The bulk modulus of rubber

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It is well known that there is an enormous disparity between the tensile elastic modulus E of a rubber and its bulk modulus K. For a typical rubber, E is of order $10^5\,\mathrm{N\,m^{-2}}$ and is primarily due to entropic effects. By contrast, K is of order $10^9\,\mathrm{N\,m^{-2}}$. This paper suggests that K arises from van der Waals interactions between groups in one chain and groups in neighbouring chains. Using a Lennard-Jones type of potential, $U=-C/r^6+D/r^{12}$, and assuming pairwise addition, the free surface energy γ of rubber may be calculated and compared with typical experimental values ($\gamma=35\,\mathrm{mJ\,m^{-2}}$). From this, a typical value is obtained for C of order $60\times10^{-79}\,\mathrm{J\,m^6}$ (corresponding to a Hamaker constant $\simeq 9.3\times10^{-20}\,\mathrm{J}$). This value may be used to calculate the bulk modulus, assuming a regular arrangement of interacting groups. The result agrees with the experimental value of K to better than an order of magnitude.

(Keywords: bulk modulus; compressibility; rubber)

INTRODUCTION

The elastic properties of solids reflect their resistance to tension (Young's modulus E), to compression (bulk modulus K) and to shear (shear modulus n): they are due to the atomic or molecular forces between their constituent parts. If these forces are all of one kind—e.g. covalent, ionic, metallic, or van der Waals—the elastic properties are more or less isotropic, and E, K and n are all of the same order of magnitude and readily interrelated. With layer-like materials such as graphite or molybdenum disulfide, the forces between the layers are weak while the forces within the layers are strong. The elastic properties are markedly anisotropic and the relations between E, K and n are complex and orientation-dependent. Nevertheless, it is a valid generalization that the elastic properties of solids are determined by the strength of the relevant interatomic forces.

This is not the case with rubber: neither E nor n is due to interatomic forces, but K is. This paper discusses, in particular, the immense difference between E and K in terms of very simple modelling.

THE TENSILE (YOUNG'S) MODULUS E OF RUBBER

A carbon-based rubber consists of an enormous number of monomers linked together to form a chain. If there is free rotation about the carbon–carbon bonds, the chain adopts as many random configurations as possible in order to increase its entropy. If an attempt is made to stretch the chain, the configurations are restricted. The entropy is reduced and the polymer resists the stretching action. This is the mechanism for the elastic tensile properties of the chain. In the rubber, the polymer chains are crosslinked at various points to form a three-dimensional network. Each segment or strand between two link points attempts to contract for the reasons already described. If there are N monomers in the strand and the molecular volume of a monomer is v, the effective Young's modulus E of the whole is given[1,2] by:

$$E=\alpha\frac{k_B T}{Nv} \tag{1}$$

where k_B is the Boltzmann constant and α is a numerical factor (still the subject of some debate) close to unity.

Unlike almost all other solids, the modulus increases with increasing temperature, a natural consequence of the fact that the tensile elasticity is associated with entropy, not with interatomic forces. A similar consideration applies to the shear modulus n for the following reason. The high bulk modulus (see below) implies that rubber is almost incompressible. If a cube of rubber is held on its base and the opposite face subjected to a shear stress, the distance between the faces must remain constant to conserve the volume. Thus every (virtual) filament in the rubber from the base to the opposite face is subjected to tension. It is then easy to show that the shear modulus n is simply equal to $E/3$.

For a typical rubber of polybutadiene, in which the segments or strands contain, say, 250 monomers, the value of E is of order $10^5\,\mathrm{N\,m^{-2}}$. However, the bulk modulus K is about $2\times10^9\,\mathrm{N\,m^{-2}}$. If we link E and K by the standard elasticity relation:

$$E=3K(1-2\nu) \tag{2}$$

where ν is Poisson's ratio, we find that $\nu=0.499992$. But Poisson's ratio for rubber is rather meaningless, since E and K arise from two completely different mechanisms, leading to vastly disparate values. The same comment applies to the shear modulus n, which is linked to E by the standard relation:

$$n=\frac{E}{2(1+\nu)} \tag{3}$$

As we have seen, for an 'incompressible' material $n=E/3$: the introduction of ν is irrelevant.

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THE BULK MODULUS K OF RUBBER

The high value of K must be due to relatively strong forces within the rubber, and we now consider various possibilities. First, there are covalent bonds between the carbon atoms in the polymer chain: they are extremely strong. The most extreme example of this is diamond, where every carbon is linked to its neighbour by a covalent bond. For diamond we find:

$$E = 10 \times 10^{11}\,\mathrm{N\,m^{-2}}$$

$$K \approx 5 \times 10^{11}\,\mathrm{N\,m^{-2}}$$

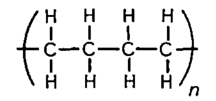
$$\nu \approx 0.16$$

It seems unlikely that these are the cause of the rubber bulk modulus, though it is possible to invoke some fraction of these forces in the polymer backbone as operating in compression. We shall assume that this is negligible. A second possibility is that compression produces some biased rotation of polymer groups about the C–C bond, say a *cis* to a *trans* configuration to accommodate the changes in volume involved. We shall assume that, in hydrostatic compression, this too, on average, is not an important factor. Finally, we ignore any possible Coulombic forces.

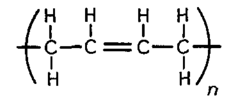
This leaves as a plausible alternative that the bulk modulus is due mainly to van der Waals forces between CH_2 groups (or their equivalent) in one rubber molecule with those of its neighbours. At room temperature the strands in the rubber between each crosslink have almost complete configurational freedom (that is why the material behaves in a rubber-like manner). It is only the crosslinks that give it solid-like properties: the strands themselves are virtually liquid. We may therefore expect the van der Waals forces to produce an internal pressure p_i in the rubber analogous to the a/V^2 term in the van der Waals equation of state for an imperfect gas. Analytically $p_i = -\partial U/\partial V$, where U is the internal energy of the material and V its volume. There is, of course, a positive pressure in the rubber due to its kinetic (or thermal) energy, and it is the balance between these pressures that leaves the surface in equilibrium with the surroundings. The internal pressure p_i is a measure of the compressibility of the rubber, but its calculation is very difficult. We shall simplify the model and assume that the constituent parts are in atomic contact, their centre-to-centre separation being equal to their effective diameter. This is equivalent to assuming that the thermal energy may be ignored, so that this is, in effect, a static molecular model[3]. Then the hydrostatic stress resisting compression is the bulk modulus K of the material, where $K = V\mathrm{d}^2U/\mathrm{d}V^2$ (see ref. 2, ch. 7). This clearly gives an overestimate of K, but it should be of the right order of magnitude: later we shall consider how to allow for some increase in the separation between the groups. At this stage we note that, for a typical butadiene rubber, the bulk modulus at room temperature is 2.4 GPa; below its T_g it is greater by a factor of less than 3.

We start by recognizing that, though, at room temperature, the strands are continuously changing their configuration, there must be a statistically mean separation between the individual CH_2 groups corresponding to the bulk density of rubber. In this sense the simplest analogue to rubber at room temperature is linear polyethylene in its rubbery range; while below its T_g polyethylene resembles rubber in its glassy state.

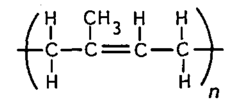
Polyethylene



Polybutadiene



Polyisoprene



If we compare the arrangement of groups in polyethylene (PE) with those in typical rubbers such as polybutadiene or polyisoprene, we see that some groups are CH or CCH_3 instead of CH_2. We make the simplifying assumption that they are all equivalent to a CH_2 group. In molten PE we assume that each CH_2 group occupies a volume v of about $23 \times 10^{-30}\,\mathrm{m}^3$ corresponding to a bulk density of molten PE of about $1000\,\mathrm{kg\,m^{-3}}$. For polybutadiene the equivalent volume is $25 \times 10^{-30}\,\mathrm{m}^3$. Assuming that the groups are in molecular contact, the forces between the CH_2 groups are, as mentioned above, a balance between van der Waals attractive forces and a repulsive force arising from the overlap of orbitals (see below). Unfortunately, it is not easy to calculate the van der Waals interaction between CH_2 groups *ab initio*, particularly as the carbon atom itself is also linked by covalent bonds to a carbon atom on each side of it. The simplest assumption is that each HCH unit behaves like a single spherical 'atom' with orbital electrons. Fluctuations in electron configuration give rise to an instantaneous dipole, which interacts with its neighbours to give a pairwise potential of the Lennard-Jones type:

$$U = -\frac{C}{r^6} + \frac{D}{r^{12}} \qquad (4)$$

Apart from the dipole interaction, there are quadrupole and more involved interactions giving additional attraction terms of the type $-C'/r^8$, $-C''/r^{10}$ as well as more elaborate forms of the repulsion potential[4]. There is also a modelling problem. A sphere of volume $23 \times 10^{-30}\,\mathrm{m}^3$ has a diameter of σ of over $3.5 \times 10^{-10}\,\mathrm{m}$. This is considerably greater than the length (about $1.53 \times 10^{-10}\,\mathrm{m}$) of the covalent bond between neighbouring CH_2 groups in the molecular chain. We accept this as part of the inadequacy of the simple treatment given here and apply the model using equation (4). The general behaviour is thus assumed to resemble that of an inert gas. Sanchez[5] has discussed the application of van der Waals forces to correlate the bulk density ρ_B, compressibility Q and surface tension γ of a wide range of liquids, including saturated hydrocarbons, aromatic hydrocarbons, alcohols as well as the inert gases and water. He finds that for each family of liquids a parameter $\gamma(Q/\rho_B)^{1/2}$ is more or less constant. Although this parameter is not a dimensionless quantity, his results suggest that van der Waals interactions are applicable to the intermolecular forces of these materials. Later in this paper some of his data will be dealt with in a different way.

THE MAGNITUDE OF THE COEFFICIENT *C*

We shall need the value of C in order to compute the bulk modulus. To do this we first consider the van der Waals energy per unit area between two (semi-infinite) flat parallel surfaces at a distance H apart. For a uniform distribution of dipoles of number density ρ_n per unit volume, we may calculate the potential due to the attractive part of the van der Waals force[2,6,7]. Assuming pairwise addition, i.e. ignoring many-body effects, we obtain (see ref. 2, equation (12.6)):

$$U = -\frac{C\pi\rho_n^2}{12H^2} = -\frac{C\pi}{12H^2v^2} \tag{5}$$

If the surfaces are brought into atomic contact ($H = H_0$) and then separated to infinity, the work done will be:

$$\frac{C\pi}{12H_0^2v^2} \tag{6}$$

and this corresponds to the work done in creating two unit areas of rubber, i.e. it is equal to 2γ where γ is the free surface energy of the solid. Hence:

$$\gamma = \frac{C\pi}{24H_0^2v^2} \tag{7}$$

We have neglected the repulsive term. If we assume that it can be expressed as a power relation D/r^{12}, this reduces the value of γ by about 25% (see ref. 2, equation (6.12)). This overestimates the effect of the repulsive forces, but if we include it we obtain:

$$\gamma = \frac{C\pi}{32H_0^2v^2} \tag{8}$$

If we assume that this analysis applies to rubber and that $v = 25 \times 10^{-30}\,\mathrm{m}^3$, we can deduce the value of C from the observed value of γ. This has been determined directly by measuring the adhesion between two rubber specimens[8]. The value obtained is $35\,\mathrm{mJ\,m^{-2}}$, and a similar value has been deduced from measurements of the critical surface tension for wetting. We also need a value for H_0. It clearly cannot be greater than the effective diameter σ of the CH_2 'sphere' ($\sigma = 3.5 \times 10^{-10}\,\mathrm{m}$): it cannot be less than, say, $10^{-10}\,\mathrm{m}$. The problem arises because in the derivation of equation (5) the dipoles are not treated as individual entities: they are replaced by a smeared-out uniform density of matter[6,7], giving an average number density ρ_n. In this way the interaction energy is obtained by integration rather than by adding every pairwise energy term. For bulk properties this is a reasonable assumption. But for the atoms at the two nascent surfaces as they are separated, the 'graininess' of matter reappears and the local interaction is much stronger than that deduced from the smeared-out distribution from which equation (5) is deduced. Another way of describing this is to recognize that the potential due to quadrupoles, octupoles, etc., falls off more rapidly with distance than the dipoles, so that their contribution is important only at short separations. There is also the problem of surface relaxation. Tabor[6] suggested that to allow for these factors it would be more realistic to give H_0 a value of $\sigma/2$, while Israelachvili[7] suggested a value $\sigma/2.5$. In fact he showed that for a variety of hydrocarbons a 'good' value for H_0 is $1.65 \times 10^{-10}\,\mathrm{m}$. It must be realized that this is an empirical value, though it has a semi-theoretical basis.

Inserting this value in equation (8) we obtain:

$$C = 60 \times 10^{-79}\,\mathrm{J\,m^6} \tag{9}$$

for rubber. For polyethylene, assuming that in the molten state $\gamma = 30\,\mathrm{mJ\,m^{-2}}$, we deduce a value for C of about $43 \times 10^{-79}\,\mathrm{J\,m^6}$.

In colloid and surface chemistry, intermolecular and interparticle forces are often quoted in terms of the Hamaker constant A_H, where $A_H = C\pi^2\rho_n^2$. The usual range is $(4 \text{ to } 40) \times 10^{-20}\,\mathrm{J}$. The above value of C for rubber gives a value of $A_H = 9.3 \times 10^{-20}\,\mathrm{J}$; for polyethylene $A_H = 8.0 \times 10^{-20}\,\mathrm{J}$. For bulk properties there is an alternative way of calculating A_H, due to Lifshitz. It side-steps the atomic or particulate structure of the solid and treats it as a continuous medium. It is then possible to derive A_H in terms of macroscopic bulk properties such as the dielectric constant and refractive index. This approach automatically overcomes the 'many-body' problem of interacting dipoles. (For an informative discussion see Israelachvili[7].) Israelachvili has calculated the value of A_H for liquid hexadecane, which may be regarded as a typical assembly of CH_2 groups (ignoring the terminal hydrogens) such as one would find in molten polyethylene. He quotes a value of $A_H = 5.2 \times 10^{-20}\,\mathrm{J}$. Since the density of hexadecane at 23°C is $772\,\mathrm{kg\,m^{-3}}$, this implies an average volume v per CH_2 group of $30 \times 10^{-30}\,\mathrm{m}^3$. Since $C = A_H/\pi^2\rho_n^2 = A_Hv^2/\pi^2$, we have $C = 47 \times 10^{-79}\,\mathrm{J\,m^6}$. This gives us confidence in using the value $43 \times 10^{-79}\,\mathrm{J\,m^6}$ derived from equation (8) and the value $60 \times 10^{-79}\,\mathrm{J\,m^3}$ for rubber.

To calculate the bulk modulus we need to know how the internal energy U of an assembly of CH_2 particles varies with separation, since $K = V\,\mathrm{d}^2U/\mathrm{d}V^2$. This can be achieved most simply by assuming a regular arrangement of the particles. It is convenient to put the CH_2 particles on a f.c.c. lattice, since this has been analysed for typical van der Waals solids such as Ar, Kr and Xe. In this connection we note that the experimentally determined bulk moduli for Ar, Kr and Xe are respectively 2.9, 3.4 and 3.6 GPa (ref. 9), as compared with a value of 2.5 GPa for rubber. Similarly, theoretical calculations by Shuttleworth[10] of the surface energy of the crystalline inert gases give values lying between 18 and $63\,\mathrm{mJ\,m^{-2}}$, which straddle the value for rubber. These similarities are not fortuitous, as the following shows.

If the lattice spacing is $2a$ (this implies a particle or atom diameter $\sigma = a\sqrt{2}$), it may be shown, using the 6–12 potential, that:

$$K = \frac{1.8C}{a^9} \tag{10}$$

In this structure the volume v per particle or atom is $2a^3$, so that:

$$K = \frac{14.4C}{v^3} \tag{11}$$

Using the values of v and C in *Table 1* we see that for the inert gases the calculated values of K are somewhat smaller than the observed values but agree to within a factor of 2. (We may recognize that other sources give larger values for C, which could provide better agreement.) For molten polyethylene the calculated value is more than five times larger than the experimental value: for rubber it is more than twice as big. However the derivations of equations (8), (10) and (11) assume a regular

Table 1 Properties of inert gases, polyethylene and polybutadiene

						Bulk modulus K (GPa)		
						Solid		Liquid
Species	Molecular volume (10^{-6} m^3)	v (10^{-30} m^3)	Refractive index (visible λ)	Surface energy (mJ m^{-2})	Coefficient C (10^{-79} J m^6)	Calc.	Exp.	Exp.
Ne	19^a	31	1.2	18^c	–	–	1.1^{a,i}	0.6^j
Ar	24^a	40	1.8	43^c	108^g	2.4	2.9^{a,i}	0.9^j
Kr	38^a	63	1.9	55^c	220^g	1.3	3.4^{a,i}	1.2^j
Xe	49^a	81	2.0	63^c	520^g	1.4	3.6^{a,i}	1.5^j
CH_2 (polyethylene)	15^b	23	1.51	30^d	43^h	5	2.0^i	1.0^{f,i}
$CH_2CHCHCH_2$ (polybutadiene)		25 per 'CH_2'	1.52	35^{d,e,f}	60^h	5.5		2.4^{i,k} rubber

[a] Single crystal at 0 K[9]
[b] Amorphous, semicrystalline, per monomer
[c] Single crystal at 0 K, theoretical[10]
[d] Experimental, wetting
[e] Experimental, adhesion[8]
[f] Rubbery state
[g] Ref. 4
[h] This paper, derived from the surface energy
[i] Experimental
[j] Above triple point[11]
[k] Crosslinked, rubbery state

rigid f.c.c. structure, whereas the CH_2 groups (or their equivalents in rubber) are in continuous thermal motion and are somewhat disordered. We should not expect better agreement. A similar calculation may be made of the latent heat of vaporization from the liquid state of $C_{28}H_{58}$ using an Arrhenius plot of the vapour pressure at various temperatures. The observed value is 0.62×10^{-20} J per CH_2 compared with a value of 1.3×10^{-20} J calculated from the value of $C = 43 \times 10^{-79}$ J m^6 for the CH_2 group.

Equation (11) also indicates how the bulk modulus of the inert gases would change on melting. A 10% expansion would lead to a 30% reduction of K. There would also be a reduction in the number of nearest neighbours and probably some entropic effects associated with local packing. We would thus expect melting to produce a reduction in K (taken as the reciprocal of the compressibility) of not more than 2. This is observed with the inert gases near their triple point[11]. Similarly, the compressibility of molten polyethylene in the rubbery state differs from that of the solid semicrystalline polymer by a factor of about 2 (refs. 12, 13).

We may take the analysis one stage further. By combining equations (8) and (11) and taking H_0 as $\sigma/2$, i.e. $a\sqrt{2}$, for a model f.c.c. structure, we obtain:

$$\frac{K}{\gamma} = \frac{146 H_0^2}{v} \approx \frac{45}{v^{1/3}} \tag{12}$$

This relation is followed qualitatively by the inert gases using the data of *Table 1*, though the constant is nearer 25 than 45. This may be due to inconsistent basic data and to other factors discussed above. We may conclude that the CH_2 groups (or their equivalent) interact by van der Waals forces, and that in rubber and molten polyethylene their interaction energy and bulk modulus resemble that of a 'small' inert gas just above its melting point.

Table 2 Surface tension γ and bulk modulus K of liquid hydrocarbons

Liquid	Temp. (°C)	ρ_B^{a} (kg m^{-3})	K (GPa)	γ (mJ m^{-2})	K/γ (10^{-10} m)	$Kv^{1/3}/\gamma$
n-Pentane	20	626	0.49	16	3.1	10.4
n-Hexane	25	655	0.60	18	3.3	10.5
n-Hexane	60	622	0.42	14.3	3.4	10.2
Octane	25	698	0.96	23.6	4.1	12.7
Dodecane	23	728	1.11	25.2	4.4	12.9
Hexadecane	23	772	1.35	27.4	4.9	15.5
Octadecane	60	755	1.06	25	4.2	12.9
PE molten	135	1000	1.0	~30	3.3	~10

[a] From the density the mean value of the volume v of the CH_2 unit has been calculated ignoring the effect of the bulky CH_3 end-groups. This becomes less important the longer the chain. The value of v ranges from 38×10^{-30} m^3 for pentane to 23×10^{-30} m^3 for molten polyethylene

THE SURFACE TENSION AND BULK MODULUS OF LIQUID HYDROCARBONS

Equation (12) suggests that it would be interesting to know if:

$$\frac{Kv^{1/3}}{\gamma} = \text{constant} \tag{13}$$

is applicable to the organic liquids studied by Sanchez. We consider here only his data for saturated liquid hydrocarbons. *Table 2* gives the bulk density ρ_B (kg m^{-3}), the surface tension (mJ m^{-2}) and the reciprocal of the compressibility, which is equivalent to the bulk modulus, K (GPa). The temperatures in some cases are very much higher than melting points, in other cases rather close. In spite of this unsatisfactory feature of the data, very clear conclusions emerge. The ratio K/γ is almost constant and varies only by ±20% over the whole range. Physically this is because the surface energy represents the work done in separating two unit areas against the bulk forces in the liquid. It has the dimensions of L^{-1}. This conclusion is not basically altered if we consider the more acceptable dimensionless ratio $Kv^{1/3}/\gamma$: it has a value of $11 \pm 10\%$ (if we omit the result for hexadecane) from pentane to liquid polyethylene. The theoretical value if the liquid consisted of isolated interacting spheres in a regular f.c.c. structure is approximately 45. Considering the crudity of the model, we cannot expect better numerical agreement.

CONCLUSIONS

The ideas discussed in this paper indicate that van der Waals forces between CH_2 groups (or their equivalents) can play an important part in explaining certain properties of polymers and rubber. For example, in the flow of molten polyethylene, the resistance to flow is attributed, in part, to the occurrence of transient entanglements. These could simply be the van der Waals interactions between short rows of CH_2 groups in one chain with similar groups in a neighbouring chain. Thus it may be possible to quantify the effect.

Again, the very large value of the bulk modulus of rubber compared with its tensile modulus is shown to be due to the fact that the tensile modulus is an entropic property whereas the bulk modulus involves intermolecular forces. These are van der Waals forces and, like the inert gases, are reasonably well represented by a 6–12 potential. The basic qualitative difference between these moduli is shown most markedly by the results of Wood and Martin[14], who studied the compressibility of latex and of a lightly peroxide-linked latex rubber. The compressibilities were almost identical. Further a rise in temperature from 0 to 40°C produced a decrease in K from about 2.6 to 2.1 GPa, i.e. a drop of nearly 20%. Over the same temperature range the tensile modulus of rubber increases by approximately 15%. These results emphasize the general view expressed in this paper and hinted at by Treloar[1] that the bulk modulus of rubber is in no way related to the tensile elastic modulus. The present paper, although relatively crude, attempts to bridge the 10 000-fold gap between E and K.

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