ATOMISTIC BASIS OF ELASTICITY

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Introduction

The *Introduction to Elastic Response* Module introduced two very important material properties, the ultimate tensile strength σ_f and the Young's modulus E. To the effective mechanical designer, these aren't just numerical parameters that are looked up in tables and plugged into equations. The very nature of the material is reflected in these properties, and designers who try to function without a sense of how the material really works are very apt to run into trouble. Whenever practical in these modules, we'll make an effort to put the material's mechanical properties in context with its processing and microstructure. This module will describe how for most engineering materials the modulus is controlled by the atomic bond energy function.

For most materials, the amount of stretching experienced by a tensile specimen under a small fixed load is controlled in a relatively simple way by the tightness of the chemical bonds at the atomic level, and this makes it possible to relate stiffness to the chemical architecture of the material. This is in contrast to more complicated mechanical properties such as fracture, which are controlled by a diverse combination of microscopic as well as molecular aspects of the material's internal structure and surface. Further, the stiffness of some materials — notably rubber — arises not from bond stiffness but from disordering or entropic factors. Some principal aspects of these atomistic views of elastic response are outlined in the sections to follow.

Energetic effects

Chemical bonding between atoms can be viewed as arising from the electrostatic attraction between regions of positive and negative electronic charge. Materials can be classified based on the nature of these electrostatic forces, the three principal classes being

1. *Ionic materials,* such as NaCl, in which an electron is transferred from the less electronegative element (Na) to the more electronegative (Cl). The ions therefore differ by one electronic charge and are thus attracted to one another. Further, the two ions feel an attraction not only to each other but also to other oppositely charged ions in their vicinity; they also feel a repulsion from nearby ions of the same charge. Some ions may gain or lose more than one electron.

2. *Metallic materials,* such as iron and copper, in which one or more loosely bound outer electrons are released into a common pool which then acts to bind the positively charged atomic cores.

3. Covalent materials, such as diamond and polyethylene, in which atomic orbitals overlap to form a region of increased electronic charge to which both nuclei are attracted. This bond is directional, with each of the nuclear partners in the bond feeling an attraction to the negative region between them but not to any of the other atoms nearby.

In the case of ionic bonding, Coulomb's law of electrostatic attraction can be used to develop simple but effective relations for the bond stiffness. For ions of equal charge e the attractive force f_{attr} can be written:

$$f_{attr} = \frac{Ce^2}{r^2} \tag{1}$$

Here C is a conversion factor; For e in Coulombs, $C = 8.988 \times 10^9$ N-m^2/Coul^2. For singly ionized atoms, $e = 1.602 \times 10^{-19}$ Coul is the charge on an electron. The *energy* associated with the Coulombic attraction is obtained by integrating the force, which shows that the bond energy varies inversely with the separation distance:

$$U_{attr} = \int f_{attr} \, dr = \frac{-Ce^2}{r} \tag{2}$$

where the energy of atoms at infinite separation is taken as zero.
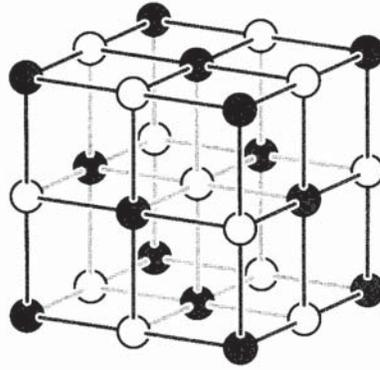

Figure 1: The interpenetrating cubic NaCl lattice.

If the material's atoms are arranged as a perfect crystal, it is possible to compute the electrostatic binding energy field in considerable detail. In the interpenetrating cubic lattice of the ionic NaCl structure shown in Fig. 1, for instance, each ion feels attraction to oppositely charged neighbors and repulsion from equally charged ones. A particular sodium atom is surrounded by 6 Cl$^-$ ions at a distance r, 12 Na$^+$ ions at a distance $r\sqrt{2}$, 8 Cl$^-$ ions at a distance $r\sqrt{3}$, etc. The total electronic field sensed by the first sodium ion is then:

$$U_{attr} = -\frac{Ce^2}{r} \left(\frac{6}{\sqrt{1}} - \frac{12}{\sqrt{2}} + \frac{8}{\sqrt{3}} - \frac{6}{\sqrt{4}} + \frac{24}{\sqrt{5}} - \cdots \right) \tag{3}$$

$$= \frac{-ACe^2}{r}$$

where $A = 1.747558 \cdots$ is the result of the previous series, called the *Madelung constant*[1]. Note that it is not sufficient to consider only nearest-neighbor attractions in computing the bonding energy; in fact the second term in the series is larger in magnitude than the first. The specific value for the Madelung constant is determined by the crystal structure, being 1.763 for CsCl and 1.638 for cubic ZnS.

At close separation distances, the attractive electrostatic force is balanced by mutual repulsion forces that arise from interactions between overlapping electron shells of neighboring ions; this force varies much more strongly with the distance, and can be written:

$$U_{rep} = \frac{B}{r^n} \tag{4}$$

Compressibility experiments have determined the exponent n to be 7.8 for the NaCl lattice, so this is a much steeper function than U_{attr}.
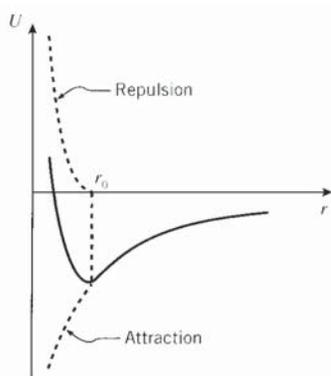

Figure 2: The bond energy function.

As shown in Fig. 2, the total binding energy of one ion due to the presence of all others is then the sum of the attractive and repulsive components:

$$\boxed{U = -\frac{ACe^2}{r} + \frac{B}{r^n}} \tag{5}$$

Note that the curve is *anharmonic* (not shaped like a sine curve), being more flattened out at larger separation distances. The system will adopt a configuration near the position of lowest energy, computed by locating the position of zero slope in the energy function:

$$(f)_{r=r_0} = \left(\frac{dU}{dr}\right)_{r=r_0} = \left(\frac{ACe^2}{r^2} - \frac{nB}{r^{n+1}}\right)_{r=r_0} = 0$$

$$r_o = \left(\frac{nB}{ACe^2}\right)^{\frac{1}{n-1}} \tag{6}$$

The range for n is generally 5–12, increasing as the number of outer-shell electrons that cause the repulsive force.

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[1]C. Kittel, *Introduction to Solid State Physics,* John Wiley & Sons, New York, 1966. The Madelung series does not converge smoothly, and this text includes some approaches to computing the sum.
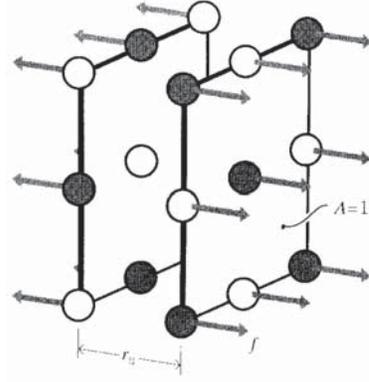
Example 1

Figure 3: Simple tension applied to crystal face.

In practice the n and B parameters in Eqn. 5 are determined from experimental measurements, for instance by using a combination of X-ray diffraction to measure r_0 and elastic modulus to infer the slope of the $U(r)$ curve. As an illustration of this process, picture a tensile stress σ applied to a unit area of crystal $(A = 1)$ as shown in Fig. 3, in a direction perpendicular to the crystal cell face. (The [100] direction on the (100) face, using crystallographic notation[2].) The total force on this unit area is numerically equal to the stress: $F = \sigma A = \sigma$.

If the interionic separation is r_0, there will be $1/r_0^2$ ions on the unit area, each being pulled by a force f. Since the total force F is just f times the number of ions, the stress can then be written

$$\sigma = F = f\,\frac{1}{r_0^2}$$

When the separation between two adjacent ions is increased by an amount δ, the strain is $\epsilon = \delta/r_0$. The differential strain corresponding to a differential displacement is then

$$d\epsilon = \frac{dr}{r_0}$$

The elastic modulus E is now the ratio of stress to strain, in the limit as the strain approaches zero:

$$E = \left.\frac{d\sigma}{d\epsilon}\right|_{\epsilon\to 0} = \left.\frac{1}{r_0}\frac{df}{dr}\right|_{r\to r_0} = \left.\frac{1}{r_0}\frac{d}{dr}\left(\frac{ACe^2}{r^2} - \frac{nB}{r^{n+1}}\right)\right|_{r\to r_0}$$

Using $B = ACe^2 r_0^{n-1}/n$ from Eqn. 6 and simplifying,

$$E = \frac{(n-1)ACe^2}{r_0^4}$$

Note the very strong dependence of E on r_0, which in turn reflects the tightness of the bond. If E and r_0 are known experimentally, n can be determined. For NaCl, $E = 3 \times 10^{10}$ N/m^2; using this along with the X-ray diffraction value of $r_0 = 2.82 \times 10^{-10}$ m, we find $n = 1.47$.

Using simple tension in this calculation is not really appropriate, because when a material is stretched in one direction, it will *contract* in the transverse directions. This is the *Poisson effect,* which will be treated in a later module. Our tension-only example does not consider the transverse contraction, and the resulting value of n is too low. A better but slightly more complicated approach is to use hydrostatic

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[2]See the *Module on Crystallographic Notation* for a review of this nomenclature.

compression, which moves all the ions closer to one another. Problem 3 outlines this procedure, which yields values of n in the range of 5–12 as mentioned earlier.
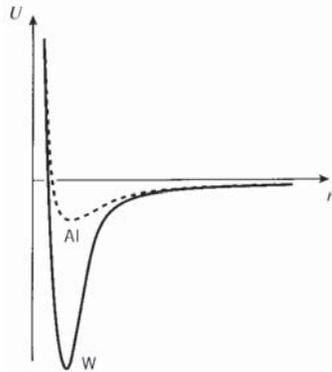

Figure 4: Bond energy functions for aluminum and tungsten.

The stiffnesses of metallic and covalent systems will be calculated differently than the method used above for ionic crystals, but the concept of electrostatic attraction applies to these non-ionic systems as well. As a result, bond energy functions of a qualitatively similar nature result from all these materials. In general, the "tightness" of the bond, and hence the elastic modulus E, is related to the curvature of the bond energy function. Steeper bond functions will also be deeper as a rule, so that within similar classes of materials the modulus tends to correlate with the energy needed to rupture the bonds, for instance by melting. Materials such as tungsten that fill many bonding and few antibonding orbitals have very deep bonding functions[3], with correspondingly high stiffnesses and melting temperatures, as illustrated in Fig. 4. This correlation is obvious in Table 1, which lists the values of modulus for a number of metals, along with the values of melting temperature T_m and melting energy ΔH.

Table 1: Modulus and bond strengths for transition metals.

Material	E	T_m	ΔH	α_L
	GPa (Mpsi)	°C	kJ/mol	$\times 10^{-6}$,° C^{-1}
Pb	14 (2)	327	5.4	29
Al	69 (10)	660	10.5	22
Cu	117 (17)	1084	13.5	17
Fe	207 (30)	1538	15.3	12
W	407 (59)	3410	32	4.2

The system will generally have sufficient thermal energy to reside at a level somewhat above the minimum in the bond energy function, and will oscillate between the two positions labeled A and B in Fig. 5, with an average position near r_0. This simple idealization provides a rationale for why materials expand when the temperature is raised. As the internal energy is increased by the

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[3]A detailed analysis of the cohesive energies of materials is an important topic in solid state physics; see for example F. Seitz, *The Modern Theory of Solids,* McGraw-Hill, 1940.

addition of heat, the system oscillates between the positions labeled A' and B' with an average separation distance r_0'. Since the curve is anharmonic, the average separation distance is now greater than before, so the material has expanded or stretched. To a reasonable approximation, the relative thermal expansion $\Delta L/L$ is often related linearly to the temperature rise ΔT, and we can write:

$$\boxed{\frac{\Delta L}{L} = \epsilon_T = \alpha_L\,\Delta T} \tag{7}$$

where ϵ_T is a *thermal strain* and the constant of proportionality α_L is the *coefficient of linear thermal expansion*. The expansion coefficient α_L will tend to correlate with the depth of the energy curve, as is seen in Table 1.
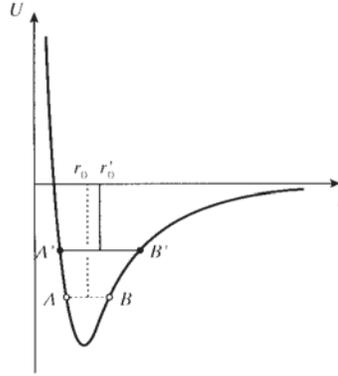

Figure 5: Anharmonicity of the bond energy function.

Example 2

A steel bar of length L and cross-sectional area A is fitted snugly between rigid supports as shown in Fig. 6. We wish to find the compressive stress in the bar when the temperature is raised by an amount ΔT.
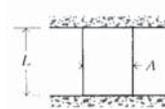

Figure 6: Bar between rigid supports.

If the bar were free to expand, it would increase in length by an amount given by Eqn. 7. Clearly, the rigid supports have to push on the bar – i.e. put in into compression – to suppress this expansion. The magnitude of this thermally induced compressive stress could be found by imagining the material free to expand, then solving $\sigma = E\epsilon_T$ for the stress needed to "push the material back" to its unstrained state. Equivalently, we could simply set the sum of a thermally induced strain and a mechanical strain ϵ_σ to zero:

$$\epsilon = \epsilon_\sigma + \epsilon_T = \frac{\sigma}{E} + \alpha_L\Delta T = 0$$

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$$\sigma = -\alpha_L E \Delta T$$

The minus sign in this result reminds us that a negative (compressive) stress is induced by a positive temperature change (temperature rises.)

Example 3

A glass container of stiffness E and thermal expansion coefficient α_L is removed from a hot oven and plunged suddenly into cold water. We know from experience that this "thermal shock" could fracture the glass, and we'd like to see what materials parameters control this phenomenon. The analysis is very similar to that of the previous example.

In the time period just after the cold-water immersion, before significant heat transfer by conduction can take place, the outer surfaces of the glass will be at the temperature of the cold water while the interior is still at the temperature of the oven. The outer surfaces will try to contract, but are kept from doing so by the still-hot interior; this causes a tensile stress to develop on the surface. As before, the stress can be found by setting the total strain to zero:

$$\epsilon = \epsilon_\sigma + \epsilon_T = \frac{\sigma}{E} + \alpha_L \Delta T = 0$$

$$\sigma = -\alpha_L E \Delta T$$

Here the temperature change ΔT is negative if the glass is going from hot to cold, so the stress is positive (tensile). If the glass is not to fracture by thermal shock, this stress must be less than the ultimate tensile strength σ_f; hence the maximum allowable temperature difference is

$$-\Delta T_{max} = \frac{\sigma_f}{\alpha_L E}$$

To maximize the resistance to thermal shock, the glass should have as low a value of $\alpha_L E$ as possible. "Pyrex" glass was developed specifically for improved thermal shock resistance by using boron rather than soda and lime as process modifiers; this yields a much reduced value of α_L.

Material properties for a number of important structural materials are listed in the *Module on Material Properties*. When the column holding Young's Modulus is plotted against the column containing the Thermal Expansion Coefficients (using log-log coordinates), the graph shown in Fig. 7 is obtained. Here we see again the general inverse relationship between stiffness and thermal expansion, and the distinctive nature of polymers is apparent as well.

Not all types of materials can be described by these simple bond-energy concepts: *intra*molecular polymer covalent bonds have energies entirely comparable with ionic or metallic bonds, but most common polymers have substantially lower moduli than most metals or ceramics. This is due to the *inter*molecular bonding in polymers being due to secondary bonds which are much weaker than the strong intramolecular covalent bonds. Polymers can also have substantial entropic contributions to their stiffness, as will be described below, and these effects do not necessarily correlate with bond energy functions.

Entropic effects

The internal energy as given by the function $U(r)$ is sufficient to determine the atomic positions in many engineering materials; the material "wants" to minimize its internal energy, and it does this by optimizing the balance of attractive and repulsive electrostatic bonding forces.
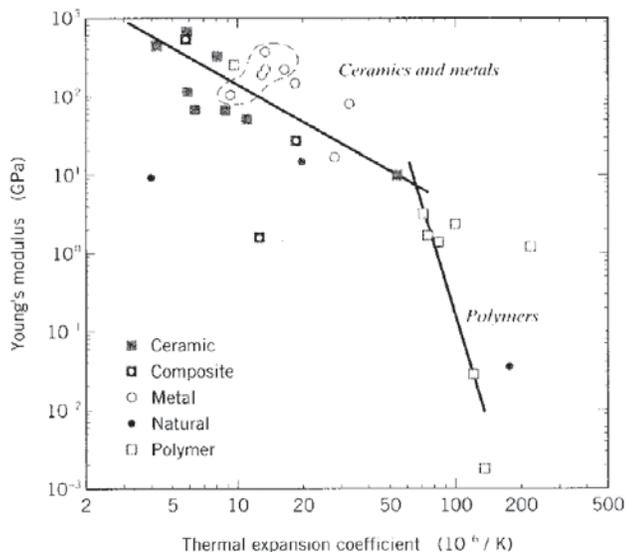
Figure 7: Correlation of stiffness and thermal expansion for materials of various types.

But when the absolute temperature is greater than approximately two-thirds of the melting temperature, there can be sufficient molecular mobility that entropic or disordering effects must be considered as well. This is often the case for polymers even at room temperature, due to their weak intermolecular bonding.

When the temperature is high enough, polymer molecules can be viewed as an interpenetrating mass of (extremely long) wriggling worms, constantly changing their positions by rotation about carbon-carbon single bonds. This wriggling does not require straining the bond lengths or angles, and large changes in position are possible with no change in internal bonding energy.

Figure 8: Conformational change in polymers.

The shape, or "conformation" of a polymer molecule can range from a fully extended chain to a randomly coiled sphere (see Fig. 8). Statistically, the coiled shape is much more likely than the extended one, simply because there are so many ways the chain can be coiled and only one way it can be fully extended. In thermodynamic terms, the entropy of the coiled conformation is very high (many possible "microstates"), and the entropy of the extended conformation is very low (only one possible microstate). If the chain is extended and then released, there will be more wriggling motions tending to the most probable state than to even more highly stretched states; the material would therefore shrink back to its unstretched and highest-entropy state. Equivalently, a person holding the material in the stretched state would feel a tensile force as the material tries to unstretch and is prevented from doing so. These effects are due to entropic

factors, and not internal bond energy.

It is possible for materials to exhibit both internal energy and entropic elasticity. Energy effects dominate in most materials, but rubber is much more dependent on entropic effects. An *ideal rubber* is one in which the response is completely entropic, with the internal energy changes being negligible.

When we stretch a rubber band, the molecules in its interior become extended because they are *crosslinked* by chemical or physical junctions as shown in Fig. 9. Without these links, the molecules could simply slide past one another with little or no uncoiling. "Silly Putty " is an example of uncrosslinked polymer, and its lack of junction connections cause it to be a viscous fluid rather than a useful elastomer that can bear sustained loads without continuing flow. The crosslinks provide a means by which one molecule can pull on another, and thus establish load transfer within the materials. They also have the effect of limiting how far the rubber can be stretched before breaking, since the extent of the entropic uncoiling is limited by how far the material can extend before pulling up tight against the network of junction points. We will see below that the stiffness of a rubber can be controlled directly by adjusting the crosslink density, and this is an example of process-structure-property control in materials.
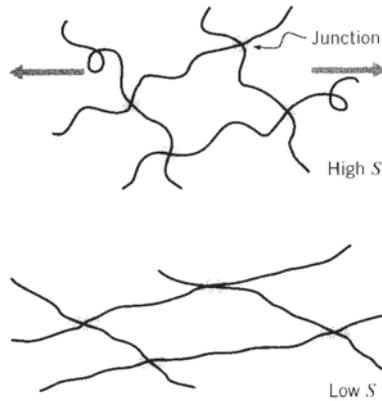

Figure 9: Stretching of crosslinked or entangled polymers.

As the temperature is raised, the Brownian-type wriggling of the polymer is intensified, so that the material seeks more vigorously to assume its random high-entropy state. This means that the force needed to hold a rubber band at fixed elongation *increases* with increasing temperature. Similarly, if the band is stretched by hanging a fixed weight on it, the band will *shrink* as the temperature is raised. In some thermodynamic formalisms it is convenient to model this behavior by letting the coefficient of thermal expansion be a variable parameter, with the ability to become negative for sufficiently large tensile strains. This is a little tricky, however; for instance, the stretched rubber band will contract only along its long axis when the temperature is raised, and will become thicker in the transverse directions. The coefficient of thermal expansion would have to be made not only stretch-dependent but also dependent on direction ("anisotropic").

Example 4

An interesting demonstration of the unusual thermal response of stretched rubber bands involves replacing the spokes of a bicycle wheel with stretched rubber bands as seen in Fig. 10, then mounting

the wheel so that a heat lamp shines on the bands to the right or left of the hub. As the bands warm up, they contract. This pulls the rim closer to the hub, causing the wheel to become unbalanced. It will then rotate under gravity, causing the warmed bands to move out from under the heat lamp and be replaced other bands. The process continues, and the wheel rotates in a direction opposite to what would be expected were the spokes to expand rather than contract on heating.
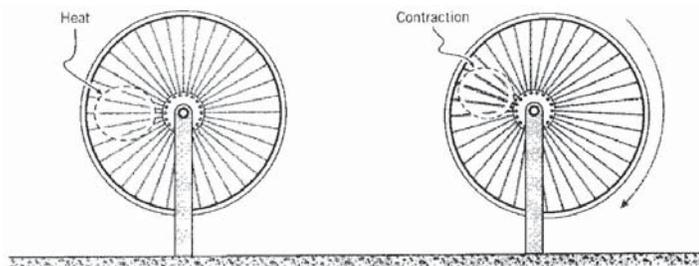

Figure 10: A bicycle wheel with entropic spokes.

The bicycle-wheel trick produces a rather weak response, and it is easy to stop the wheel with only a light touch of the finger. However, the same idea, using very highly stretched urethane bands and employing superheated geothermal steam as a heat source, becomes a viable route for generating mechanical energy.

It is worthwhile to study the response of rubbery materials in some depth, partly because this provides a broader view of the elasticity of materials. But this isn't a purely academic goal. Rubbery materials are being used in increasingly demanding mechanical applications (in addition to tires, which is a very demanding application itself). Elastomeric bearings, vibration-control supports, and biomedical prostheses are but a few examples. We will outline what is known as the "kinetic theory of rubber elasticity," which treats the entropic effect using concepts of statistical thermodynamics. This theory stands as one of the very most successful atomistic theories of mechanical response. It leads to a result of satisfying accuracy without the need for adjustable parameters or other fudge factors.

When pressure-volume changes are not significant, the competition between internal energy and entropy can be expressed by the Helmholtz free energy $A = U - TS$, where T is the temperature and S is the entropy. The system will move toward configurations of lowest free energy, which it can do either by reducing its internal energy or by increasing its entropy. Note that the influence of the entropic term increases explicitly with increasing temperature. With certain thermodynamic limitations in mind (see Prob. 5), the mechanical work $dW = F\,dL$ done by a force F acting through a differential displacement dL will produce an increase in free energy given by

$$F\,dL = dW = dU - T\,dS \tag{8}$$

or

$$F = \frac{dW}{dL} = \left(\frac{\partial U}{\partial L}\right)_{T,V} - T\left(\frac{\partial S}{\partial L}\right)_{T,V} \tag{9}$$

For an ideal rubber, the energy change dU is negligible, so the force is related directly to the temperature and the change in entropy dS produced by the force. To determine the force-deformation relationship, we obviously need to consider how S changes with deformation.

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We begin by writing an expression for the conformation, or shape, of the segment of polymer molecule between junction points as a statistical probability distribution. Here the length of the *segment* is the important molecular parameter, not the length of the entire molecule. In the simple form of this theory, which turns out to work quite well, each covalently bonded segment is idealized as a freely-jointed sequence of n rigid links each having length a.
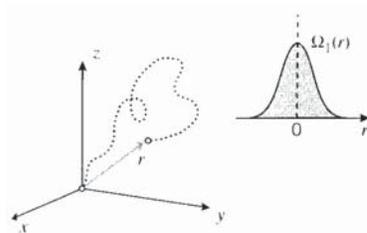

Figure 11: Random-walk model of polymer conformation

A reasonable model for the end-to-end distance of a randomly wriggling segment is that of a "random walk" Gaussian distribution treated in elementary statistics. One end of the chain is visualized at the origin of an xyz coordinate system as shown in Fig. 11, and each successive link in the chain is attached with a random orientation relative to the previous link. (An elaboration of the theory would constrain the orientation so as to maintain the 109° covalent bonding angle.) The probability $\Omega_1(r)$ that the other end of the chain is at a position $r = \left(x^2 + y^2 + z^2\right)^{1/2}$ can be shown to be

$$\Omega_1(r) = \frac{\beta^3}{\sqrt{\pi}} \exp(-\beta^2 r^2) = \frac{\beta^3}{\sqrt{\pi}} \exp\left[-\beta^2 \left(x^2 + y^2 + z^2\right)\right]$$

The parameter β is a scale factor related to the number of units n in the polymer segment and the bond length a; specifically it turns out that $\beta = \sqrt{3/2n}/a$. This is the "bell-shaped curve" well known to seasoned test-takers. The most probable end-to-end distance is seen to be zero, which is expected because the chain will end up a given distance to the left (or up, or back) of the origin exactly as often as it ends up the same distance to the right.

When the molecule is now stretched or otherwise deformed, the relative positions of the two ends are changed. Deformation in elastomers is usually described in terms of *extension ratios,* which are the ratios of stretched to original dimensions, L/L_0. Stretches in the x, y, and z directions are denoted by λ_x, λ_y, and λ_z respectively, The deformation is assumed to be *affine,* i.e. the end-to-end distances of each molecular segment increase by these same ratios. Hence if we continue to view one end of the chain at the origin the other end will have moved to $x_2 = \lambda_x x, y_2 = \lambda_y y, z_2 = \lambda_z z$. The configurational probability of a segment being found in this stretched state is then

$$\Omega_2 = \frac{\beta^3}{\sqrt{\pi}} \exp\left[-\beta^2 \left(\lambda_x^2 x^2 + \lambda_y^2 y^2 + \lambda_z^2 z^2\right)\right]$$

The relative change in probabilities between the perturbed and unperturbed states can now be written as

$$\ln \frac{\Omega_2}{\Omega_1} = -\beta^2 \left[\left(\lambda_x^2 - 1\right) x^2 + \left(\lambda_y^2 - 1\right) y^2 + \left(\lambda_z^2 - 1\right) z^2\right]$$

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Several strategems have been used in the literature to simplify this expression. One simple approach is to let the initial position of the segment end x, y, z be such that $x^2 = y^2 = z^2 = \overline{r_0^2}/3$, where $\overline{r_0^2}$ is the initial mean square end-to-end distance of the segment. (This is not zero, since when squares are taken the negative values no longer cancel the positive ones.) It can also be shown (see Prob. 8) that the distance $\overline{r_0^2}$ is related to the number of bonds n in the segment and the bond length a by $\overline{r_0^2} = na^2$. Making these substitutions and simplifying, we have

$$\ln \frac{\Omega_2}{\Omega_1} = -\frac{1}{2} \left(\lambda_x^2 + \lambda_y^2 + \lambda_z^2 - 3 \right) \tag{10}$$

As is taught in subjects in statistical thermodynamics, changes in configurational probability are related to corresponding changes in thermodynamic entropy by the "Boltzman relation" as

$$\Delta S = k \ln \frac{\Omega_2}{\Omega_1}$$

where $k = 1.38 \times 10^{-23}$ J/K is Boltzman's constant. Substituting Eqn. 10 in this relation:

$$\Delta S = -\frac{k}{2} \left(\lambda_x^2 + \lambda_y^2 + \lambda_z^2 - 3 \right)$$

This is the entropy change for one segment. If there are N chain segments per unit volume, the total entropy change per unit volume ΔS_V is just N times this quantity:

$$\Delta S_V = -\frac{Nk}{2} \left(\lambda_x^2 + \lambda_y^2 + \lambda_z^2 - 3 \right) \tag{11}$$

The associated work (per unit volume) required to change the entropy by this amount is

$$\boxed{\Delta W_V = -T \Delta S_V = +\frac{NkT}{2} \left(\lambda_x^2 + \lambda_y^2 + \lambda_z^2 - 3 \right)} \tag{12}$$

The quantity ΔW_V is therefore the strain energy per unit volume contained in an ideal rubber stretched by $\lambda_x, \lambda_y, \lambda_z$.

Example 5

Recent research by Prof. Christine Ortiz has demonstrated that the elasticity of individual polymer chains can be measured using a variety of high-resolution force spectroscopy techniques, such as atomic force microscopy (AFM). At low to moderate extensions, most polymer chains behave as ideal, entropic, random coils; i.e. molecular rubber bands. This is shown in Fig. 12, which displays AFM data (retraction force, F_{chain}, versus chain end-to-end separation distance) for stretching and uncoiling of single polystyrene chains of different lengths. By fitting experimental data with theoretical polymer physics models of freely-jointed chains (red lines in Fig. 12) or worm-like chains, we can estimate the "statistical segment length" or local chain stiffness and use this parameter as a probe of chemical structure and local environmental effects (e.g. electrostatic interactions, solvent quality, etc.). In addition, force spectroscopy can be used to measure noncovalent, physisorption forces of single polymer chains on surfaces and covalent bond strength (chain "fracture").

To illustrate the use of Eqn. 12 for a simple but useful case, consider a rubber band, initially of length L_0 which is stretched to a new length L. Hence $\lambda = \lambda_x = L/L_0$. To a very good approximation, rubbery materials maintain a constant volume during deformation, and this lets us compute the transverse contractions λ_y and λ_z which accompany the stretch λ_x. An
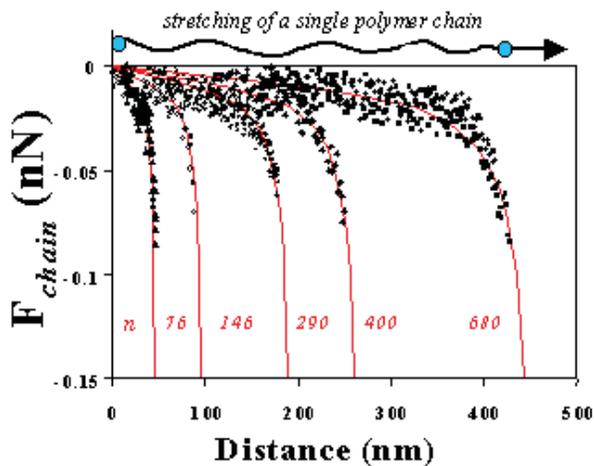
Figure 12: Experimental measurements from numerous force spectroscopy (AFM) experiments of force-elongation response of single polystyrene segments in toluene, compared to the freely-jointed chain model. The statistical segment length is 0.68, and n = number of molecular units in the segment.

expression for the change ΔV in a cubical volume of initial dimensions a_0, b_0, c_0 which is stretched to new dimensions a, b, c is

$$\Delta V = abc - a_0 b_0 c_0 = (a_0 \lambda_x)(b_0 \lambda_y)(c_0 \lambda_z) - a_0 b_0 c_0 = a_0 b_0 c_0 (\lambda_x \lambda_y \lambda_z - 1)$$

Setting this to zero gives

$$\lambda_x \lambda_y \lambda_z = 1 \tag{13}$$

Hence the contractions in the y and z directions are

$$\lambda_y^2 = \lambda_z^2 = \frac{1}{\lambda}$$

Using this in Eqn. 12, the force F needed to induce the deformation can be found by differentiating the total strain energy according to Eqn. 9:

$$F = \frac{dW}{dL} = \frac{d(V\,\Delta W_V)}{L_0\,d\lambda} = A_0 \frac{NkT}{2}\left(2\lambda - \frac{2}{\lambda^2}\right)$$

Here $A_0 = V/L_0$ is the original area. Dividing by A_0 to obtain the engineering stress:

$$\boxed{\sigma = NkT\left(\lambda - \frac{1}{\lambda^2}\right)} \tag{14}$$

Clearly, the parameter NkT is related to the stiffness of the rubber, as it gives the stress σ needed to induce a given extension λ. It can be shown (see Prob. 10) that the initial modulus — the slope of the stress-strain curve at the origin — is controlled by the temperature and the crosslink density according to $E = 3NkT$.

Crosslinking in rubber is usually done in the "vulcanizing" process invented by Charles Goodyear in 1839. In this process sulfur abstracts reactive hydrogens adjacent to the double

bonds in the rubber molecule, and forms permanent bridges between adjacent molecules. When crosslinking is done by using approximately 5% sulfur, a conventional rubber is obtained. When the sulfur is increased to $\approx$ 30–50%, a hard and brittle material named ebonite (or simply "hard rubber") is produced instead.

The volume density of chain segments N is also the density of junction points. This quantity is related to the specimen density ρ and the molecular weight between crosslinks M_c as $M_c = \rho N_A / N$, where N is the number of crosslinks per unit volume and $N_A = 6.023 \times 10^{23}$ is Avogadro's Number. When N is expressed in terms of moles per unit volume, we have simply $M_c = \rho / N$ and the quantity NkT in Eqn. 14 is replaced by NRT, where $R = kN_A = 8.314$ J/mol-°K is the Gas Constant.

Example 6

The Young's modulus of a rubber is measured at $E = 3.5$ MPa for a temperature of $T = 300$ °K. The molar crosslink density is then

$$N = \frac{E}{3RT} = \frac{3.5 \times 10^6 \text{ N/m}^2}{3 \times 8.314 \frac{\text{N·m}}{\text{mol·K}} \times 300 \text{ K}} = 468 \text{ mol/m}^3$$

The molecular weight per segment is

$$M_c = \frac{\rho}{N} = \frac{1100 \text{ kg/m}^3}{468 \text{ mol/m}^3} = 2350 \text{ gm/mol}$$

Example 7

A person with more entrepreneurial zeal than caution wishes to start a bungee-jumping company, and naturally wants to know how far the bungee cord will stretch; the clients sometimes complain if the cord fails to stop them before they reach the asphalt. It's probably easiest to obtain a first estimate from an energy point of view: say the unstretched length of the cord is L_0, and that this is also the distance the jumper free-falls before the cord begins to stretch. Just as the cord begins to stretch, the the jumper has lost an amount of potential energy wL_0, where w is the jumper's weight. The jumper's velocity at this time could then be calculated from $(mv^2)/2 = wL_0$ if desired, where $m = w/g$ is the jumper's mass and g is the acceleration of gravity. When the jumper's velocity has been brought to zero by the cord (assuming the cord doesn't break first, and the ground doesn't intervene), this energy will now reside as entropic strain energy within the cord. Using Eqn. 12, we can equate the initial and final energies to obtain

$$wL_0 = \frac{A_0 L_0 \cdot NRT}{2} \left(\lambda^2 + \frac{2}{\lambda} - 3 \right)$$

Here $A_0 L_0$ is the total volume of the cord; the entropic energy per unit volume ΔW_V must be multiplied by the volume to give total energy. Dividing out the initial length L_0 and using $E = 3NRT$, this result can be written in the dimensionless form

$$\frac{w}{A_0 E} = \frac{1}{6} \left(\lambda^2 + \frac{2}{\lambda} - 3 \right)$$

The closed-form solution for λ is messy, but the variable $w/A_0 E$ can easily be plotted versus λ (see Fig. 13.) Note that the length L_0 has canceled from the result, although it is still present implicitly in the extension ratio $\lambda = L/L_0$.

Taking a typical design case for illustration, say the desired extension ratio is taken at $\lambda = 3$ for a rubber cord of initial modulus $E = 100$ psi; this stops the jumper safely above the pavement and is verified
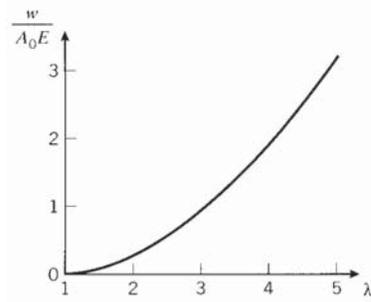
Figure 13: Dimensionless weight versus cord extension.

to be well below the breaking extension of the cord. The value of the parameter w/AE corresponding to $\lambda = 3$ is read from the graph to be 1.11. For a jumper weight of 150 lb, this corresponds to $A = 1.35$ in^2, or a cord diameter of 1.31 in.

If ever there was a strong case for field testing, this is it. An analysis such as this is nothing more than a crude starting point, and many tests such as drops with sandbags are obviously called for. Even then, the insurance costs would likely be very substantial.

Note that the stress-strain response for rubber elasticity is nonlinear, and that the stiffness as given by the stress needed to produce a given deformation is predicted to increase with increasing temperature. This is in accord with the concept of more vigorous wriggling with a statistical bias toward the more disordered state. The rubber elasticity equation works well at lower extensions, but tends to deviate from experimental values at high extensions where the segment configurations become nongaussian.

Deviations from Eqn. 14 can also occur due to crystallization at high elongations. (Rubbers are normally noncrystalline, and in fact polymers such as polyethylene that crystallize readily are not elastomeric due to the rigidity imparted by the crystallites.) However, the decreased entropy that accompanies stretching in rubber increases the crystalline melting temperature according to the well-known thermodynamic relation

$$T_m = \frac{\Delta U}{\Delta S} \tag{15}$$

where ΔU and ΔS are the change in internal energy and entropy on crystallization. The quantity ΔS is reduced if stretching has already lowered the entropy, so the crystallization temperature rises. If it rises above room temperature, the rubber develops crystallites that stiffen it considerably and cause further deviation from the rubber elasticity equation. (Since the crystallization is exothermic, the material will also increase in temperature; this can often be sensed by stretching a rubber band and then touching it to the lips.) Strain-induced crystallization also helps inhibit crack growth, and the excellent abrasion resistance of natural rubber is related to the ease with which it crystallizes upon stretching.

Problems

1. Justify the first two terms of the Madelung series given in Eqn. 3.

2. Using Eqn. 6 to write the parameter B in terms of the equilibrium interionic distance r_0, show that the binding energy of an ionic crystal, per bond pair, can be written as

$$U = -\frac{(n-1)ACe^2}{nr_0}$$

where A is the Madelung constant, C is the appropriate units conversion factor, and e is the ionic charge.

3. Measurements of bulk compressibility are valuable for probing the bond energy function, because unlike simple tension, hydrostatic pressure causes the interionic distance to decrease uniformly. The *modulus of compressibility* K of a solid is the ratio of the pressure p needed to induce a relative change in volume dV/V:

$$K = -\frac{dp}{(dV)/V}$$

The minus sign is needed because positive pressures induce reduced volumes (volume change negative).

(a) Use the relation $dU = pdV$ for the energy associated with pressure acting through a small volume change to show

$$\frac{K}{V_0} = \left(\frac{d^2U}{dV^2}\right)_{V=V_0}$$

where V_0 is the crystal volume at the equilibrium interionic spacing $r = a_0$.

(b) The volume of an ionic crystal containing N negative and N positive ions can be written as $V = cNr^3$ where c is a constant dependent on the type of lattice (2 for NaCl). Use this to obtain the relation

$$\frac{K}{V_0} = \left(\frac{d^2U}{dV^2}\right)_{V=V_0} = \frac{1}{9c^2N^2r^2} \cdot \frac{d}{dr}\left(\frac{1}{r^2}\frac{dU}{dr}\right)$$

(c) Carry out the indicated differentiation of the expression for binding energy to obtain the expression

$$\frac{K}{V_0} = \frac{K}{cNr_0^3} = \frac{N}{9c^2Nr_0^2}\left[\frac{-4ACe}{r_0^5} + \frac{n(n+3)B}{r_0^{n+4}}\right]$$

Then using the expression $B = ACe^2r_0^{n-1}/n$, obtain the formula for n in terms of compressibility:

$$n = 1 + \frac{9cr_0^4K}{ACe^2}$$

4. Complete the spreadsheet below, filling in the values for repulsion exponent n and lattice energy U.

type	r_0 (pm)	K (GPa)	A	n	U(kJ/mol)	U_{expt}
LiF	201.4	6.710e+01	1.750			-1014
NaCl	282.0	2.400e+01	1.750			-764
KBr	329.8	1.480e+01	1.750			-663

The column labeled U_{expt} lists experimentally obtained values of the lattice energy.

5. Given the definition of Helmholtz free energy:

$$A = U - TS$$

along with the first and second laws of thermodynamics:

$$dU = dQ + dW$$

$$dQ = TdS$$

where U is the internal energy, T is the temperature, S is the entropy, Q is the heat and W is the mechanical work, show that the force F required to hold the ends of a tensile specimen a length L apart is related to the Helmholtz energy as

$$F = \left(\frac{\partial A}{\partial L}\right)_{T,V}$$

6. Show that the temperature dependence of the force needed to hold a tensile specimen at fixed length as the temperature is changed (neglecting thermal expansion effects) is related to the dependence of the entropy on extension as

$$\left(\frac{\partial F}{\partial T}\right)_L = -\left(\frac{\partial S}{\partial L}\right)_T$$

7. (a) Show that if an ideal rubber ($dU = 0$) of mass M and specific heat c is extended adiabatically, its temperature will change according to the relation

$$\frac{\partial T}{\partial L} = \frac{-T}{Mc}\left(\frac{\partial S}{\partial L}\right)$$

i.e. if the entropy is reduced upon extension, the temperature will rise. This is known as the *thermoelastic effect*.

(b) Use this expression to obtain the temperature change dT in terms of an increase $d\lambda$ in the extension ratio as

$$dT = \frac{\sigma}{\rho c}\, d\lambda$$

where σ is the engineering stress (load divided by original area) and ρ is the mass density.

8. Show that the end-to-end distance r_0 of a chain composed of n freely-jointed links of length a is given by $r_o = na^2$.

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9. Evalute the temperature rise in a rubber specimen of $\rho = 1100$ kg/m^3, $c = 2$ kJ/kg·K, $NkT = 500$ kPa, subjected to an axial extension $\lambda = 4$.

10. Show that the initial engineering modulus of a rubber whose stress-strain curve is given by Eqn. 14 is $E = 3NRT$.

11. Calculate the Young's modulus of a rubber of density 1100 gm/mol and whose inter-crosslink segments have a molecular weight of 2500 gm/mol. The temperature is 25°C.

12. Show that in the case of biaxial extension (λ_x and λ_y prescribed), the x-direction stress based on the original cross-sectional dimensions is

$$\sigma_x = NkT \left(\lambda_x - \frac{1}{\lambda_x^3 \lambda_y^2} \right)$$

and based on the deformed dimensions

$$_t\sigma_x = NkT \left(\lambda_x^2 - \frac{1}{\lambda_x^2 \lambda_y^2} \right)$$

where the t subscript indicates a "true" or current stress.

13. Estimate the initial elastic modulus E, at a temperature of 20C, of an elastomer having a molecular weight of 7,500 gm/mol between crosslinks and a density of 1.0 gm/cm^3. What is the percentage change in the modulus if the temperature is raised to 40C?

14. Consider a line on a rubber sheet, originally oriented at an angle ϕ_0 from the vertical. When the sheet is stretched in the vertical direction by an amount $\lambda_y = \lambda$, the line rotates to a new inclination angle ϕ'. Show that

$$\tan \phi' = \frac{1}{\lambda^{3/2}} \tan \phi_0$$

15. Before stretching, the molecular segments in a rubber sheet are assumed to be distributed uniformly over all directions, so the the fraction of segments $f(\phi)$ oriented in a particular range of angles $d\phi$ is

$$f(\phi) = \frac{dA}{A} = \frac{2\pi r^2 \sin \phi \, d\phi}{2\pi r}$$

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The *Herrman orientation parameter* is defined in terms of the mean orientation as

$$f = \frac{1}{2}\left(3\langle\cos^2\phi'\rangle - 1\right), \qquad \langle cos^2\phi'\rangle = \int_0^{\pi/2} \cos^2\phi'\, f(\phi)\, d\phi$$

Using the result of the previous problem, plot the orientation function f as a function of the extension ratio λ.

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