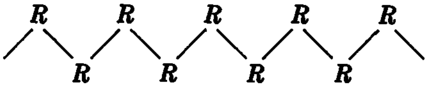
CHAPTER 13

CONFIGURATION OF POLYMER MOLECULES AND RUBBER ELASTICITY

In this chapter we present a brief introduction to polymer configuration problems and to the theory of rubber elasticity. The treatment is based to a considerable extent on the work of James and Guth (Supplementary Reading list). A number of other topics having to do primarily with polymer molecules in solution will be discussed in Chapter 21.

The basic prototype for polymer chains can be represented as



where R is the monomer unit, and the chain continues indefinitely at both ends. The configuration shown above is the fully extended configuration. Actually, because of rotation of the attached groups of R's around each R—R bond, a great many configurations are possible, of which the extended configuration is only one. One of the fundamental problems in polymer statistics is to deduce the relative number of configurations of a long polymer chain consistent with a specified end-to-end distance (Fig. 13–1). This problem is closely related to problems in brownian motion, random walks, diffusion, etc.

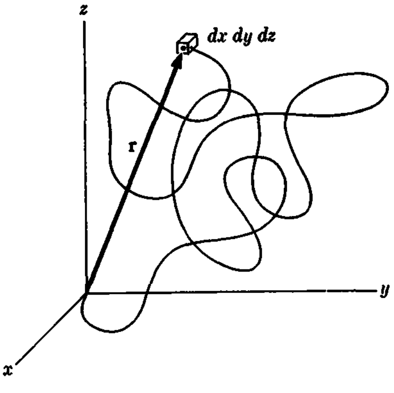
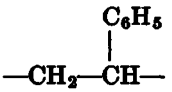


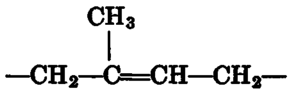
Fig. 13–1. Long polymer chain with end-to-end vector $\mathbf{r}$.

One of the simplest polymer chains, polymethylene, has $R = CH_2$. Other well-known possibilities for R are:



$$-CH_2-\overset{\overset{C_6H_5}{|}}{CH}-$$

Polystyrene



$$-CH_2-\overset{\overset{CH_3}{|}}{C}=CH-CH_2-$$

Rubber

In typical cases the number of monomers in a chain might be from 100 to 10,000.

13-1 Freely jointed chain. To handle this problem we first have to generalize the formalism of Section 7-4. Consider a linear polymer chain made up of M units, where M is large enough so that one chain can be considered a thermodynamic system. Each unit can exist in the states $i = 1, 2, \ldots, n$ with partition functions $j_i(T)$ and lengths l_i. The total length of the chain is l. The system (chain) is characterized thermodynamically by l, M, T. The canonical ensemble partition function is then

$$Q(l, M, T) = \sum_{\mathbf{M}} M! \prod_{i=1}^{n} \frac{j_i^{M_i}}{M_i!}, \tag{13-1}$$

where M_i is the number of units with length l_i, and the sum is over all sets $\mathbf{M} = M_1, M_2, \ldots, M_n$ consistent with the restrictions

$$\sum_{i=1}^{n} M_i = M, \tag{13-2}$$

$$\sum_{i=1}^{n} l_i M_i = l. \tag{13-3}$$

Equation (13-1) is a rather obvious generalization of Eq. (7-58). Here, for purposes of symmetry, we choose l as independent variable instead of one of the M_i [M_α was used in Eq. (7-58)]. The appropriate thermodynamic equation is

$$dA = -S\,dT + \tau\,dl + \mu\,dM, \tag{13-4}$$

with

$$A = -kT \ln Q \tag{13-5}$$

and τ = force pulling on the chain.

The restriction (13-3) is troublesome; to avoid it we change to another partition function. We use the partition function

$$\Delta(\tau, M, T) = \sum_{l} Q(l, M, T) e^{\tau l/kT} \tag{13-6}$$

This is the analog of Eq. (1–87). The connection with thermodynamics is

$$dF = -S\,dT - l\,d\tau + \mu\,dM, \tag{13–7}$$

$$F = A - \tau l = \mu M = -kT \ln \Delta. \tag{13–8}$$

We substitute Eqs. (13–1) and (13–3) in Eq. (13–6) and obtain

$$\Delta(\tau, M, T) = \sum_{\mathbf{M}} M! \prod_{i=1}^{n} \frac{(j_i e^{\tau l_i/kT})^{M_i}}{M_i!},$$

where now the only restriction on sets **M** is (13–2). The sum can be carried out immediately, and we have

$$\Delta(\tau, M, T) = \left(\sum_{i=1}^{n} j_i e^{\tau l_i/kT}\right)^{M} = \xi(\tau, T)^{M}, \tag{13–9}$$

This gives, for example, for the average length $\bar{l}$ of the chain at a given force τ,

$$\bar{l} = -\left(\frac{\partial F}{\partial \tau}\right)_{M,T} = kT\left(\frac{\partial \ln \Delta}{\partial \tau}\right)_{M,T} = MkT\left(\frac{\partial \ln \xi}{\partial \tau}\right)_{T}$$

$$= \frac{\sum_l lQ(l, M, T)e^{\tau l/kT}}{\sum_l Q(l, M, T)e^{\tau l/kT}} = M\,\frac{\sum_i l_i j_i e^{\tau l_i/kT}}{\sum_i j_i e^{\tau l_i/kT}}. \tag{13–10}$$

Equations (13–1) through (13–10) are formally the same as Eqs. (7–23) through (7–29). Therefore the notation $\Delta = \xi^M$ in Eq. (13–9) is appropriate. The partition function ξ for one unit has the same form as Δ in Eq. (13–6) for the entire chain [just as ξ in Eq. (7–27) resembles Ξ in Eq. (7–25)].

We now consider a special case, a chain of M units, each of length a, with "free" joints between units. That is, if we choose one end of any unit as origin, the other end of the unit moves freely (in the absence of a force on the chain) over the surface of a sphere with radius a (Fig. 13–2). The ends of the chain are a distance l apart and are on the x-axis. If the left end of the chain is considered fixed, we want to calculate, among other things, the equilibrium force τ along the x-axis necessary to hold the chain extended a distance l (Fig. 13–2). Real polymer chains do not have free joints between monomers (R units), but an approximate connection can be established between real chains and this idealized model (see Section 13–2).

The contribution of any one unit to l can range from $-a$ to $+a$. Thus l_i in Eq. (13–9) can vary continuously between these limits. We use x for this continuous variable. It is clear from Eq. (13–10) that j_i is proportional to the probability of a length l_i being observed when there is no force on

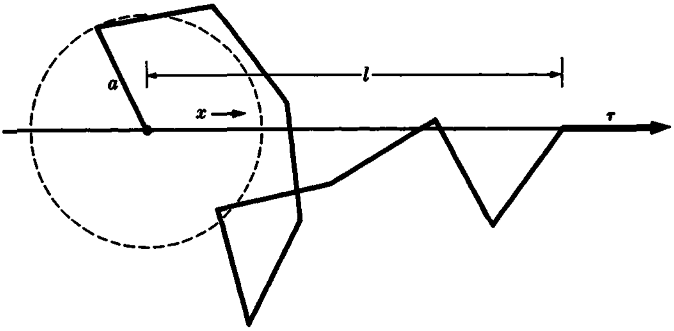


FIG. 13–2. Two-dimensional version of freely jointed chain. Each unit is of length a. The ends are on the x-axis and are a distance l apart.

the chain ($\tau = 0$). When there is a force, $j_i e^{\tau l_i/kT}$ is proportional to this probability. In the present problem, then, we let $j(x, T)\,dx$ be proportional to the probability that the end of a freely moving unit (Fig. 13–2) will have an x-component in dx. It is easy to see (Problem 13–1) that this probability is in fact independent of x (in the range $-a \leq x \leq +a$). Therefore we have

$$\begin{aligned} \xi &= \int_{-a}^{+a} j(T) e^{\tau x/kT}\,dx \\ &= \frac{2ja}{t}\sinh t, \qquad (13\text{–}11) \end{aligned}$$

where $t = \tau a/kT$. From Eq. (13–10) we find for the length-force relation

$$\bar{l} = MkT\left(\frac{\partial \ln \xi}{\partial \tau}\right)_T = Ma\mathcal{L}(t), \qquad (13\text{–}12)$$

or

$$t = \mathcal{L}^{-1}\left(\frac{\bar{l}}{Ma}\right), \qquad (13\text{–}13)$$

where $\mathcal{L}$ is the Langevin function defined in Eq. (12–30) and $\mathcal{L}^{-1}$ is the inverse Langevin function. The maximum extension is Ma; to achieve this we need $t \to \infty$. Figure 12–3 provides us with a plot of $\bar{l}/Ma$ (ordinate) against t (abscissa).

The occurrence of the same (Langevin) function here and in Section 12–3 is not surprising. In Section 12–3 we were dealing with freely rotating dipoles perturbed in their rotation by an electric field. Here we have freely rotating units of a chain perturbed in their rotation by a force pulling on the chain.

At small extensions ($\bar{l} \ll Ma$), we use $\mathcal{L}(t) = t/3$ and find the linear relationship

$$t = \frac{3\bar{l}}{Ma} \quad \text{or} \quad \tau = \frac{3kT\bar{l}}{Ma^2}. \tag{13-14}$$

Thus $\bar{l} = 0$ when $\tau = 0$, which is what we should expect on symmetry grounds (l can be positive or negative; with $\tau > 0$ we have $\bar{l} > 0$).

The question of fluctuations is of some interest. For example, when $\tau = 0$ does the value of l fluctuate much about $\bar{l} = 0$? By the methods of Section 2-1 we find (Problem 13-2) from Eq. (13-10) for the fluctuation in l at fixed τ,

$$\overline{l^2} - (\bar{l})^2 = kT\left(\frac{\partial \bar{l}}{\partial \tau}\right)_{M,T}. \tag{13-15}$$

From Fig. 12-3, we see that $\partial\bar{l}/\partial\tau$ is largest at small extensions. In the limit as $\tau \rightarrow 0$ (Eq. 13-14),

$$\frac{\overline{l_0^2}}{(Ma)^2} = \frac{\sigma_l^2}{(Ma)^2} = \frac{1}{3M}, \tag{13-16}$$

where we compare the fluctuation $\overline{l_0^2}$ with the maximum extension Ma instead of $\bar{l}$, since $\bar{l} \rightarrow 0$ as $\tau \rightarrow 0$. The subscript on $\overline{l_0^2}$ refers to $\tau = 0$. Thus, if $M = 3000$, $\sigma_l/Ma = 10^{-2}$, a rather significant fluctuation. The conclusion we draw from this is that chains of this size are not quite macroscopic in the thermodynamic sense. Hence, although quantities such as τ, $\bar{l}$, $\overline{l^2}$, T, etc., are well defined (see Sections 3-4 and 7-2) and equations of the type (13-10), (13-13), and (13-15) are valid, functions such as E, F, S, A, etc., for a single chain are slightly fuzzy in their thermodynamic significance. These latter functions become sharply defined, of course, for a system consisting of a *large number* of chains (as is always the case in practice).

From Eq. (13-16) we have that $\overline{l_0^2} = Ma^2/3$. Then Eq. (13-14) can be written

$$\tau = \frac{kT\bar{l}}{\overline{l_0^2}}. \tag{13-17}$$

Actually, the length-force equation in this form is applicable to small extensions of *any kind* of chain with $\bar{l}_0 = 0$. This relation follows directly from Eq. (13-15) and the necessary (by symmetry) linear dependence of τ on $\bar{l}$ at small $\bar{l}$.

The generalization of Eq. (13-17) to $\bar{l}_0 \neq 0$ (as, for example, in Section 7-4) and extensions that are not small can be deduced by a method which has very wide applicability in statistical mechanics. Define Δ_0 from Eq. (13-6) by

$$\Delta_0(M, T) \equiv \Delta(0, M, T) = \sum_l Q(l, M, T),$$

and rewrite Eq. (13-10) as

$$\bar{l} = \frac{1}{\Delta/\Delta_0}\left(\frac{\partial \Delta/\Delta_0}{\partial \tau/kT}\right)_{M,T}. \qquad (13\text{-}18)$$

Now if we expand the exponential in Eq. (13-6), we find

$$\frac{\Delta}{\Delta_0} = \frac{\sum_{i=0}^{\infty} (1/i!) \sum_l Q(l, M, T)(\tau l/kT)^i}{\sum_l Q(l, M, T)} = \sum_{i=0}^{\infty} \frac{1}{i!}\left(\frac{\tau}{kT}\right)^i \overline{l_0^i},$$

where $\overline{l_0^i}$, a function of M and T in general, is the average value of l^i at *zero force*. This follows from Eq. (13-10), which states that the probability of the chain having a length l is proportional to $Qe^{\tau l/kT}$ when the force is τ and to Q when $\tau = 0$ [see also Eq. (2-13)]. The occurrence of "unperturbed" ($\tau = 0$) averages is the essential point here, since these are not so difficult to calculate. Equation (13-18) becomes, then,

$$\bar{l} = \frac{\sum_{i=1}^{\infty} [1/(i-1)!](\tau/kT)^{i-1}\overline{l_0^i}}{\sum_{i=0}^{\infty} (1/i!)\,(\tau/kT)^i\,\overline{l_0^i}}. \qquad (13\text{-}19)$$

This gives $\bar{l} - \bar{l}_0$ as a power series in τ/kT, or vice versa. We shall not pursue this method further here (but see Problem 13-3).

As just indicated, $Q(l, M, T)$ is proportional to the probability that the free ($\tau = 0$) chain has a length l (for given M and T). An equivalent statement is that $Q(l, M, T)$ is proportional to the number of configurations (a configurational degeneracy) the chain can assume consistent with a length l, for given M and T. The dependence of this probability on l is perhaps the most important single property of a polymer chain. We are now in a position to deduce this dependence for a freely jointed chain (and more general chains) from Q. The same results can be obtained from the theory of random walks, without use of any of our statistical thermodynamical formalism.

The general method we employ is to integrate the length-force relation to obtain A and hence Q, using Eqs. (13-4) and (13-5). It should be noted that at this point we make use of macroscopic thermodynamics; hence in the following we are dealing implicitly with the limit of very long chains ($M \rightarrow \infty$). For the freely jointed chain,

$$dA = \tau\, dl = \frac{kT}{a}\,\mathcal{L}^{-1}\left(\frac{l}{Ma}\right) dl \qquad (T, M \text{ constant}),$$

and therefore

$$\frac{Q(l, M, T)}{Q(0, M, T)} = \exp\left[-\frac{1}{a}\int \mathcal{L}^{-1}\left(\frac{l}{Ma}\right) dl\right]. \tag{13-20}$$

This is the probability of a free chain having a length l relative to the probability of a length $l = 0$. It is also the ratio of the number of configurations of the chain with length l to the number with length zero. If we use the expansion (Problem 13–4)

$$\mathcal{L}^{-1}(x) = 3x + \tfrac{9}{5}x^3 + \cdots, \tag{13-21}$$

which can be deduced from Eq. (12–31), Eq. (13–20) becomes

$$\frac{Q(l, M, T)}{Q(0, M, T)} = \exp\left\{-M\left[\frac{3}{2}\left(\frac{l}{Ma}\right)^2 + \frac{9}{20}\left(\frac{l}{Ma}\right)^4 + \cdots\right]\right\}. \tag{13-22}$$

When $l \ll Ma$, we keep just the first term in this expansion and obtain the gaussian probability distribution ordinarily used,

$$\frac{Q(l, M, T)}{Q(0, M, T)} = e^{-3l^2/2Ma^2}. \tag{13-23}$$

This equation also follows directly on integrating the linear length-force equation, (13–14). Thus the gaussian probability distribution for the length of a free chain and the linear length-force relation for a chain under an extending force have the same limits of validity (Problem 13–5). To go beyond the linear length-force range, configurations of the chain with values of l outside the gaussian region become involved. That the "gaussian region" is in fact quite extensive can be seen as follows. The ratio of the correction term in Eq. (13–22) to the gaussian term is $(3/10)(l/Ma)^2$. Even for a very large extension, this quantity is small compared with unity. For example, take $M = 1000$ and an extension l' of ten times the root mean-square extension $(Ma^2/3)^{1/2}$. Then

$$\frac{3}{10}\left(\frac{l'}{Ma}\right)^2 = \frac{10}{M} = \frac{1}{100}.$$

We have been emphasizing the probability significance of Q and $Qe^{\tau l/kT}$ for the length of a chain with *fixed force*. But one must also keep in mind that Q has the usual connections with the thermodynamic properties of a chain with *fixed length* (fluctuating force). An example is the deduction of the linear $l - \tau$ relation from $Q(l)$ in Eq. (13–23) (Problem 13–6). Another example is the derivation of an equation for the dependence of the entropy S of a chain on its length l. In the present model, $Q(l, M, T)$ has the functional form (Eq. 13–20)

$$Q(l, M, T) = Q(0, M, T)f(l, M). \tag{13–24}$$

This relation, combined with Eq. (1–33) for S, leads immediately to

$$S(l, M, T) - S(0, M, T) = k \ln f = k \ln [Q/Q(0)]$$

$$= -\frac{k}{a} \int \mathcal{L}^{-1}\left(\frac{l}{Ma}\right) dl \tag{13–25}$$

$$= -\frac{3kl^2}{2Ma^2} = -\frac{3}{2} Mk\left(\frac{l}{Ma}\right)^2 \qquad (l \ll Ma). \tag{13–26}$$

The entropy is a maximum (largest number of configurations) at $l = 0$ and decreases with increasing l. The right side of Eq. (13–25) approaches $-\infty$ when $l \to Ma$. This, however, is pushing the model too far: a real polymer molecule, when fully extended, will not be rigid, but will have internal vibrational motion. The analog of this situation for an ideal gas is letting $V \to 0$ in Eq. (4–20).

It is possible to write Eq. (13–20) in an alternative and more explicit form. Thus, from Eqs. (13–11) and (13–13),

$$Q = e^{-A/kT} = \Delta\, e^{-\tau l/kT}$$

$$= \left[\frac{2ja \sinh \mathcal{L}^{-1}(l/Ma)}{\mathcal{L}^{-1}(l/Ma)}\right]^M \exp\left[-\frac{l}{a}\mathcal{L}^{-1}\left(\frac{l}{Ma}\right)\right],$$

or

$$\frac{Q(l, M, T)}{Q(0, M, T)} = \left[\frac{\sinh \mathcal{L}^{-1}(l/Ma)}{\mathcal{L}^{-1}(l/Ma)}\right]^M \exp\left[-\frac{l}{a}\mathcal{L}^{-1}\left(\frac{l}{Ma}\right)\right]. \tag{13–27}$$

Here again we should note that the limit $M \to \infty$ is implicit, since we have made use of the thermodynamic equivalence of the partition functions Q and Δ. Equation (13–22) may also be obtained from Eq. (13–27) (Problem 13–7).

From Eq. (13–19) we can derive a more general version of Eq. (13–23) [or Eq. (13–22)] for any polymer chain (see also Problem 13–3). We integrate $dA = \tau\, dl$, where

$$\tau = \frac{kT(l - l_0)}{\overline{l_0^2} - (\bar{l}_0)^2}, \tag{13–28}$$

and obtain

$$\frac{Q(l, M, T)}{Q(l_0, M, T)} = \exp\left[-\frac{1}{2}\frac{(l - l_0)^2}{\overline{l_0^2} - (\overline{l_0})^2}\right], \tag{13-29}$$

where M is a number proportional to the mass of the polymer molecule. Thus a gaussian probability distribution about $l = l_0 \equiv \overline{l_0}$, for small extensions, is *always* found. Since in general $\overline{l_0}$ and $\overline{l_0^2}$ are functions of temperature, Eq. (13–26) is somewhat more complicated here. For example, if $\overline{l_0}(T) \equiv 0$, we find (Problem 13–8)

$$S(l, M, T) - S(0, M, T) = -\frac{Mk}{2}\frac{l^2}{M\overline{l_0^2}}\left[1 - \left(\frac{\partial \ln \overline{l_0^2}}{\partial \ln T}\right)_M\right]. \tag{13-30}$$

We should expect $\overline{l_0^2}$ to increase with temperature for a real molecule owing to increased freedom of rotation about chemical bonds in the chain.

As a final topic in this section, we consider briefly the one-dimensional version of a freely jointed chain. The chain has M units, each of length a. Each unit must now always lie on the x-axis so that the possible contributions of a unit to l are the two values $-a$ or $+a$. Thus the chain resembles a folding ruler. In random-walk language, this is a random walk along a line with each step of length $+a$ or $-a$. In Eq. (13–9), we take $l_1 = +a$, $l_2 = -a$, and $j_1 = j_2 = j$. Then

$$\Delta = \left(2j \cosh \frac{\tau a}{kT}\right)^M \tag{13-31}$$

and, from Eq. (13–10),

$$\bar{l} = Ma \tanh t, \qquad t = \tau a/kT, \tag{13-32}$$

$$t = \tanh^{-1}\left(\frac{\bar{l}}{Ma}\right) = \frac{\bar{l}}{Ma} + \frac{1}{3}\left(\frac{\bar{l}}{Ma}\right)^3 + \cdots. \tag{13-33}$$

Just as the three-dimensional freely jointed chain under a pulling force resembles a gas of dipolar molecules oriented by an electric field (Section 12–3), the one-dimensional freely jointed chain under a force resembles a system of magnetic dipoles in a magnetic field (Section 12–4). In particular, Eqs. (12–45) and (13–32) should be compared. Figure 12–4 is also a plot of $\bar{l}/Ma$ (ordinate) against t (abscissa).

The present one-dimensional problem is a special case of the model discussed at the beginning of Section 7–4 using different independent variables. The connection in notation is $l_\alpha = -a$, $l_\beta = +a$, and $j_\alpha = j_\beta = j$.

By the same methods as for the three-dimensional case, we find (Problem 13-9)

$$\frac{Q(l, M, T)}{Q(0, M, T)} = \exp\left[-\frac{1}{a}\int \tanh^{-1}\left(\frac{l}{Ma}\right) dl\right] \tag{13-34}$$

$$= \cosh^{M}\left(\tanh^{-1}\frac{l}{Ma}\right)\exp\left(-\frac{l}{a}\tanh^{-1}\frac{l}{Ma}\right) \tag{13-35}$$

$$= \exp\left\{-M\left[\frac{1}{2}\left(\frac{l}{Ma}\right)^2 + \frac{1}{12}\left(\frac{l}{Ma}\right)^4 + \cdots\right]\right\}, \tag{13-36}$$

and $\overline{l_0^2} = Ma^2$.

13-2 Gaussian probability distribution for free polymer molecules. In this section we discuss further the gaussian probability distribution for free ($\tau = 0$) polymer molecules with the usual property $\overline{l_0} = 0$. Since the whole section is concerned with free chains, we drop the subscript zero on $\overline{l_0}$, $\overline{l_0^2}$, etc.

We saw in the preceding section that if one end of a long polymer molecule is chosen as origin and the other end is forced to lie on a preassigned line passing through the origin, say the x-axis, then according to Eq. (13-29), the probability that the ends of the molecule will be separated by a distance l is proportional, for l not too large, to $\exp(-l^2/2\overline{l^2})$. Since the direction of the preassigned line is arbitrary, we can make the equivalent alternative statement that if one end of a polymer molecule is chosen as origin, the probability that the other end will lie in a specified volume element $dx\,dy\,dz$, a distance r from the origin (Fig. 13-1), is proportional to

$$e^{-r^2/2\overline{l^2}}\,dx\,dy\,dz.$$

As a next step, we can conclude that if one end of a polymer molecule is chosen as origin, the probability that the other end is at a distance between r and $r + dr$, *irrespective of direction*, is

$$P(r)\,dr = \frac{e^{-r^2/2\overline{l^2}}4\pi r^2\,dr}{\int_0^\infty e^{-r^2/2\overline{l^2}}4\pi r^2\,dr} = (2\pi\overline{l^2})^{-3/2}e^{-r^2/2\overline{l^2}}4\pi r^2\,dr. \tag{13-37}$$

This probability is normalized to unity. The average values of r^2 and r are

$$\overline{r^2} = \int_0^\infty r^2P(r)\,dr = 3\overline{l^2}, \tag{13-38}$$

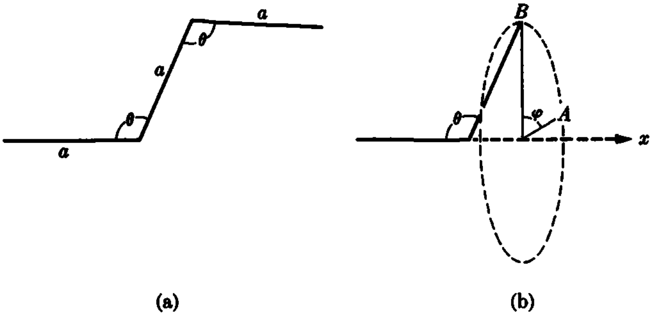


FIG. 13-3. Chain with fixed angle θ between units. In part (b), if the left unit is on the x-axis, the end of the right unit (point B) can be anywhere on the dotted circle. The angle φ is measured from some fixed point A.

$$\bar{r} = \int_0^\infty rP(r)\,dr = \left(\frac{8\overline{l^2}}{\pi}\right)^{1/2} = \left(\frac{8\overline{r^2}}{3\pi}\right)^{1/2}. \qquad (13\text{–}39)$$

Thus $\bar{l} = 0$ but $\bar{r} > 0$ (l can be positive or negative, but r is always positive). Using Eq. (13-38), Eq. (13-37) takes the more appropriate form

$$P(r)\,dr = \left(\frac{3}{2\pi\overline{r^2}}\right)^{3/2} e^{-3r^2/2\overline{r^2}}\,4\pi r^2\,dr. \qquad (13\text{–}40)$$

Equation (13-40), it will be recalled, follows from the very general equation (13-29) and is therefore not restricted to any particular model. In various special cases, an explicit expression can be given for $\overline{r^2}$. For example, for the freely jointed chain of Section 13-1, $\overline{l^2} = Ma^2/3$, and hence $\overline{r^2} = Ma^2$. We now list, without proof,* some further results for idealized models of polymer molecules, which, however, are considerably more realistic than the freely jointed chain.

(1) If the chain has M units or bonds of length a, and θ is the fixed bond angle between successive bonds (Fig. 13-3a), and if rotation about bonds (see the angle φ in Fig. 13-3b) is free, then for large M,

$$\overline{r^2} = Ma^2\frac{(1-\cos\theta)}{(1+\cos\theta)}. \qquad (13\text{–}41)$$

The tetrahedral angle $\theta = 109.5°$ is the case of most interest: $\overline{r^2} = 2Ma^2$. If $\theta = 90°$, $\overline{r^2} = Ma^2$, as for a freely jointed chain.

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* See Flory, pp. 414-422, for more details.

(2) If fixed bond angles θ_1 and θ_2 alternate (e.g., O—Si—O and Si—O—Si in the silicone chain), then

$$\overline{r^2} = Ma^2 \frac{(1 - \cos\theta_1)(1 - \cos\theta_2)}{(1 - \cos\theta_1 \cos\theta_2)} \tag{13-42}$$

for large M.

(3) Here we have the same situation as in (1) except that rotation about φ is hindered (see Section 9-5). For a hindering potential $V(\varphi)$ which is symmetrical about $\varphi = 0$,

$$\overline{r^2} = Ma^2 \frac{(1 - \cos\theta)(1 + \overline{\cos\varphi})}{(1 + \cos\theta)(1 - \overline{\cos\varphi})} \tag{13-43}$$

for large M and $\overline{\cos\varphi}$ not too near unity, where

$$\overline{\cos\varphi} = \frac{\int_0^\pi \cos\varphi\, e^{-V(\varphi)/kT}\, d\varphi}{\int_0^\pi e^{-V(\varphi)/kT}\, d\varphi}. \tag{13-44}$$

If $V(\varphi) \equiv 0$ or if $V(\varphi) = V(\varphi + 2\pi m^{-1})$, where $m \geq 2$, as in Eq. (9-18), then $\overline{\cos\varphi} = 0$ and Eq. (13-43) reduces to Eq. (13-41). However, actual polymer chains will not have this symmetry, and the $\overline{\cos\varphi}$ correction will be significant.

Although the models leading to Eqs. (13-41) through (13-43) are much more realistic than a freely jointed chain, they still cannot be taken too seriously. For example, bending and stretching of bonds have not been taken into account. Much more important, van der Waals (or other) attractions and, especially, repulsions between different units of the chain have been ignored. The neglect of van der Waals repulsions enters all the above models with the implicit assumption that the chain has a length but no thickness. Because of this complication alone, the polymer configuration problem differs significantly from ordinary random-walk problems: in a given polymer configuration, two parts of the chain cannot cross each other (occupy the same space), but there is no such restriction on random-walk (or diffusion) paths. In polymer language, this is called the excluded volume problem, and much recent theoretical work has been done on it.*

For the above reasons, detailed theories providing expressions for $\overline{r^2}$ in terms of a model are not very practical. Instead, one can regard $\overline{r^2}$

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* See, for example, F. T. Wall and J. J. Erpenbeck, *J. Chem. Phys.* **30**, 634, 637 (1959). These authors find that $\overline{r^2} \propto M^b$, where $b = 1.18$ for a tetrahedral lattice.

in Eq. (13–40) as an empirical quantity to be determined by some physical property of the polymer molecules that can be related to $\overline{r^2}$.

An *approximate* semiempirical device that may be used to relate a real chain of *unknown* $\overline{r^2}$ to the simplest model above, the freely jointed chain, is the following. Bond angle restrictions exist between one monomer and the next in a real polymer molecule. But if we call, say, five or ten (depending on the stiffness of the chain) monomers one "statistical unit," then the (end-to-end) direction of one statistical unit is essentially independent of the direction of neighboring statistical units in the chain. In fact, enough monomers are included in a statistical unit to ensure this independence. Thus we can replace the actual restricted chain of monomers by an equivalent chain of freely jointed statistical units. If M is the number of monomers in the chain and n the number in a statistical unit, then the number of statistical units is $M' = M/n$. The length of a statistical unit, a', is estimated as the root mean-square end-to-end distance of a statistical unit (i.e., a chain of n monomers). Then, finally, in Eq. (13–40) we put

$$\overline{r^2} = M'a'^2, \tag{13–45}$$

as for a freely jointed chain. The excluded volume problem is ignored here.

If $\overline{r^2}$ is *known*, then M' and a' can be chosen in a unique way so that not only does the product $M'a'^2$ equal $\overline{r^2}$ but also so that the fully extended length of the effective freely jointed chain, $M'a'$, is equal to the fully extended length of the real chain, l_{max}. That is, from the equations

$$\overline{r^2} = M'a'^2 \qquad \text{and} \qquad l_{\text{max}} = M'a',$$

we deduce

$$M' = \frac{l_{\text{max}}^2}{\overline{r^2}} \qquad \text{and} \qquad a' = \frac{\overline{r^2}}{l_{\text{max}}}. \tag{13–46}$$

Again the excluded volume problem is ignored.

13–3 Rubber elasticity. Rubber consists of an isotropic network of long polymer chains. The space-filling property of the chains, referred to in Section 13–2 in connection with the excluded volume problem, is important here, for rubber is a condensed phase with some liquidlike properties. A rather good analogy to a sample of rubber is a large tightly packed collection of very long actively wiggling worms, with each end of each worm attached to one end of each of three other worms (to form a network). The junctions joining the ends of four chains (worms) together are called cross-links. A real network will of course have imperfections (chains with free ends, etc.) just as a real crystal has imperfections.

It is commonplace that rubber has rather unique elastic behavior. This behavior is a consequence of the special configurational properties of polymer molecules considered in the preceding sections. We shall give here only a very brief and semiphenomenological discussion of rubber elasticity. An adequate treatment of the details of polymer network theory would take us far beyond the scope of this book. The reader interested in this subject should see the papers of James and Guth (Supplementary Reading list). The alternative, simpler, but less satisfactory theory of rubber elasticity, due to Wall, will be presented in Chapter 21. This latter theory provides the starting point for the only existing theories of polymer and polyelectrolyte gels, etc.

Let us begin by summarizing the observed thermodynamic behavior of rubber for extensions up to the order of 300%. First, rubber is approximately incompressible (as are typical liquids); when rubber is stretched, the volume stays almost constant. We can therefore use the following rather accurate thermodynamic equations for a sample of rubber of definite mass (L = length of sample):

$$dE = T\,dS + \tau\,dL, \tag{13-47}$$

$$dA = -S\,dT + \tau\,dL, \tag{13-48}$$

$$\tau = \left(\frac{\partial A}{\partial L}\right)_T = \tau_E + \tau_S, \tag{13-49}$$

$$\tau_E = \left(\frac{\partial E}{\partial L}\right)_T, \tag{13-50}$$

$$\tau_S = -T\left(\frac{\partial S}{\partial L}\right)_T = T\left(\frac{\partial \tau}{\partial T}\right)_L, \tag{13-51}$$

where τ_E and τ_S are the energy and entropy contributions to the force τ. By measuring τ as a function of both L and T, τ_S can be calculated from $(\partial\tau/\partial T)_L$, and hence τ_E can be obtained from Eq. (13-49). It is found in this way that τ_E is approximately zero: the elasticity of rubber is an entropy effect. Thus E depends on T but not on L. The implication of this is that when rubber is extended, the intermolecular potential energy remains constant, which is not surprising for a condensed phase of constant volume, and also that the extension is made possible by sufficient uncoiling of the polymer chains but does not involve any bending or stretching of chemical bonds. This behavior is equivalent to that of an ideal gas: E is a function of T but not V; and in the equation analogous to Eq. (13-49), $p = p_E + p_S$, $p_E = 0$.

An alternative and equivalent experimental observation is that the force τ is directly proportional to T at constant L. From the relation

$$\tau \cong \tau_S = -T\left(\frac{\partial S}{\partial L}\right)_T, \tag{13-52}$$

we conclude, then, that $(\partial S/\partial L)_T$ is a function of L only. This is consistent with a split of the entropy into two parts:

$$S = S_1(T) + S_2(L), \tag{13-53}$$

where $S_2(L)$ is the entropy associated with the configurational degeneracy of the polymer chains of the network. Again there is an analogy with an ideal gas: $(\partial S/\partial V)_T$ is a function of V only; $S = S_1(T) + S_2(V)$. For an ideal gas, replace, in Eq. (13-52), τ by p, τ_S by p_S, and $-(\partial S/\partial L)_T$ by $(\partial S/\partial V)_T = Nk/V$.

On the basis of the above discussion, we postulate that the essential molecular mechanism determining the elasticity of rubber is the elasticity of the individual chains making up the network, and this in turn is determined by the configurational properties of the chains (Section 13-2). We have to superimpose on this postulate the facts that the volume is constant on stretching and that a hydrostatic pressure exists in the rubber, just as in any liquid.

Consider an isotropic cube of rubber, with edge L_0, when under no force. The volume is $V = L_0^3$. Now let a force τ extend the rubber in the x-direction so that $L \equiv L_x > L_0$. Then

$$L_y = L_z, \qquad V = L_0^3 = LL_yL_z = LL_y^2. \tag{13-54}$$

Let us examine the mechanical equilibrium at a surface of the stretched rubber perpendicular to the z-axis. There is an outward force pLL_y owing to the hydrostatic pressure, but this is just balanced by the inward force of the molecular chains. We cannot write a satisfactory and completely explicit expression for this inward force without a detailed study of the properties of the network. However, for the small extensions we are interested in, we can deduce from Eq. (13-17) for a single chain that the inward force exerted by a network of N chains will have the form $CNkTL_z$, since L_z will be proportional to l_z for a single chain. Here, C is a constant which depends on the structure of the network. On equating the inward and outward forces, and putting $L_z = L_y$, we find

$$p = \frac{CNkT}{L}. \tag{13-55}$$

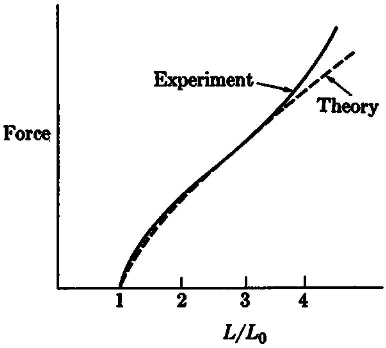

FIG. 13-4. Comparison of experimental and theoretical length-force relations for rubber in a typical case. The vertical scale has been adjusted to give best fit.

Next, consider the mechanical equilibrium at the surface (perpendicular to the x-axis) which is being pulled by an external force τ. Here $\tau + pL_y^2$ (outward force) is balanced by $CNkTL$ (inward force). Then

$$\tau = CNkTL - pL_y^2. \tag{13-56}$$

From Eqs. (13-54) and (13-55) this becomes

$$\tau = CNkTL_0\left(\alpha - \frac{1}{\alpha^2}\right), \tag{13-57}$$

where $\alpha = L/L_0$. This is the desired length-force equation, valid for small (up to about $\alpha = 3$) extensions. Of course $\alpha = 1$ when $\tau = 0$. The initial slope, $(d\tau/d\alpha)_{\alpha=1}$, is $3CNkTL_0$. Experiment and theory are compared in Fig. 13-4, where the vertical scale has been adjusted to give the best fit. The experimental "knee" is well reproduced by the theory. Deviations occur, as expected, at high extensions.

In the Wall theory of Chapter 21, $C = L_0^{-2}$.

PROBLEMS

13–1. Show that the function $j(x, T)$ for a unit in a three-dimensional freely jointed chain is independent of x in the range $-a \leq x \leq +a$. (Page 217.)

13–2. Derive Eq. (13–15) for the fluctuation in length of a chain under a constant force. (Page 218.)

13–3. For any molecule with $\overline{l_0} = \overline{l_0^3} = \cdots = 0$, show from Eq. (13–19) that

$$l = \overline{l_0^2}\left(\frac{\tau}{kT}\right) + \frac{1}{2}\left[\frac{1}{3}\overline{l_0^4} - (\overline{l_0^2})^2\right]\left(\frac{\tau}{kT}\right)^3 + \cdots \qquad (13\text{–}58)$$

Invert this series to get τ/kT in powers of $\bar{l}$, then integrate $dA = \tau\, dl$ to find

$$\frac{Q(l, T)}{Q(0, T)} = \exp -\left\{\frac{l^2}{2\overline{l_0^2}} + \frac{1}{8}\left[\frac{1}{(\overline{l_0^2})^2} - \frac{\overline{l_0^4}}{3(\overline{l_0^2})^4}\right]l^4 + \cdots\right\}. \qquad (13\text{–}59)$$

Equation (13–59) is exact only for $M \to \infty$, but Eq. (13–58) is exact in general. By comparing Eqs. (13–12) and (13–58), show that, for a freely jointed chain,

$$\overline{l_0^2} = \frac{Ma^2}{3} \quad \text{and} \quad \overline{l_0^4} = \frac{M^2a^4}{3}\left(1 - \frac{2}{5M}\right). \qquad (13\text{–}60)$$

(Page 219.)

13–4. Deduce the expansion of $\mathcal{L}^{-1}(x)$ from that of $\mathcal{L}(y)$ in Eq. (12–31). (Page 220.)

13–5. Use the gaussian form for $Q(l)$ (Eq. 13–29) to deduce Δ from Eq. (13–6) and $\bar{l}$ from Eq. (13–10). The result should agree with Eq. (13–28), of course. (Page 220.)

13–6. Derive the length-force equation, (13–14), from the canonical ensemble equations (13–4), (13–5), and (13–23). (Page 220.)

13–7. Deduce the probability expansion (13–22) from Eq. (13–27). (Page 221.)

13–8. Deduce the entropy equation (13–30) from Eqs. (1–33) and (13–29). (Page 222.)

13–9. Derive Eqs. (13–34) through (13–36) for a one-dimensional freely jointed chain. (Page 223.)

13–10. Obtain the equivalent of Eqs. (13–60) in Problem 13–3 for the one-dimensional freely jointed chain.

13–11. Discuss the problem of a two-dimensional freely jointed chain.

13–12. Derive Eq. (13–33) as a special case of Eq. (7–59).

13–13. Discuss the problem of a three-dimensional freely jointed chain in which each unit can have two lengths, a_α and a_β, with partition functions $j_\alpha(T)$ and $j_\beta(T)$ [in the notation of Eq. (13–11)]. Consider also the problem in which each unit can have any length between $a = 0$ and $a = a_m$ with equal probability. Incidentally, in an equivalent chain of statistical units, a gaussian distribution in a for the length of a statistical unit would be an appropriate approximation (in the text, we use a single length a').

13–14. Calculate $\overline{l_0^2}$ and $\overline{l_0^4}$ from the gaussian function (13–23). Compare with Problem 13–3.

13–15. Show the identity of Eqs. (13–34) and (13–35).

Supplementary Reading

Chandrasekhar, S., *Revs. Mod. Phys.* **15,** 1 (1943).

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