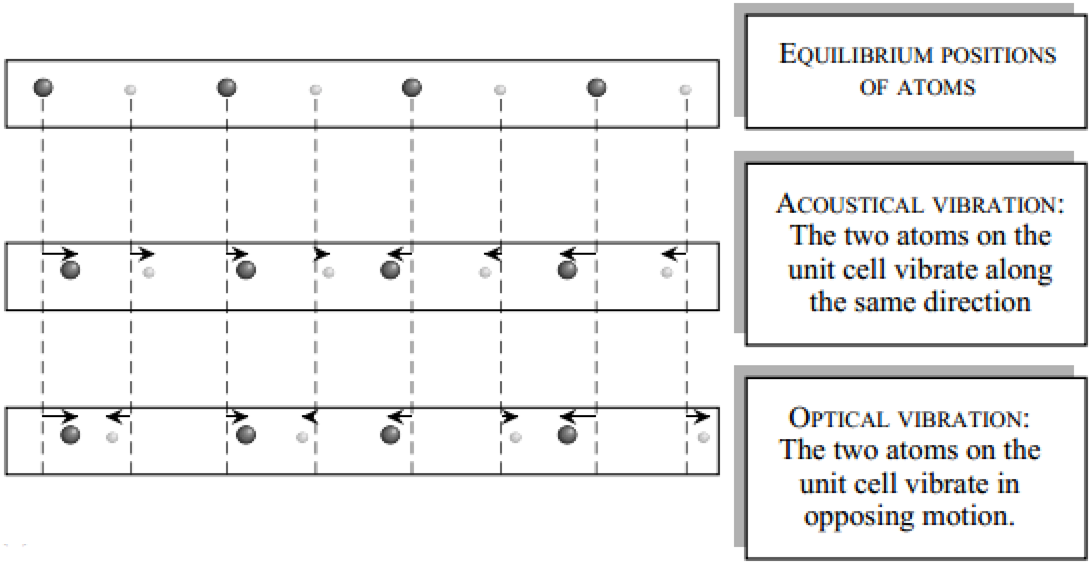


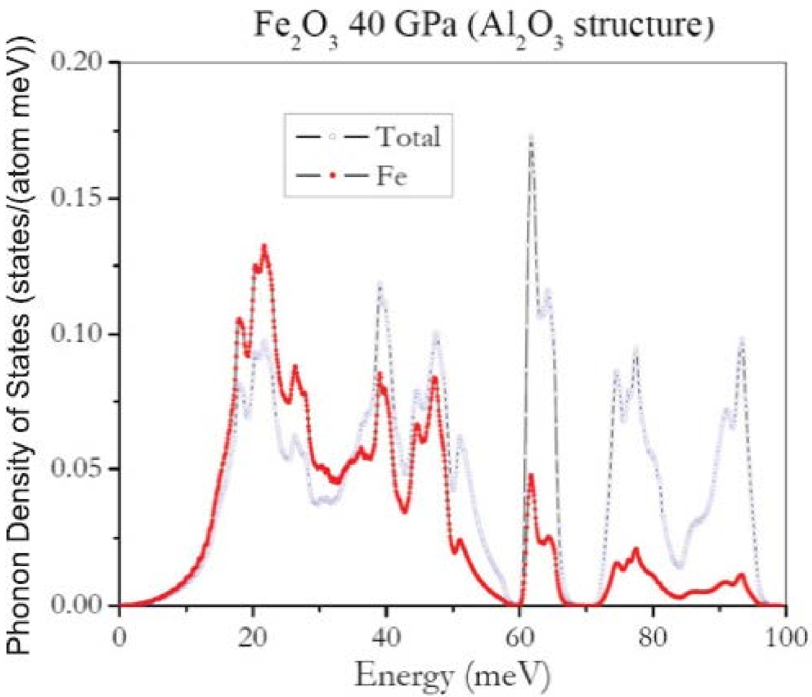


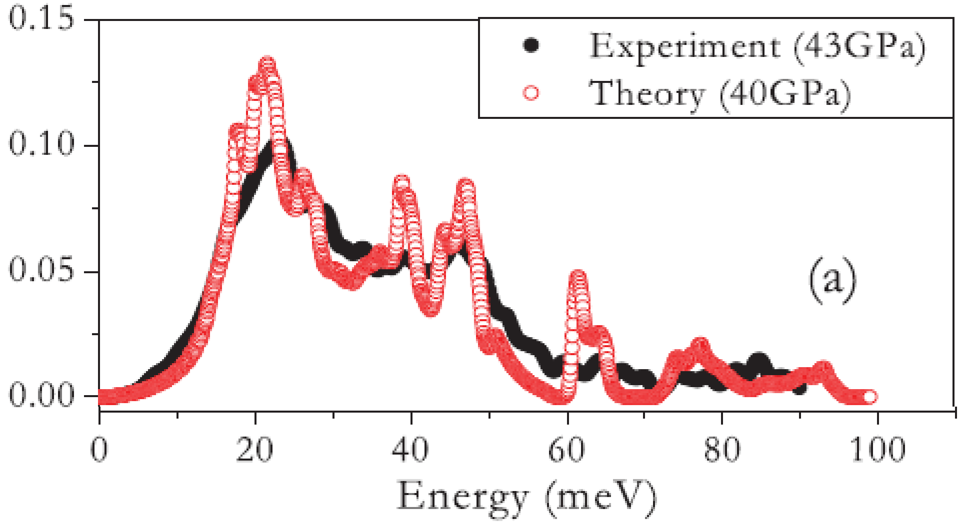


J.F. Lin, J.S. Tse, et.al., *Phys. Rev*. B **84**, 064424 (2011).

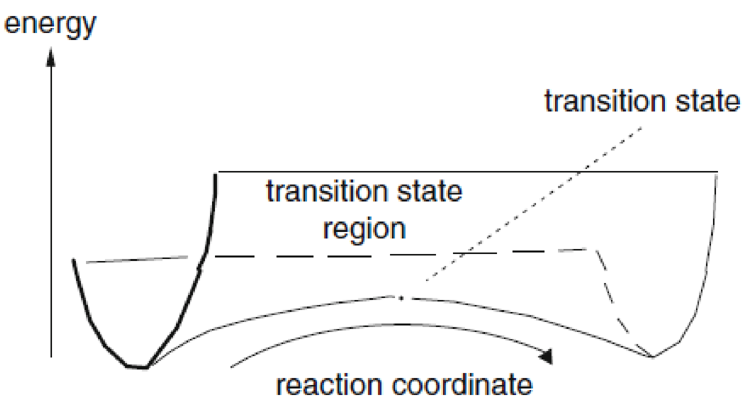
Why it works for multi-component systems?







Soft mode and Gruneisen parameter



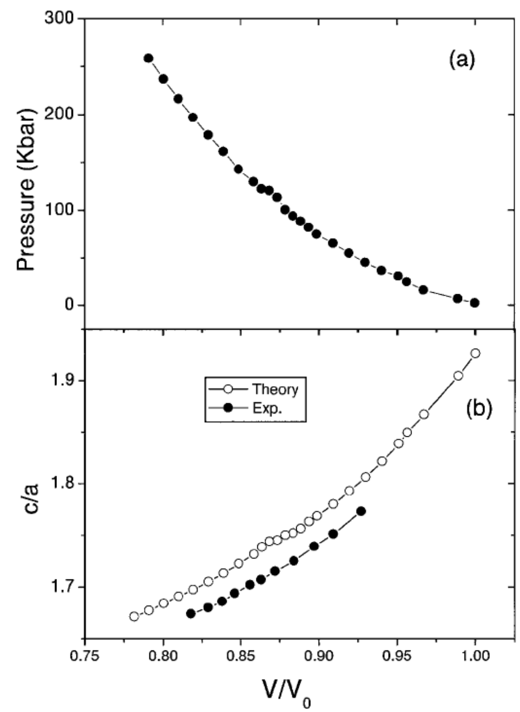
$$\gamma_i(\boldsymbol{q}) = -\frac{\partial \ln \omega(\boldsymbol{q})_i}{\partial \ln V}$$

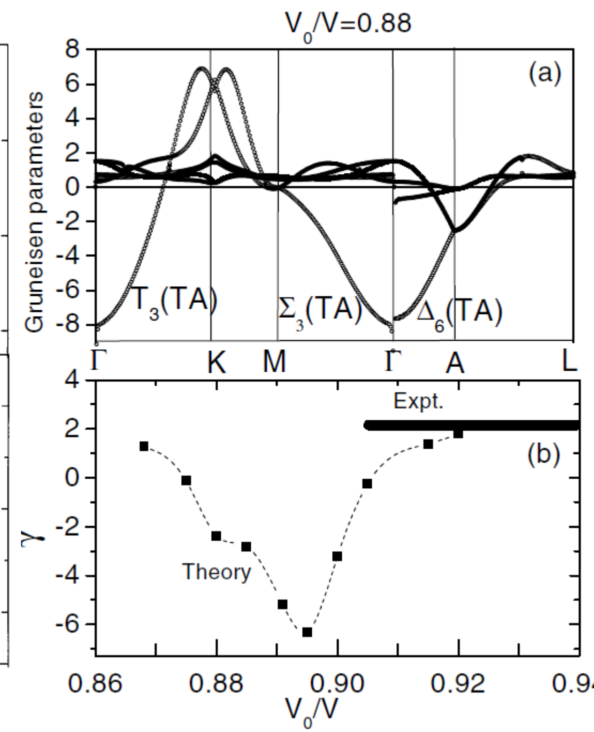
$$\tilde{\nu} = \frac{1}{2\pi c}\left(\frac{k}{\mu}\right)^{1/2}$$

$$\boldsymbol{F} = -\boldsymbol{k}\boldsymbol{q} \quad \Rightarrow \quad -\boldsymbol{k} = \frac{\partial \boldsymbol{F}}{\partial \boldsymbol{q}} = \frac{\partial^2 \boldsymbol{E}}{\partial \boldsymbol{q}^2}$$

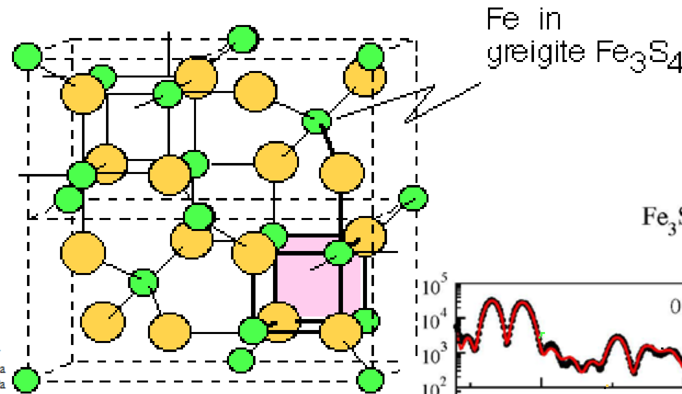
For a *transition state* $\quad \frac{\partial^2 \boldsymbol{E}}{\partial \boldsymbol{q}^2} > 0$

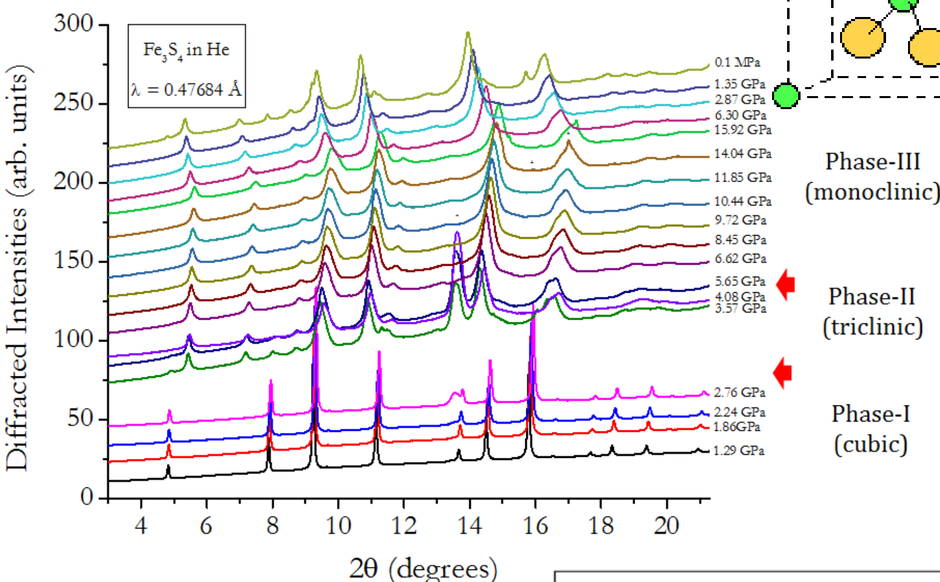
$\boldsymbol{k} < 0$ and $\tilde{\nu}$ is imaginary

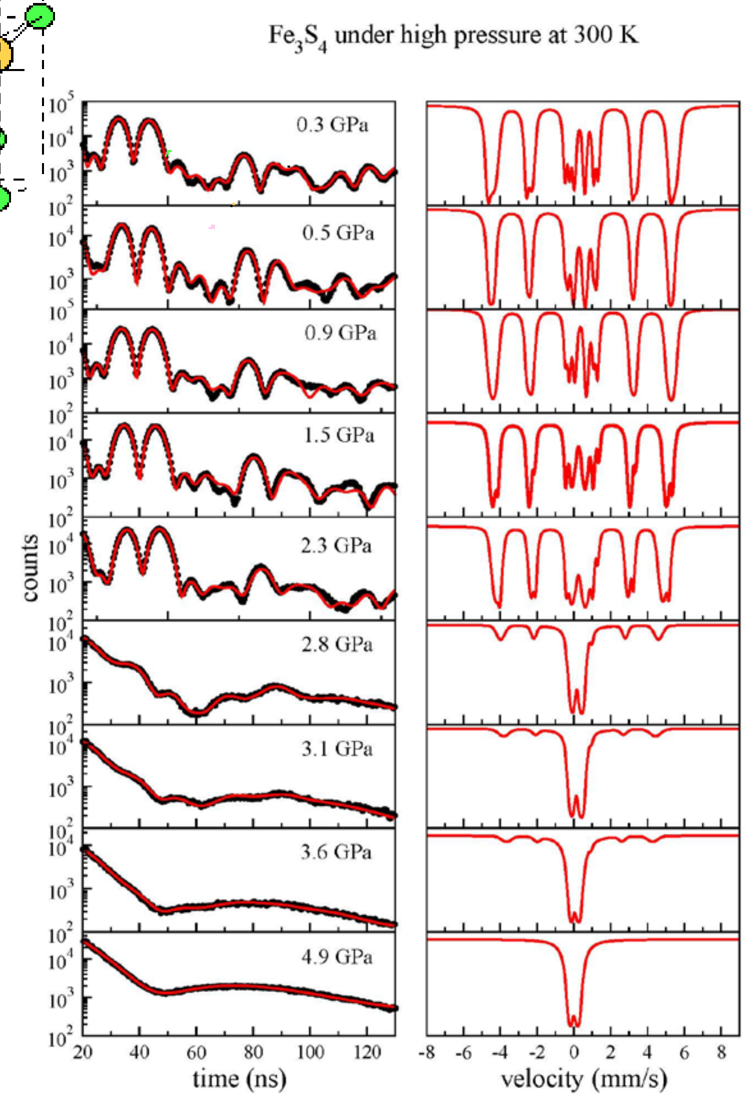


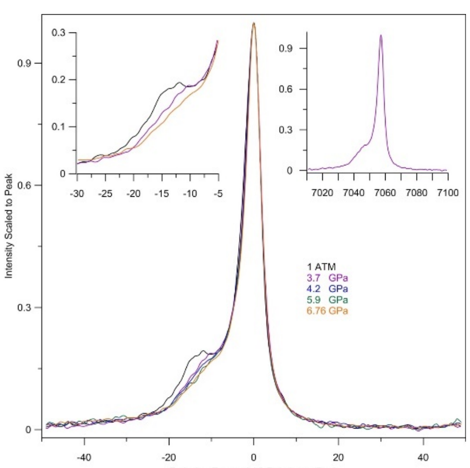


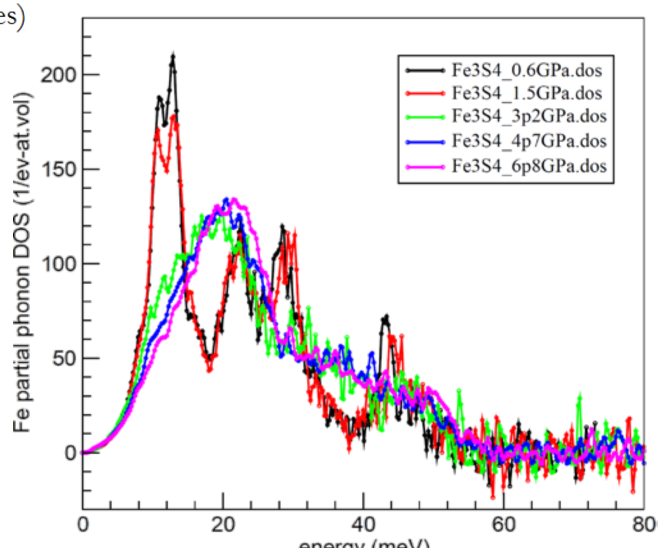
Structural phase Transition



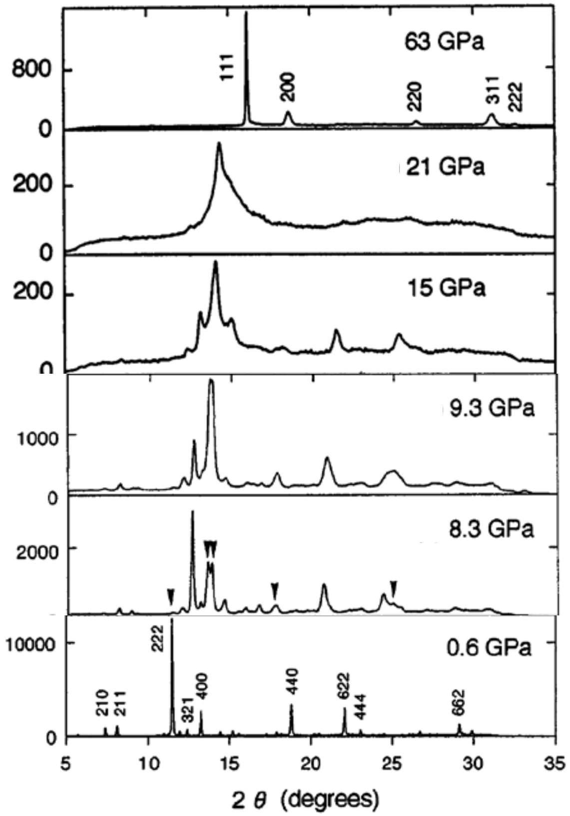


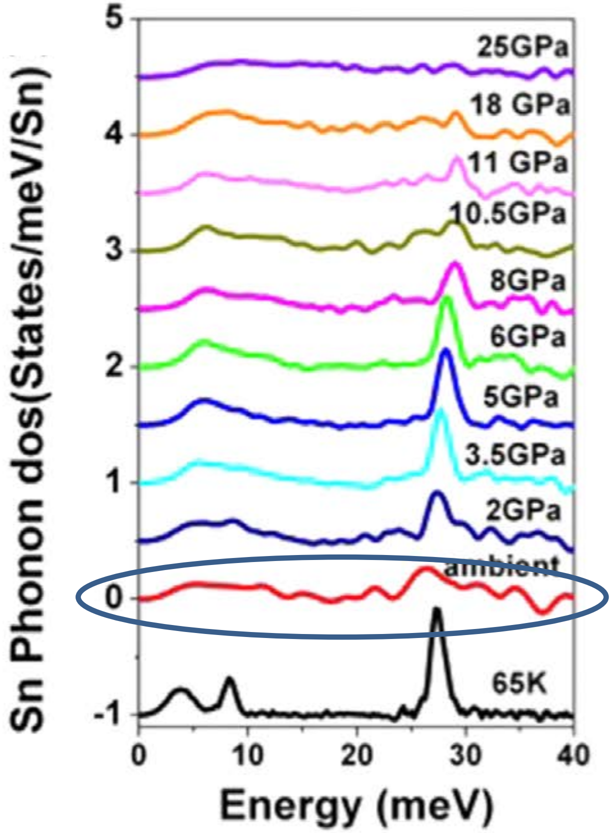


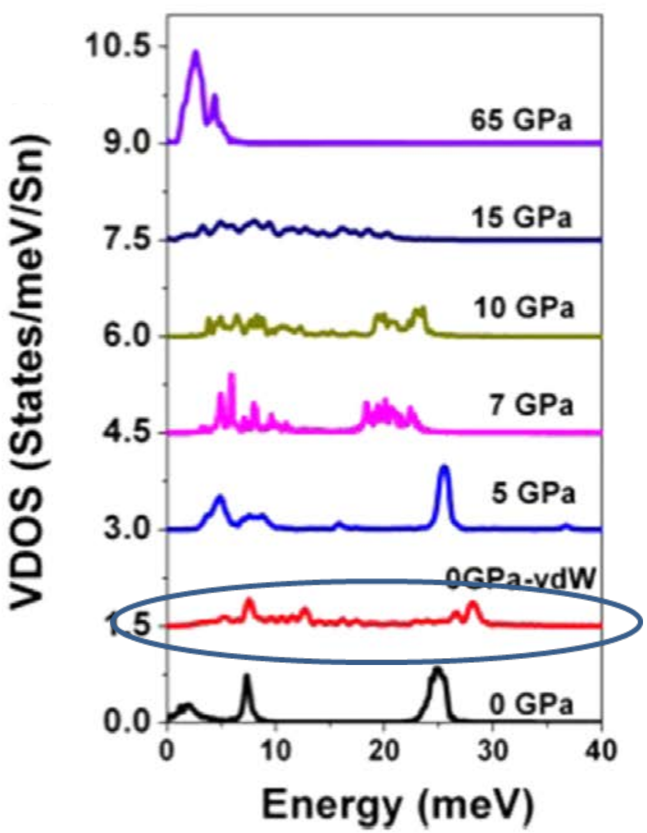




SnI_4 – effect of temperature





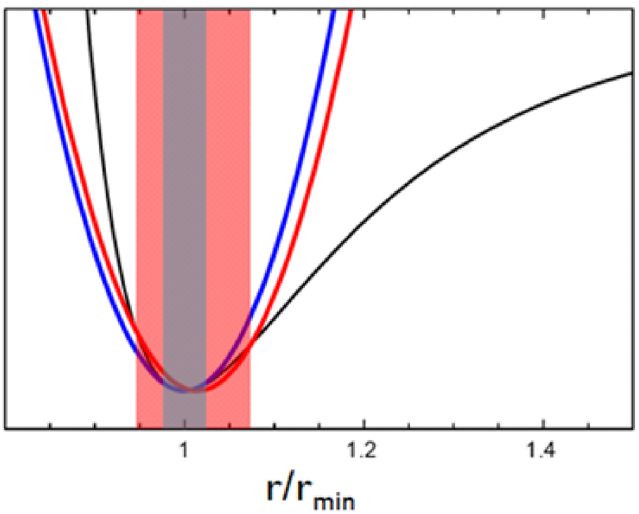


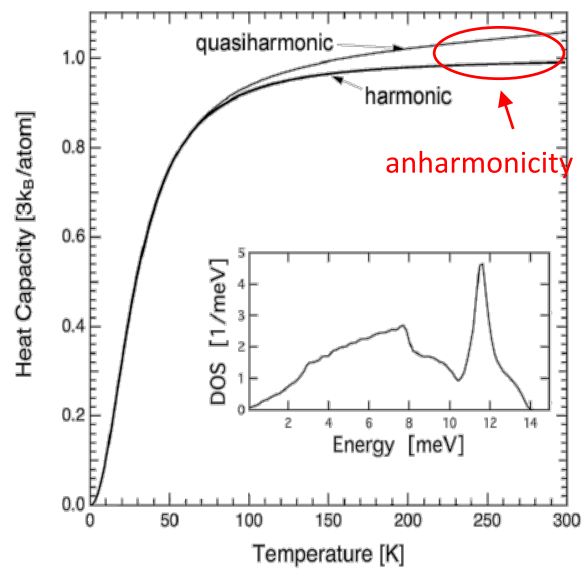
H. Liu, J. S. Tse, M. Y. Hu, W. Bi, J. Zhao, E. E. Alp, M. Pasternak, R. D. Taylor, and J. C. Lashley
J. Chem. Phys., **143**, 164508 (2015);

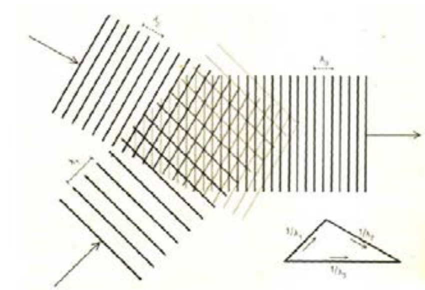
Phonon anharmonicity

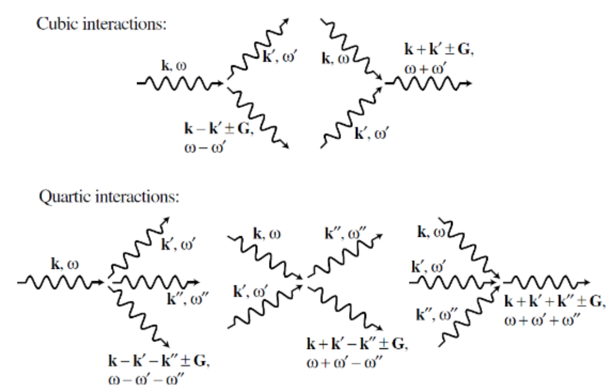
1. The heat capacity becomes T independent for T>T_D.
2. There is no thermal expansion of solids.
3. Thermal conductivity of solids is infinite

$$U(x) = U_{harm}(x) + U_{anharm}(x) = cx^2 - gx^3 - fx^4$$



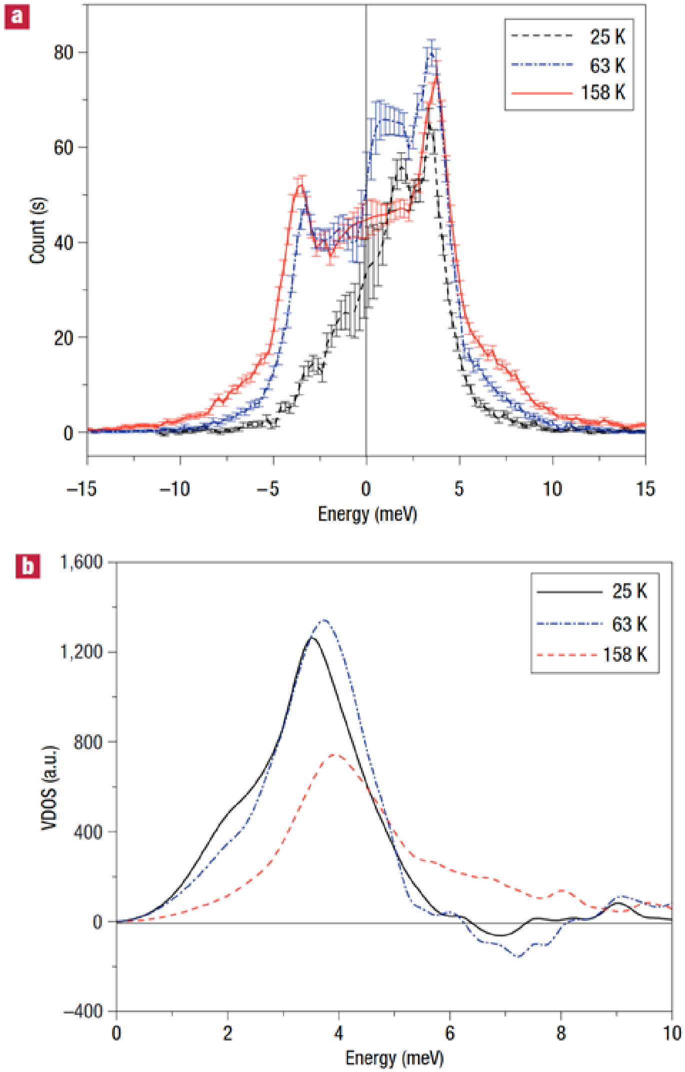


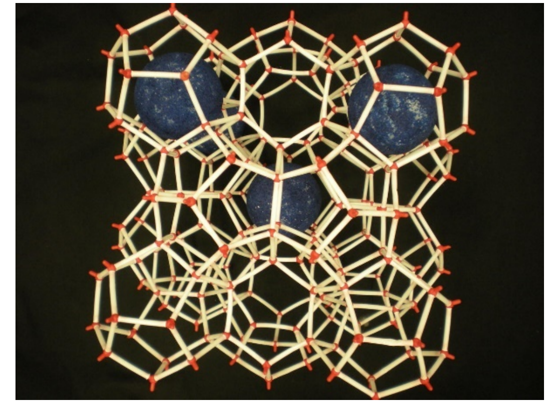


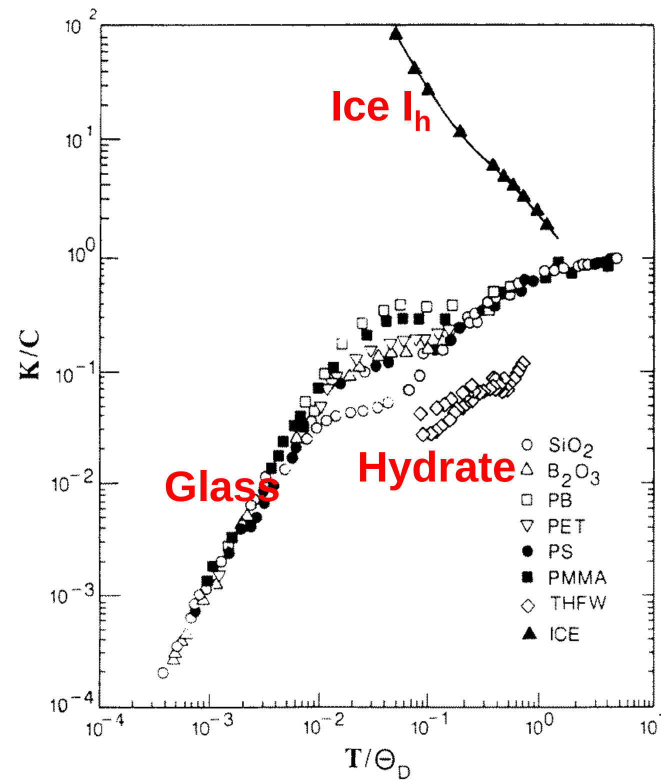


If the lattice potential is harmonic, the phonon frequencies are volume-independent, and the thermal expansion coefficient is zero at all temperatures.

Anharmonic motions of Kr in the clathrate hydrate







J. S. Tse, D. D. Klug, J. Y. Zhao, W. Sturhahn, E. E. Alp, J. Baumert, C. Gutt, M. R. Johnson and W. Press, *Nature Materials,* 4, 917 - 921 (2005)

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