A DEEPER LOOK 10 Establishing the relation between bulk and molecular properties

The isothermal compressibility is defined as $\kappa_T = -(\partial V/\partial p)_T/V$, and the bulk modulus K is simply $1/\kappa_T$, so it follows that $K = -V(\partial p/\partial V)_T$. The following calculation supposes that T is fixed at 0, so T is no longer a variable and the partial derivative becomes a complete derivative: $K = -V(\mathrm{d}p/\mathrm{d}V)$ at $T = 0$.

Step 1 *Express the pressure in terms of the internal energy*

You need to start from the fundamental thermodynamic equation $\mathrm{d}U = T\mathrm{d}S - p\mathrm{d}V$ (this is eqn 3E.1 of Topic 3E), and impose the condition $T = 0$; it follows that $p = -\mathrm{d}U/\mathrm{d}V$ at $T = 0$. This relation is now combined with the definition of K to give

$$K = -V\frac{\mathrm{d}p}{\mathrm{d}V} = V\frac{\mathrm{d}^2U}{\mathrm{d}V^2} \qquad \text{(at } T = 0\text{)}$$

This expression shows that the bulk modulus (and through eqn 15D.3, the other two moduli) depends on the curvature of a plot of the internal energy against volume.

Step 2 *Relate the change in volume to the change in a lattice parameter*

Now express the variation of internal energy with volume in terms of its variation with a lattice parameter, a, such as the length of the side of a unit cell:

$$\frac{\mathrm{d}U}{\mathrm{d}V} = \frac{\mathrm{d}U}{\mathrm{d}a}\frac{\mathrm{d}a}{\mathrm{d}V}$$

Then

$$\frac{\mathrm{d}^2U}{\mathrm{d}V^2} = \frac{\mathrm{d}}{\mathrm{d}V}\left(\frac{\mathrm{d}U}{\mathrm{d}a}\frac{\mathrm{d}a}{\mathrm{d}V}\right)$$

$$= \frac{\mathrm{d}U}{\mathrm{d}a}\left(\frac{\mathrm{d}^2a}{\mathrm{d}V^2}\right) + \left(\frac{\mathrm{d}^2U}{\mathrm{d}V\mathrm{d}a}\right)\frac{\mathrm{d}a}{\mathrm{d}V}$$

Now use

$$\frac{\mathrm{d}^2U}{\mathrm{d}V\mathrm{d}a} = \frac{\mathrm{d}}{\mathrm{d}a}\left(\frac{\mathrm{d}U}{\mathrm{d}V}\right) = \frac{\mathrm{d}}{\mathrm{d}a}\left(\frac{\mathrm{d}U}{\mathrm{d}a}\frac{\mathrm{d}a}{\mathrm{d}V}\right)$$

$$= \left(\frac{\mathrm{d}^2U}{\mathrm{d}a^2}\right)\left(\frac{\mathrm{d}a}{\mathrm{d}V}\right) + \left(\frac{\mathrm{d}U}{\mathrm{d}a}\right)\frac{\mathrm{d}^2a}{\mathrm{d}V\mathrm{d}a}$$

and so obtain

$$\frac{\mathrm{d}^2U}{\mathrm{d}V^2} = \left(\frac{\mathrm{d}U}{\mathrm{d}a}\right)\left(\frac{\mathrm{d}^2a}{\mathrm{d}V^2}\right) + \left(\frac{\mathrm{d}^2U}{\mathrm{d}a^2}\right)\left(\frac{\mathrm{d}a}{\mathrm{d}V}\right)^2$$

$$+ \left(\frac{\mathrm{d}U}{\mathrm{d}a}\right)\overbrace{\left(\frac{\mathrm{d}^2a}{\mathrm{d}V\mathrm{d}a}\right)\left(\frac{\mathrm{d}a}{\mathrm{d}V}\right)}^{(\mathrm{d}^2a/\mathrm{d}V^2)}$$

$$= 2\left(\frac{\mathrm{d}U}{\mathrm{d}a}\right)\left(\frac{\mathrm{d}^2a}{\mathrm{d}V^2}\right) + \left(\frac{\mathrm{d}^2U}{\mathrm{d}a^2}\right)\left(\frac{\mathrm{d}a}{\mathrm{d}V}\right)^2$$

To calculate K at the equilibrium volume of the sample, a is set to its equilibrium value, a_{eq}, and recognize that, at equilibrium, $\mathrm{d}U/\mathrm{d}a = 0$. Therefore, the first (blue) term on the right is zero leaving

$$\frac{\mathrm{d}^2U}{\mathrm{d}V^2} = \left(\frac{\mathrm{d}^2U}{\mathrm{d}a^2}\right)\left(\frac{\mathrm{d}a}{\mathrm{d}V}\right)^2$$

This relation now implies that, at $T = 0$,

$$K = V\left(\frac{\mathrm{d}^2U}{\mathrm{d}V^2}\right)_0 = V\left(\frac{\mathrm{d}^2U}{\mathrm{d}a^2}\right)_0\left(\frac{\mathrm{d}a}{\mathrm{d}V}\right)_0^2 \tag{1}$$

where the subscript 0 denotes that the derivatives are evaluated at the equilibrium dimensions of the unit cell by setting $a = a_{eq}$ after the derivative has been calculated. At this stage, write the volume V as $V = a_{eq}^3$; it follows that $\mathrm{d}a/\mathrm{d}V = 1/3a^2$, so

$$K = \frac{V}{(3a_{eq}^2)^2}\left(\frac{\mathrm{d}^2U}{\mathrm{d}a^2}\right)_0 = \frac{1}{9a_{eq}}\left(\frac{\mathrm{d}^2U}{\mathrm{d}a^2}\right)_0$$

Step 3 *Relate the internal energy to the intermolecular potential energy*

If the molecules in the solid interact by a pairwise Lennard-Jones (12,6)-potential energy $E_{LJ} = 4\varepsilon\{(R_0/R)^{12} - (R_0/R)^6\}$ where R is the internuclear distance between atoms (eqn 14B.12 in Topic 14B), it follows that the internal energy of the solid is $U = nN_A E_{LJ}$, where n is the amount of substance. The size of the unit cell scales with R, so $a = kR$, where k is a constant that depends on the type of unit cell; similarly, $a_{eq} = kR_{eq}$. The minimum potential energy is at $R_{eq} = 2^{1/6}R_0$. With these points in mind, take the second derivative of U with respect to a and obtain

$$\frac{\mathrm{d}^2U}{\mathrm{d}a^2} = \frac{1}{k^2}\frac{\mathrm{d}^2U}{\mathrm{d}R^2} = \frac{4\varepsilon nN_A}{k^2}\frac{\mathrm{d}}{\mathrm{d}R}\left\{-12\frac{R_0^{12}}{R^{13}} + 6\frac{R_0^6}{R^7}\right\}$$

$$= \frac{4\varepsilon nN_A}{k^2}\left\{12\times13\frac{R_0^{12}}{R^{14}} - 6\times7\frac{R_0^6}{R^8}\right\}$$

Now set R to its equilibrium value:

$$\left(\frac{\mathrm{d}^2U}{\mathrm{d}a^2}\right)_0 = \frac{4\varepsilon nN_A}{k^2}\left\{12\times13\frac{R_0^{12}}{R_{eq}^{14}} - 6\times7\frac{R_0^6}{R_{eq}^8}\right\}$$

$$= \frac{4\varepsilon nN_A}{k^2}\left\{\frac{12\times13}{2^{7/3}R_0^2} - \frac{6\times7}{2^{4/3}R_0^2}\right\} = \frac{72\varepsilon nN_A}{2^{1/3}k^2R_0^2}$$

In terms of the equilibrium internuclear distance R_{eq},

$$\left(\frac{d^2U}{da^2}\right)_0 = \frac{72\varepsilon nN_A}{2^{1/3}k^2(2^{-1/6}R_{eq})^2} = \frac{72\varepsilon nN_A}{k^2R_{eq}^2}$$

It then follows from eqn 1 that

$$K = \frac{1}{9a_{eq}} \times \underbrace{\frac{72\varepsilon nN_A}{k^2R_{eq}^2}}_{a_{eq}^2} = \frac{8\varepsilon nN_A}{\underbrace{a_{eq}^3}_{V}} = \frac{8\varepsilon nN_A}{V}$$

The molar volume is $V_m = V/n$, so finally

$$K = \frac{8\varepsilon N_A}{V_m}$$

That is, the bulk modulus is large if the interaction between molecules is strong and the molar volume is small.