

Elastic Properties of Solids

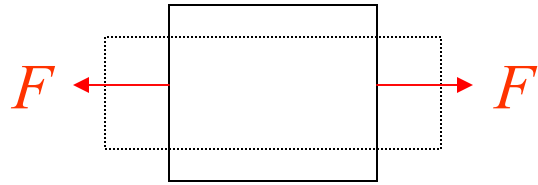
We continue our quest to relate bulk (macroscopic) properties of materials to interatomic interactions/potentials (microscopic properties).

Materials show elasticity, i.e. will deform by an amount proportional to the applied force but will return to its original form when the force is removed

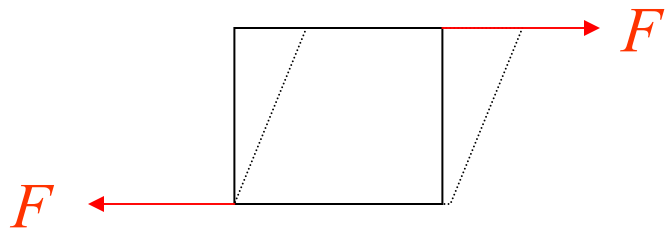
For the moment let us consider **hydrostatic compression** only (see next slide). If we apply a uniform pressure increment dP to a sample of volume V , we will produce a change (reduction) in volume dV

Definition: BULK MODULUS = $\kappa = -V \frac{dP}{dV}$

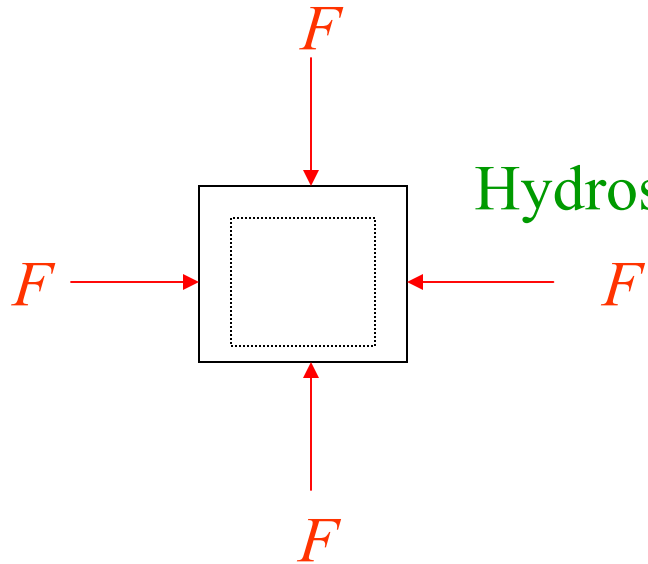
1/ κ - COMPRESSIBILITY



Stretching (YOUNG'S MODULUS)



Shearing (SHEAR MODULUS)



Hydrostatic compression (BULK MODULUS)

How is bulk modulus related to interatomic forces? Clearly, we have to measure energy conversion and to relate P and V to the energy.

$$\Delta E = E(\text{AFTER}) - E(\text{BEFORE}) = Q + W$$

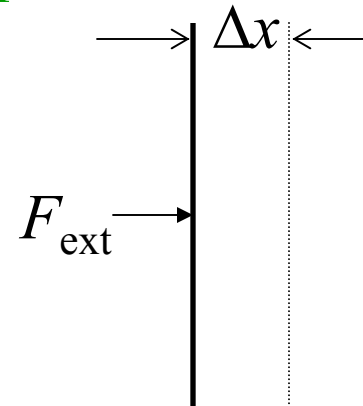
Heat absorbed

Work done on sample

The point is that at low temperature the energy E is dominated by the microscopic potential energy. Let P denote the pressure inside the material. To compress the material we have to apply an external force $|F_{\text{ext}}| = P.A$, A – surface area over which pressure P is applied.

$$\begin{aligned} W &= (\text{Force}).(\text{Displacement}) = -P(A \Delta x) \\ &= -P. \Delta V \end{aligned}$$

$$\Delta E = Q - P. \Delta V$$



There are two different possible experimental situations:

1) ISOTHERMAL = constant temperature ($Q \neq 0$), $\kappa_T = -V \left(\frac{dP}{dV} \right)_T$

2) ADIABATIC = thermally isolated ($Q = 0$), $\kappa_S = -V \left(\frac{dP}{dV} \right)_S$

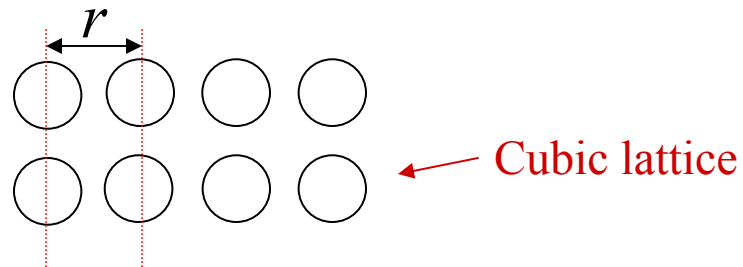
At low temperature, however, Q will be small compared to ΔE = so we can neglect it

$$\Delta E \approx -P \cdot \Delta V \Rightarrow P = - \left(\frac{dE}{dV} \right)$$

$$\kappa_T = \kappa_S = \kappa = +V \left(\frac{d^2 E}{dV^2} \right)$$

At low temperature when E is dominated by potential energy

For a molecular solid



$$E = E(r) = \frac{1}{2}nNV(r)$$

↖
Pair potential

1 molecule fills $\approx r^3$ volume $\Rightarrow V = \text{volume} = Nr^3$

$$\frac{dE}{dV} = \frac{dr}{dV} \cdot \frac{dE}{dr}$$

$$\frac{d^2E}{dV^2} = \left(\frac{d^2r}{dV^2}\right) \cdot \frac{dE}{dr} + \frac{dr}{dV} \cdot \frac{d}{dV} \left(\frac{dE}{dr}\right) = \left(\frac{d^2r}{dV^2}\right) \cdot \frac{dE}{dr} + \left(\frac{dr}{dV}\right)^2 \cdot \frac{d^2E}{dr^2}$$

↑

$$\left(\frac{dr}{dV}\right) \cdot \frac{d}{dr} \left(\frac{dE}{dV}\right)$$

For small compressions $r = a_0$ (MINIMUM OF PAIR POTENTIAL)

$$\frac{dE}{dr} = \frac{1}{2} nN \frac{dV(r)}{dr} = 0 \quad \text{at } r = a_0$$

$$\frac{d^2E}{dV^2} = \left(\frac{dr}{dV} \right)^2 \frac{d^2V(r)}{dr^2} \Big|_{r=a_0} = \left(\frac{1}{3Nr^2} \right)^2 \frac{1}{2} nN \frac{d^2V(r)}{dr^2} \Big|_{r=a_0}$$

$$V = Nr^3 \Rightarrow \frac{dV}{dr} = 3Nr^2 \Rightarrow \frac{dr}{dV} = \frac{1}{3Nr^2}$$

$$\frac{d^2E}{dV^2} = \left(\frac{n}{18Na_0^4} \right)^2 \frac{d^2V(r)}{dr^2} \Big|_{r=a_0}$$

$$\kappa = V \frac{d^2 E}{dV^2} = (Na_0^4) \frac{d^2 E}{dV^2} = \frac{n}{18a_0} \left. \frac{d^2 V(r)}{dr^2} \right|_{r=a_0}$$

$$L-J \quad V(r) = 4\varepsilon \left[\left(\frac{\sigma}{r} \right)^{12} - \left(\frac{\sigma}{r} \right)^6 \right] \quad (a_0 = 2^{\frac{1}{6}} \sigma)$$

$$\frac{dV(r)}{dr} = 4\varepsilon \left[-12 \frac{\sigma^{12}}{r^{13}} + 6 \frac{\sigma^6}{r^7} \right]$$

$$\frac{d^2 V(r)}{dr^2} = 4\varepsilon \left[156 \frac{\sigma^{12}}{r^{14}} - 42 \frac{\sigma^6}{r^8} \right]$$

$$\left. \frac{d^2V(r)}{dr^2} \right|_{r=a_0} = \varepsilon [156 - 84] = \frac{72\varepsilon}{a_0^2}$$

$$\kappa = \frac{4n\varepsilon}{a_0^3} = \frac{8\left(\frac{1}{2}nN_A\varepsilon\right)}{N_A a_0^3} = \frac{8L_0}{V_0}$$

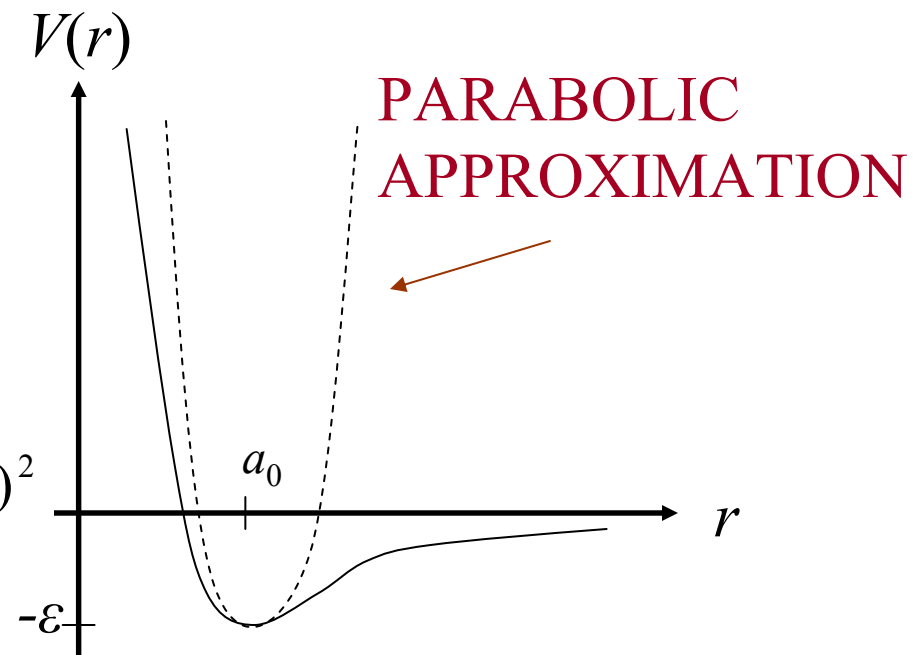
$$\kappa = 8 \frac{\text{MOLAR BINDING ENERGY}}{\text{MOLAR VOLUME}}$$

The quantity $\left. \frac{d^2V(r)}{dr^2} \right|_{r=a_0} = V''(a_0)$ can give us information

About the DYNAMICS of a microscopic particle, i.e. it can tell us how the particles move when slightly displaced from equilibrium

Consider an *L-J* type potential. We can approximate the potential by a simple parabola:

$$V_{\text{Approx}}(r) = -\varepsilon + b(r - a_0) + \frac{1}{2}c(r - a_0)^2$$



$$V_{\text{Approx}}(a_0) = -\varepsilon = V(a_0)$$

$$\left. \frac{dV_{\text{Approx}}(r)}{dr} \right|_{r=a_0} = b + c(r - a_0) \Big|_{r=a_0} = b = \left. \frac{dV(r)}{dr} \right|_{r=a_0} = 0$$

$$\left. \frac{d^2V_{\text{Approx}}(r)}{dr^2} \right|_{r=a_0} = c = \left. \frac{d^2V(r)}{dr^2} \right|_{r=a_0} = V''(a_0)$$

$$\Rightarrow V_{\text{Approx}}(r) = -\varepsilon + \frac{1}{2} V''(a_0)(r - a_0)^2$$

In Mathematics you will soon learn that V_{Approx} is just the first few terms of a Taylor's series representation of $V(r)$. If $r - a_0$ is small enough V_{Approx} is very close to $V(r)$.


What about the force F_{Approx} ?

$$F_{\text{Approx}}(r) = -\frac{dV_{\text{Approx}}}{dr} = -V''(a_0)(r - a_0)$$

Let $x = r - a_0$

$$F_{\text{Approx}}(x) = -V''(a_0)x = -cx$$

There is a **LINEAR RESTORING FORCE!** This means that if the molecule (or atom) is displaced from equilibrium and let go with the other molecule fixed it will undergo **SIMPLE HARMONIC MOTION**, i.e. of the form $mX'' = -cX$)

SHM frequency $\nu = \frac{1}{2\pi} \sqrt{\frac{c}{m}}$ 

Einstein showed that in a real crystal with many molecules (or atoms)
The total restoring force is:

$$F^{Tot}_{Approx}(x) = -\frac{24n\varepsilon}{a_0^2} \cdot x$$

Force constant

Therefore the frequency associated with SHM is:

$$\nu_E = \frac{1}{2\pi} \sqrt{\frac{24n\varepsilon}{ma_0^2}}$$

ν_E = EINSTEIN FREQUENCY

The EINSTEIN FREQUENCY is an approximate expression for how fast a molecule will vibrate when displaced from equilibrium

Summary

Next Topic: Liquids

Elastic Properties of Solids