Part II. Mechanical Properties of Polymers

Chapter 5. The nature of rubber elasticity

• In 1805, Gough found that the length of rubber sample held under constant tension decreased as its temperature was increased and demonstrated that heat was evolved as a result of adiabatic extension.

• Until 1930, by that time the macromolecular character of the rubber molecules was completely accepted, the theory of rubber elasticity became possible to develope.

• The rubber specimen departed from the Hooke’s law over such as an enormous range of extensions.

Fig. 6.1 Typical stress/strain curve for elongation of vulcanized natural rubber.
1. The Thermodynamics of Stress and Strain

When a cross-linked elastomer is subjected to a sudden stress it reaches a state of equilibrium strain almost instantaneously and, similarly, the stress remains constant for an indefinite time in a sample maintained in a state of constant strain. Such equilibrium situations naturally lend themselves to a thermodynamic treatment and this has provided an invaluable basis for the study of highly elastic behaviour. Actually the experimental attainment of a true state of equilibrium is not quite as simple as was at one time supposed. Practical difficulties however, once recognized, can usually be overcome and in the best studies of the deformation of rubber and synthetic elastomers it may confidently be accepted that reversible processes have been examined.

For a reversible process the first and second laws of thermodynamics may be combined to give

\[ dU = TdS - dW \]  \hspace{1cm} (1)

where \( W \) is the work done by the system. The Helmholtz free energy \( F \) is defined by:

\[ F = U - TS \]  \hspace{1cm} (2)

so that at constant temperature

\[ (\delta F)_T = (\delta U)_T - T(\delta S)_T \]  \hspace{1cm} (3)

Combining eq. (1) and eq. (3) gives

\[ (\delta F)_T = -(\delta W)_T \]  \hspace{1cm} (4)

for an isothermal process.

If a linear force \( f \) acts upon a sample of length \( L \) the work done by the system during a small extension \( dL \) is \(-fdL\). If the volume of the system increases by \( dV \) as a result of this strain, then

\[ dW = -fdL + PdV \]  \hspace{1cm} (5)

where \( P \) is the external pressure. Hence

\[ (\delta F)_V = f(\delta L)_V - P(\delta V)_T \]  \hspace{1cm} (6)
Combining eq. (3) and eq. (6) gives at constant volume
\[ f = \left( \frac{\partial F}{\partial L} \right)_{T,V} = \left( \frac{\partial U}{\partial L} \right)_{T,V} - T \left( \frac{\partial S}{\partial L} \right)_{T,V} \]  
(7)

Differentiation of eq. (2) to
\[ dF = dU - TdS - SdT \]  
(8)
gives with eq. (1) and eq. (5), at constant volume,
\[ \left( \frac{\partial F}{\partial V} \right)_{T,V} = f \left( \frac{\partial L}{\partial V} \right)_{T,V} - S \left( \frac{\partial T}{\partial V} \right)_{T,V} \]  
(9)
Thus, since \( \left( \frac{\partial F}{\partial V} \right)_{T,V} \) is a perfect differential,
\[ \left( \frac{\partial f}{\partial T} \right)_{L,V} = - \left( \frac{\partial S}{\partial L} \right)_{T,V} \]  
(10)
Substituting for \( \left( \frac{\partial S}{\partial L} \right)_{T,V} \) in eq. (7) leads to
\[ f - T \left( \frac{\partial f}{\partial T} \right)_{L,V} = \left( \frac{\partial U}{\partial L} \right)_{T,V} \]  
(11)
Accepting for the moment that, as \( \left( \frac{\partial F}{\partial V} \right)_{T,P} \) is small for the extension of an elastomer,
\[ \left( \frac{\partial f}{\partial T} \right)_{L,P} \simeq \left( \frac{\partial f}{\partial T} \right)_{L,V} \]  
(12)

Fig. 6.3 Force against temperature for natural rubber at constant length. Extensions per cent at the standard temperature (20°C) are indicated on the lines. (Courtesy of R. L. Anthony, R. H. Caston and E. Guth, *Journal of Physical Chemistry* [23].)
The relationship between $f_u$ and $f_s$:

\[ f_u = \frac{\partial U}{\partial L}_{T,P} \]
\[ f_s = -T \frac{\partial S}{\partial L}_{T,P} \]

Since $f$ is function of $T$ and $P$, therefore

\[ df = \left( \frac{\partial f}{\partial T} \right)_P dT + \left( \frac{\partial f}{\partial P} \right)_T dP \]
\[
\left( \frac{\partial f}{\partial T} \right)_L = \left( \frac{\partial f}{\partial T} \right)_{L,P} + \left( \frac{\partial f}{\partial P} \right)_{L,T} \left( \frac{\partial P}{\partial T} \right)_L
\]

Hence at constant volume this may be written

\[
\left( \frac{\partial f}{\partial T} \right)_{L,V} = \left( \frac{\partial f}{\partial T} \right)_{L,P} + \left( \frac{\partial f}{\partial P} \right)_{L,T} \left( \frac{\partial P}{\partial T} \right)_{L,V}
\]

Now the Gibbs and Helmholtz free energies are related by

\[dG = dF + PdV + VdP\]

and introducing eq. (6) for \((\partial F)_T\) gives

\[\left( \frac{\partial G}{\partial T} \right)_T = f(\partial L)_T + V(\partial P)_T\]

Therefore

\[\left( \frac{\partial f}{\partial P} \right)_{T,L} = \left( \frac{\partial V}{\partial L} \right)_{T,P}\]

and eq. (18) becomes after substitution and rearrangement

\[
\left( \frac{\partial f}{\partial T} \right)_{L,P} = \left( \frac{\partial f}{\partial T} \right)_{L,V} - \left( \frac{\partial V}{\partial L} \right)_{T,P} \left( \frac{\partial P}{\partial T} \right)_{L,V}
\]

Although \((\partial V/\partial L)_{P,L}\) is very small, \((\partial P/\partial T)_{L,V}\) is large and this accounts for the inadequacy of eq. (12).

Defining the coefficients of thermal expansion \(\alpha_L\) and isothermal compressibility \(\beta_L\) at constant length by

\[\alpha_L = \frac{1}{V} \left( \frac{\partial V}{\partial T} \right)_{L,P} \quad \text{and} \quad \beta_L = -\frac{1}{V} \left( \frac{\partial V}{\partial P} \right)_{L,T}\]  \hspace{1cm} (23)

and remembering that

\[
\left( \frac{\partial P}{\partial T} \right)_{L,V} \left( \frac{\partial T}{\partial V} \right)_{L,P} \left( \frac{\partial V}{\partial P} \right)_{L,T} = -1
\]

gives

\[
\left( \frac{\partial P}{\partial T} \right)_{L,V} = \frac{\alpha_L}{\beta_L}\]  \hspace{1cm} (24)

The coefficient of dilation on extension \(\lambda\) is defined by

\[\lambda = \left( \frac{\partial \ln V}{\partial \ln L} \right)_{T,P}\]  \hspace{1cm} (25)

so that eq. (22) can now be rewritten to relate the thermo-elastic coefficients at constant pressure and volume by

\[
\left( \frac{\partial f}{\partial T} \right)_{L,P} = \left( \frac{\partial f}{\partial T} \right)_{L,V} - \frac{V\lambda \alpha_L}{L \beta_L}\]  \hspace{1cm} (26)
II. The statistic thermodynamic theory of high elasticity

1. The statistics of freely-jointed chain

The freely-jointed chain consists of \( n \) identical links of length \( l \) with no restriction whatever on the angles between successive links and with zero volume in the sense that separate links do not interfere with one another in space.

\[
l_x = l \cos \psi
\]

\[
P(l_x)dl_x = \frac{2\pi \sin \psi (dl \psi)}{4\pi^2} = \sin \psi d\psi
\]

\begin{figure}[h]
\centering
\includegraphics[width=0.5\textwidth]{freely-jointed-chain.png}
\caption{A freely-jointed chain in three dimensions.}
\end{figure}

Considering first the projection \( l_x \) on the \( x \)-axis made by a single link of the chain, if this link lies at an angle \( \psi \) to the \( x \) direction then

\[
l_x = l \cos \psi
\]

(1)

The probability \( p(l_x)dl_x \) that this projection shall have a value lying between \( l_x \) and \( (l_x + dl_x) \) is given by the fraction of the total solid angle accessible to the bond which gives a value of the projection in the correct range. For a freely-jointed chain all angles are accessible, hence

\[
\frac{\sin \psi}{4\pi} \frac{l \sin \psi}{l^2} \frac{l \sin \psi}{l^2} \frac{2\pi \sin \psi d\psi}{4\pi} = \frac{1}{2} \sin \psi d\psi
\]

(2)

The extreme values of \( l_x \) are \( +l \) for bonds lying to the right, i.e. \( \psi = 0 \) and \( -l \) for bonds lying to the left i.e. \( \psi = \pi \). Clearly, the mean value of \( l_x \) is zero but the mean square \( l_x^2 \) is not and may be evaluated by integrating the product of \( l_x^2 \) and \( p(l_x)dl_x \) from \( +l \) to \( -l \). Thus

\[
l_x^2 = \frac{1}{2} l^2 \int_0^{\pi} \cos^2 \psi \sin \psi d\psi = \frac{1}{2} l^2
\]

(3)
Provided \( n \) is sufficiently large, the total projection of any chain configuration on the \( x \)-axis may be calculated by assuming that each bond makes the root-mean-square projection \( \pm 1/3^l \). If \( x \) is the projection of the displacement vector \( r \) along the \( x \)-axis, then

\[
x = (n_+ - n_-)l/3^l
\]  

(4)

where \( n_+ \) is the number of bonds lying to the right, that is with positive orientation, and \( n_- \) is the number with negative orientation. Since the positive and negative roots have equal probabilities, the probability of finding a particular value of \( x \) or of \( (n_+ - n_-) \) is the same as the probability that \( n \) randomly arranged identical counters with positive and negative faces will show \( n_+ \) positive and \( n_- \) negative faces. This is well known to be [3]

\[
\left( \frac{1}{2} \right)^n \frac{n!}{n_+!n_-!}
\]

and is known as the binomial distribution. Supposing, for simplicity, that \( n \) is an even number, then this probability is a maximum for \( n_+ = n_- = n/2 \) and it decreases symmetrically as \( |n_+ - n_-| \) increases from zero to \( n \). Thus the most probable value of \( x \) is zero and the form of its distribution about zero is such that states for which \( x \ll n/12 \) are overwhelmingly the most numerous.

Let \( W_0 \) be the probability that \( x \) is zero and \( W_m \) the probability that \( x \) has the value \( (n_+ - n_-)l/3^l \). Provided \( [(n_+ - n_-)/n]^6 \) is negligible compared with \( (n_+ - n_-)/n \), it may be shown [3] by taking logarithms of \( W_0 \) and \( W_m \) and expanding the logarithms in series that

Let \( m = n_+ - n_- \), \( \omega(n_+, n_-) = \omega(n, m) = \left( \frac{1}{2} \right)^2 \frac{n!}{\left( \frac{n + m}{2} \right)!\left( \frac{n - m}{2} \right)!} \)

From Stirling's approximation, \( n! \geq \sqrt{2\pi n} n^{n+1/2} / e^n \)

\[
\omega(n, m) = \left( \frac{2}{\pi n} \right)^{n+1/2} \left[ 1 - \left( \frac{m}{n} \right)^2 \right]^{(n+1)/2} \frac{1 - m/n}{1 + m/n}^{m/2}
\]

If \( m/n \ll 1 \),

\[
\left( \frac{1 - m/n}{1 + m/n} \right)^{m/2} = \left[ \left( \frac{1 - m/n}{1 - (m/n)^2} \right)^{m/2} \right] \approx (1 - m/n)^m
\]
\[
(1 - m / n)^m = \left(1 - \frac{m}{n} \right)^{-n/m} \approx e^{-m^2/n}
\]

Moreover,
\[
\left[ 1 - \left( \frac{m}{n} \right)^2 \right]^{n+1 \over 2} = \left[ 1 - \left( \frac{m}{n} \right)^2 \right]^{\left( \frac{m}{n} \right)^2} \approx e^{m^2/2n}
\]

So,
\[
\omega(n, m) = \left( \frac{2}{\pi n} \right)^{1/2} e^{2n} e^{-m^2} = \left( \frac{2}{\pi n} \right)^{1/2} e^{2n/2n}
\]

Since each time we increase one unit in \(n\), \(m\) will be decreased by one unit.

If we use \(x\) to replace \(m\), \(x = (n_+ - n_-) \frac{l}{\sqrt{3}} = m \frac{l}{\sqrt{3}} \) and \(\Delta x = \frac{2l}{\sqrt{3}}\)

Thus,
\[
\omega(x) = \frac{\omega(n, m)}{\Delta x} = \left( \frac{2}{\pi n} \right)^{1/2} \left( \frac{\sqrt{3}}{2l} \right)^{-3x^2} e^{2n/2n^2}
\]

\[
W(x)dx = \frac{1}{\sqrt{2\pi n}} \exp \left( -\frac{3x^2}{2n^2} \right) dx \quad (9)
\]

This continuous function is known as the **Gaussian distribution**. It should be noticed that the exponential factor, which is characteristic of a Gaussian distribution, arose from the assumption that \((n_+ - n_-)/n\) is small, i.e., \(x < n/3\), whereas the pre-exponential factor required the assumption of a large value

Note
\[
\frac{l}{\sqrt{3}}(n_+ - n_-) = x, \quad \frac{n_+ - n_-}{n} = \frac{x\sqrt{3}}{l \cdot n} \ll 1, \quad x \ll \frac{l \cdot n}{\sqrt{3}}
\]

Also,
\[
\omega(x)dx = \omega_o e^{-3x^2/2n^2} dx
\]

where
\[
\omega_o = \frac{\beta}{\sqrt{\pi}} = \left( \frac{3}{2\pi} \right)^{1/2} \frac{1}{\sqrt{nl}}
\]
\[
\beta = \left( \frac{3}{2\pi} \right)^{1/2} \frac{1}{\sqrt{nl}}
\]
Expressions precisely analogous to eq. (9) may be derived for the probabilities of particular values of the projections on the y-axis and z-axis. The magnitude of the displacement vector \( r \) is given by

\[
 r^2 = x^2 + y^2 + z^2
\]

and hence the probability that the free chain end lies in the volume element \( dx \, dy \, dz \) about the point \((x, y, z)\) in Fig. 7.2 may be expressed as

\[
 W(x,y,z)dx\,dy\,dz = W(x)dx\,W(y)dy\,W(z)dz = \left(\frac{\beta}{\pi^3}\right)^3 \exp\left(-\beta r^2\right)dx\,dy\,dz
\]

where \( \beta \) is defined by

\[
 \beta = \frac{1}{\sqrt{2\pi}}
\]

This probability is seen to be a maximum for \( r = 0 \), i.e. when the two chain ends are coincident at the origin of the co-ordinate system.

To define the displacement length of a chain only the magnitude of \( r \) is important, its direction is not. Any chain with one end fixed at the origin \( O \) and the other end lying in the shell enclosed between the surfaces of two spheres whose centres are at \( O \) and whose radii are \( r \) and \( (r + dr) \) will have a displacement length between \( r \) and \( (r + dr) \). The probability \( W(r)dr \) of a chain having such a location is the product of \( W(x,y,z) \) and the volume \( 4\pi r^2 dr \) of this spherical shell, i.e.

\[
 W(r)dr = \left(\frac{\beta}{\pi^3}\right)^3 \exp\left(-\beta r^2\right)4\pi r^2 dr
\]

\( W(r) \) is called the radial distribution function. Its maximum is not at \( r = 0 \) and it is shown plotted for a polymer chain of typical molecular dimensions in Fig. 7.3. The radial distribution function has the same mathematical form as Maxwell's equation for the distribution of the velocities of the molecules in a three dimensional gas. Differentiating it with respect to \( r \) gives

\[
 \frac{dW(r)}{dr} = 8\pi r \left(\frac{\beta}{\pi^3}\right)^3 (1 - \beta r^2) \exp\left(-\beta r^2\right)
\]

and setting this differential equal to zero gives for the turning points of \( r \) the values 0, \( \infty \), \( 1/\beta \) and \(-1/\beta \). \( r = -1/\beta \) is without physical significance, 0 and \( \infty \) are minima in \( W(r) \) and \( 1/\beta \) defines the position of the maximum in Fig. 7.3. It occurs when \( r = l(2n/3)^{1/2} \). The mean-square value of \( r \) is given by

\[
 \bar{r}^2 = \int_0^\infty r^2 W(r)dr
\]

since by dealing throughout with a single chain it has been ensured that

\[
 \int_0^\infty W(r)dr = 1
\]
The effect of bond angle restrictions

\[ r^2 = \sum_{i=1}^{n} \frac{C_i}{i} + \sum_{i=1}^{n} \frac{C_i}{i}^2 + 2 \sum_{i=1}^{n-1} \sum_{j=i+1}^{n} \frac{C_i}{i} \frac{C_j}{j} \]  \hfill (2.12)

Equation 2.12 is valid for any polymer chain regardless of structure. We have to consider an ensemble of \( N \) chains each comprising \( n \) segments. The average of the squared end-to-end distance, \( \langle r^2 \rangle \), is equal to:

\[ \langle r^2 \rangle = \frac{1}{N} \sum_{i=1}^{N} \left( \frac{C_i}{i} \right)^2 = \sum_{i=1}^{n} \left( \frac{C_i}{i} \right)^2 + 2 \sum_{i=1}^{n-1} \sum_{j=i+1}^{n} \frac{C_i}{i} \frac{C_j}{j} \]

\[ = \langle \bar{r}_1 \bar{r}_1 \rangle + \langle \bar{r}_2 \bar{r}_2 \rangle + \cdots + \langle \bar{r}_n \bar{r}_n \rangle + \]

\[ + \langle \bar{r}_1 \bar{r}_2 \rangle + \langle \bar{r}_2 \bar{r}_3 \rangle + \cdots + \langle \bar{r}_n \bar{r}_{n-1} \rangle + \]

\[ + \cdots + \cdots + \cdots + \cdots + \]

\[ + \langle \bar{r}_n \bar{r}_1 \rangle + \langle \bar{r}_n \bar{r}_2 \rangle + \cdots + \langle \bar{r}_n \bar{r}_n \rangle \]
\[
\langle r^2 \rangle = n l^2 + 2 l^2 \sum_{i=1}^{n-1} \sum_{j=i+1}^{n} \langle \cos \theta_{ij} \rangle
\]

\[
= \left[ l^2 + l^2 \langle \cos \theta_{12} \rangle + \cdots + l^2 \langle \cos \theta_{n} \rangle + \right]
\]

\[
+ l^2 \langle \cos \theta_{23} \rangle + l^2 + \cdots + l^2 \langle \cos \theta_{n2} \rangle + \right]
\]

\[
\vdots \quad \vdots \quad \vdots \quad \cdots \quad \cdots \quad \cdots \quad +
\]

\[
\vdots \quad \vdots \quad \vdots \quad \cdots \quad \cdots \quad \cdots \quad +
\]

\[
l^2 \langle \cos \theta_{n1} \rangle + l^2 \langle \cos \theta_{n2} \rangle + \cdots + l^2
\]

(2.15)

If we assume

\[
\langle \mathbf{r}_i \mathbf{r}_{i+1} \rangle = l^2 \cos(180 - \tau)
\]

\[
\langle \mathbf{r}_i \mathbf{r}_{i+2} \rangle = l^2 \cos^2(180 - \tau)
\]

\[
\langle \mathbf{r}_i \mathbf{r}_j \rangle = l^2 |\cos(180 - \tau)|^{j-i}
\]

which after combination with eqs (2.13) and (2.15) gives:

\[
\langle r^2 \rangle = n l^2 + 2 l^2 \sum_{i=1}^{n-1} \sum_{j=i+1}^{n} |\cos(180 - \tau)|^{j-i}
\]

\[
= \left[ l^2 + l^2 \cos(180 - \tau) + \cdots + l^2 |\cos(180 - \tau)|^{n-1} + \right]
\]

\[
+ l^2 \cos(180 - \tau) + l^2 + \cdots + l^2 |\cos(180 - \tau)|^{n-2} + \right]
\]

\[
\vdots \quad \vdots \quad \vdots \quad \cdots \quad \cdots \quad \cdots \quad +
\]

\[
\vdots \quad \vdots \quad \vdots \quad \cdots \quad \cdots \quad \cdots \quad +
\]

\[
l^2 |\cos(180 - \tau)|^{n-1} + \cdots \quad \cdots \quad l^2
\]

The summation can be performed over a single variable \(k\) by substituting \(j - i\) by \(k\):

\[
\langle r^2 \rangle = n l^2 \left[ 1 + \frac{2}{n} \sum_{k=1}^{n-1} (n - k) \alpha^k \right]
\]

(2.18)

where \(\alpha = \cos(180 - \tau)\).
\[ \langle r^2 \rangle = nl^2 \left[ 1 + \frac{2}{n} \sum_{k=1}^{n-1} (n-k)x^k \right] \]
\[ = nl^2 \left[ 1 + 2 \sum_{k=1}^{n-1} x^k - \frac{2}{n} \sum_{k=1}^{n-1} kx^k \right] \]
\[ = nl^2 \left[ 1 + \frac{2(\alpha - \alpha^n)}{1 - \alpha} - \frac{2}{n} \left( \frac{\alpha(1 - \alpha)^n}{(1 - \alpha)^2} - \frac{n\alpha^n}{1 - \alpha} \right) \right] \]
\[ = nl^2 \left[ 1 + \frac{2\alpha}{1 - \alpha} - \frac{2\alpha (1 - \alpha)^n}{n (1 - \alpha)^2} \right] \]

For infinitely long chains \( (n = \infty) \):

\[ \langle r^2 \rangle = nl^2 \left[ 1 + \frac{2\alpha}{1 - \alpha} \right] = nl^2 \left[ \frac{1 + \alpha}{1 - \alpha} \right] \]
\[ = nl^2 \left[ \frac{1 + \cos(180 - \tau)}{1 - \cos(180 - \tau)} \right] \]

(2.19)

Insertion of the bond angle \( (\tau) \) value for an \( sp^3 \) hybridized carbon of \( 110^\circ \) gives the following degree-of-polymerization dependence of a methylene chain with free rotation:

\[ \langle r^2 \rangle \approx 2nl^2 \]

- Chain with hindered rotation

\[ \langle r^2 \rangle = nl^2 \left[ \frac{1 + \cos(180 - \tau)}{1 - \cos(180 - \tau)} \right] \left[ 1 + \langle \cos \phi \rangle \right] \left[ \frac{1 + \langle \cos \phi \rangle}{1 - \langle \cos \phi \rangle} \right] \]
• Long range interaction

Two segments in a polymer chain can not occupy the same space.

\[
\left( \frac{r_o^2}{2} \right)^{1/2} \sim n^{0.6} l
\]
TABLE 7.3. The Characteristic Ratio $r_0^2/P_x$ for Some Common Polymers, Evaluated at the Limit of High Chain Length

<table>
<thead>
<tr>
<th>Polymer</th>
<th>$r_0^2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Polyethylene</td>
<td>6.7</td>
</tr>
<tr>
<td>Polystyrene (atactic)</td>
<td>10.0</td>
</tr>
<tr>
<td>Polypropylene (isotactic)</td>
<td>5.7</td>
</tr>
<tr>
<td>Poly(methyl methacrylate)</td>
<td></td>
</tr>
<tr>
<td>Atactic</td>
<td>6.9</td>
</tr>
<tr>
<td>Isotactic</td>
<td>9.3</td>
</tr>
<tr>
<td>Syndiotactic</td>
<td>–7</td>
</tr>
<tr>
<td>Poly(ethylene oxide)</td>
<td>4.0</td>
</tr>
<tr>
<td>6-Nylon</td>
<td>5.9</td>
</tr>
</tbody>
</table>


2. Persistent (wormlike) chains

The model of "persistent," or wormlike, chains described by Krafft–Porod [33, 34] proved to be the most suitable for describing the conformational properties of rigid-chain molecules. In contrast to the Kuhn freely jointed chain, this model takes into account the orientational short-range interaction of chain elements. The Porod model (just as the Kuhn model) is based on a chain of length $L$ consisting of $n$ rectilinear elements of length $\Delta L$ so that $L = n \Delta L$. However, in this case, in contrast to the freely jointed chain, the spatial orientations of neighboring elements are not quite mutually independent: the direction of the first element is propagated ("remembered") to a certain extent along the chain. The correlation between the elements is expressed by the fact that the average value (for all conformations) of $\langle \cos \Delta \psi \rangle = k$ where $\Delta \psi$ is the angle between the neighboring elements, is not equal to zero and is identical for all chain elements (evidently, for a freely jointed chain $k = 0$). Hence, the combination of the values of $\Delta L$ and $k$ is a measure of orientational short-range interaction, i.e., of correlation or "persistence" in the chain. Mean cosines of the angles formed between the first chain element and the subsequent elements evidently correspond to the terms of the series $k, k^2, k^3, \ldots, k^n$, and, therefore, the angle $\psi$ between the first and $n$th elements is determined by the equation
\[ \langle \cos \psi \rangle = \langle \cos \Delta \psi \rangle^{n-1} = \exp \left[ (n-1) \ln \langle \cos \Delta \psi \rangle \right] = \exp \left( -\frac{L}{a} \right) \exp \left( -\ln \langle \cos \Delta \psi \rangle \right), \]  

(1.19)

where

\[ a = -\Delta L / \ln \langle \cos \Delta \psi \rangle. \]  

(1.20)

Here \( a \) is called the "persistence length." Equation (1.20) can also be written as

\[ \langle \cos \Delta \psi \rangle = e^{-\Delta L / a}. \]  

(1.20')

If the values of \( L \) and \( a \) are left constant and one takes the limit \( \Delta L \rightarrow 0 \) [correspondingly, according to Eq. (1.20), \( \langle \cos \Delta \psi \rangle \rightarrow 1 \)], the broken persistent chain is transformed into a continuous "wormlike" chain which from Eq. (1.19) is described by the equation

\[ \langle \cos \psi \rangle = e^{-L/a}. \]  

(1.21)

Hence, the curvature of the wormlike chain is the same at all points and is determined by the value of \( a \) calculated according to Eq. (1.20), whereas the directions of bends at these points are chaotic. In other words, a wormlike chain can be characterized as a line in space having a constant curvature.

If the first chain element is directed along the \( Z \) axis, the origin of which coincides with the beginning of the chain (Fig. 1.1), evidently the averaged chain projection on the \( Z \) axis is given by

\[ \langle Z \rangle = \frac{L}{0} \langle \cos \psi \rangle dL = \int_{0}^{L} \exp \left( -\frac{L}{a} \right) dL = a \left( 1 - e^{-L/a} \right). \]  

(1.22)

With increasing chain length \( (L \rightarrow \infty) \) the length of the projection tends to a limit

\[ \langle Z \rangle_{\infty} = a. \]  

(1.23)
Besides Eq. (1.20), Eq. (1.23) also gives the persistence length as the length of projection of an infinitely long wormlike chain on the axis of its first element.

A chain with free rotation and constant bond angle $\pi - \theta$ [Eqs. (1.10) and (1.11)] is also a persistent chain since a constant value of $\cos \theta = \alpha$ corresponds to each of its elements $l$. For the limiting transition to the continuous wormlike chain it is also necessary to replace $\alpha$ in Eq. (1.10) according to Eq. (1.20'), i.e., $\alpha = \cos \theta = \exp(-l/a) \approx 1 - L/na$, after which one should neglect the term $L/na$ and those of lower orders of magnitude. Hence, for the mean-square end-to-end distance of the wormlike chain, Eq. (1.10) yields the Porod equation [33]

$$\langle R^2 \rangle / 2aL = 1 - (1 - e^{-x})/x,$$  

(1.24)

where $x = L/a$ is the reduced chain length. Similarly, the combined application of Eqs. (1.20) and (1.11) leads to the following expression for the radius of gyration $\langle R^2 \rangle$ of the wormlike chain [8]:

$$3 \langle R^2 \rangle / aL = 1 - 3 [1 - 2x^{-1} + 2x^{-2} (1 - e^{-x})]/x.$$  

(1.25)

As $x \to 0$ (i.e., a short chain), the expansion

$$e^{-x} = 1 - x + x^2/2! - x^3/3! + \ldots$$

can be used, and Eqs. (1.24) and (1.25) then give the values of $\langle R^2 \rangle = L^2$ and $\langle R^2 \rangle_0 = (1/12)L^2$, which correspond to the conformation of a straight rod.

In the other limiting case as $x \to \infty$ (i.e., a long chain), it follows from Eqs. (1.24) and (1.25) that

$$\langle R^2 \rangle_\infty = 2aL, \quad \langle R^2 \rangle_\infty = aL/3.$$  

(1.26)

Equations (1.26) are equivalent to Eqs. (1.7) and (1.8) under the condition that

$$a = A/2.$$  

(1.27)

This means that at a large length $L$, a wormlike chain becomes Gaussian with the length of the Kuhn segment equal to twice the persistence length.
3. The equation of state for a single polymer chain

For real chains with hindered rotations the configurations which are consistent with the normal bond lengths and angles, and which give rise to a particular chain-end displacement vector $\mathbf{r}$, do not all have the same internal energy and hence do not have equal probabilities. A configuration integral $Z(r,T)$ may be set down formally [17] for a chain of $n$ bonds which are represented by the vectors $\mathbf{l}_1, \mathbf{l}_2 \ldots \mathbf{l}_n$, where

$$\mathbf{r} = \sum_{i=1}^{n} \mathbf{l}_i$$

(23)

If $\varepsilon(0)$ is the internal energy associated with a particular set of values of $\mathbf{l}_i$, then

$$Z(r,T) = \int \ldots \int \exp \left( -\frac{\varepsilon(0)}{kT} \right) d\mathbf{l}_1 \, d\mathbf{l}_2 \ldots d\mathbf{l}_n$$

(24)

where the integration is taken over all possible values of the bond vectors $\mathbf{l}_i$ which are consistent with the constant displacement vector $\mathbf{r}$.

According to the basic principles of statistical thermodynamics [18] the Helmholtz free energy ($F$) of the chain with displacement vector $\mathbf{r}$ is

$$F = -kT \ln Z(r,T) + \text{constant}$$

(25)

where the constant involves all the non-configurational degrees of freedom of the chain which are assumed to be unaltered by changes of configuration. The relation between $F$ and tension was obtained in Chapter 6, eq. (7). Replacing $E$ by $r$ it is

$$f = \left( \frac{\partial F}{\partial r} \right)_{\varepsilon,\mathbf{v}} = -kT \left( \frac{\partial \ln Z(r,T)}{\partial r} \right)_{\varepsilon,\mathbf{v}}$$

(26)

in which only the magnitude of $r$ and not its direction is important.

A detailed expression for $Z(r,T)$ cannot usually be formulated. For a chain of without constraints, the probability that $r$ lies between $r$ and $(r + dr)$ is given by

$$W(r)dr = \frac{Z(r,T)dr}{\int_0^\infty Z(r,T)dr}$$

(27)

The probability $W(r)$ of eq. (27) corresponds exactly in its physical meaning with $W(x,y,z)$ of eq. (11) which was derived for the freely-jointed chain. Multiplying eq. (27) by $4\pi r^2$ removes the directional restriction on $r$, hence

$$W(r)dr = \frac{Z(r,T)dr}{\int_0^\infty Z(r,T)dr} \cdot 4\pi r^2$$

(28)
Rearranging eq. (28) and taking logarithms gives
\[
\ln Z(r, T) = \ln W(r) + \ln \int_0^r Z(r, T) dr - \ln 4\pi - \ln r^2
\] (29)
and on differentiation
\[
\left( \frac{\partial \ln Z(r, T)}{\partial r} \right)_T = \left( \frac{\partial \ln W(r)}{\partial r} \right)_T \frac{2}{r}
\] (30)
since \( \int_0^r Z(r, T) dr \) is independent of \( r \).

If \( W(r) \) may be expressed by the Gaussian expression, eq. (13), eq. (30) becomes
\[
\left( \frac{\partial \ln Z(r, T)}{\partial r} \right)_T = -2\beta^2 r
\] (31)
where for real chains \( \beta \) is a parameter of the equivalent random chain and is sensitive to temperature if the real chain has hindered rotations. Recalling the definition of the equivalent chain and using eq. (16) gives
\[
\beta^2 = \frac{3}{2r_0^2}
\] (32)
where \( r_0^2 \) is the mean-square displacement length of the equivalent random chain and so, by definition, it is also the mean-square length of the real chain when unperturbed by excluded volume effects. The latter quantity can be obtained from the intrinsic viscosity \( [\eta]_b \) of the polymer determined in a solvent whose \( \theta \)-temperature is at the temperature of interest [19]. The full relation is
\[
[\eta]_b = M \Phi \overline{r}_0^2 / M^{\frac{1}{2}}
\] (33)
where \( M \) is the molecular weight, and \( \Phi \) a universal parameter equal to 2.1(±0.2)\times10^{14} when \( r_0 \) is in cm. and \( [\eta]_b \) in decilitres/g.

Substituting eq. (31) and eq. (32) into eq. (26) gives the equation of state
\[
f = 3kT r_0^2
\] (34)
This is valid over the range for which the Gaussian distribution is valid for the equivalent random chain. As it has not been assumed that all chain configurations have the same internal energy or \textit{a priori} probability, the derivation of this equation of state is general in the statistical thermodynamic sense. Differentiation of eq. (34) gives
\[
\left( \frac{3f}{\partial r} \right)_T = 3kT r_0^2
\] (35)
so that a single chain is predicted to obey Hooke's law. This behaviour is not
observed for a macroscopic sample of an elastomer. The parameter \( \overline{r}_0^2 \) is however temperature dependent and from eq. (34) differentiation with respect to temperature leads to

\[
\left( \frac{\partial f}{\partial T} \right)_r = \frac{3kT}{\overline{r}_0^3} \left( 1 - \frac{\partial \ln \overline{r}_0^2}{\partial \ln T} \right)
\]  

(36)

Since \( \partial \ln \overline{r}_0^2/\partial \ln T \) does not vary greatly with \( T \), eq. (36) predicts that at constant length \( f \) increases linearly with \( T \). This corresponds closely with the observed thermoelastic behaviour of elastomers.

When the displacement length \( r \) becomes sufficiently large the Gaussian distribution function is no longer adequate to express \( W(r) \) and the inverse Langevin equation or its expansion, eq. (19), is necessary. In this case

\[
\left( \frac{\partial \ln W(r)}{\partial r} \right)_T = -\frac{1}{l} \left[ 3 \left( \frac{r}{nl} \right) ^3 + 9 \left( \frac{r}{nl} \right) ^5 + \frac{297}{175} \left( \frac{r}{nl} \right) ^7 + \cdots \right] + \frac{2}{r}
\]

(37)

and substituting this into eq. (30) and eq. (26) gives

\[
f = \frac{kT}{l} \left[ 3 \left( \frac{r}{nl} \right) ^3 + 9 \left( \frac{r}{nl} \right) ^5 + \frac{297}{175} \left( \frac{r}{nl} \right) ^7 + \cdots \right]
\]

(38)

- **Langevin approximation**

A segment of length \( a \) in a freely orienting chain will usually have no preferred direction or orientation. When the chain is subjected to a tension \( F \), the segment will have different potential energies as it is aligned in various directions. In order to make the problem definite, let us suppose the tension is in the \( x \) direction and equivalent to \( \vec{F} \). As a result of this tension, it will require an average energy \( 2af \) to move a segment from a position parallel to the \( x \) direction to a position that is antiparallel. If the segment is assumed to have zero potential energy when it has no component of its length in the \( x \) direction, its potential energy is therefore

\[
V = -\vec{F}a \cos \theta
\]

(2.1)

where \( \theta \) is the angle between the \( x \) axis and \( a \).

According to the Boltzmann distribution law, the probability that the segment makes an angle \( \theta \) with the \( x \) axis is proportional to

\[
\exp \left( -\frac{V}{kT} \right)
\]

(2.2)
Hence, the average value of the $x$ component of $a$ as it undergoes thermal motion will be

$$
\langle a_x \rangle = \frac{\int (a \cos \theta)(2\pi a^2 \sin \theta \, d\theta) \exp [N a \cos \theta / kT]}{\int (2\pi a^2 \sin \theta \, d\theta) \exp [N a \cos \theta / kT]}.
$$

or

$$
\langle a_x \rangle = a [\coth (aF/kT) - (kT/aF)]
$$

(2.3)

The function in brackets in the right-hand term of Eq. (2.3) is usually referred to as the “Langevin function,” encountered by Langevin in his theory of the ordering of magnetic dipoles in a magnetic field. The function is usually represented by the symbol $\mathcal{L} (aF/kT)$.

Since $\langle a_x \rangle$ is the average $x$ component of a typical chain segment, the average $x$ separation of the chain ends will be $N$ times as large. Therefore,

$$
\langle r_x \rangle = Na \mathcal{L} (aF/kT)
$$

(2.4)

The subscript for $r$ is not essential, since the average value of $r_y$ and $r_z$ will be zero because there is no tension in these directions. Solving Eq. (2.4) for $F$ gives, symbolically at least,

$$
F = (kT/a) \mathcal{L}^*(r/Na)
$$

(2.5)

where $\mathcal{L}^*(r/Na)$ is called the “inverse Langevin function” of $r/Na$. This equation gives the force $F$ needed to maintain the chain at an average elongation $r$.

On the other hand, the work spent to pull the polymer chain will be

$$
\int_0^r F \, dr = (KT/a) \int_0^r \mathcal{L}^* (r/Na) \, dr
$$

If no force was applied to pull the polymer chain, the possibility for the chain end to appear in $r$ and $r+dr$ can be expressed by

$$
\omega(r) \, dr = \text{const} \exp \left[ - \left( \frac{\int_0^r F \, dr}{KT} \right) 4\pi r^2 \right] \, dr
$$
Assuming $\ell^*(r/Na) = u$, then $r/Na = \coth u - \frac{1}{u}$

$$\ln \omega(r) = \text{const} - N \left[ \left( \frac{r}{Na} \right)^u + \frac{u}{\sinh u} \right] + \ln 4\pi^2$$

$$= \text{const} - N \left[ \frac{3}{2} \left( \frac{r}{Na} \right)^2 + \frac{9}{20} \left( \frac{r}{Na} \right)^4 + \frac{99}{350} \left( \frac{r}{Na} \right)^6 + ... \right] + \ln 4\pi^2$$

When $r/Na > 0.3$, the polymer chain does not follow the Hook's law.
The stress/strain equation of a network

Affine deformation: Upon deformation, the crosslink junctions in the network transform affinely, i.e., in the same ratio as the macroscopic deformation ratio of the rubber sample. If the network consists of \( r_0 \) active sub-chains of mean-square length \( \bar{r}_0^2 \) in the isotropic unstrained state and of mean-square length \( \bar{r}^2 \) in the strained state then for an affine deformation,

\[
\bar{r}^2 = \frac{1}{2}(\gamma_x^2 + \gamma_y^2 + \gamma_z^2)\bar{r}_0^2
\]

(57)

If the sub-chains obey eq. (34), \( W \), the total work done by the sub-chains, is therefore given by

\[
W = 3\nu_0 \left( \frac{r}{r_0} \right)^{\gamma (\bar{r}_0^2)} \int_{\gamma_1^2/\gamma}^{\gamma_2^2/\gamma} r dr = \Delta F_{\text{ai}}
\]

(58)

where from eq. (4), Chapter 6, \( \Delta F_{\text{ai}} \) is the change in Helmholtz free energy of the network due to the deformation. Hence the stored energy is

\[
\Delta F_{\text{ai}} = \nu_0 \left( \frac{\bar{r}_0^2}{\bar{r}^2} \right) \left( \gamma_x^2 + \gamma_y^2 + \gamma_z^2 - 3 \right)
\]

(59)
introduced into eq. (59) to give

$$\Delta F_d = \frac{\nu \kappa T}{2} \left( \frac{2}{3} \frac{\rho a - \frac{2}{\gamma} - 3}{\rho a} \right)$$

(60)

Differentiation of eq. (60) with respect to \( \gamma \) gives for the force of extension

$$f_z = \left( \frac{\partial F}{\partial \gamma} \right)_{\gamma_0, a} = \nu \kappa T \left( \frac{\rho a}{3} \right) \left( \frac{\gamma - 1}{\rho a} \right)^2$$

(61)

If unit volume of the network is considered then \( f_z \) is the stress and \( \nu a \) is the number of active sub-chains per unit volume. \( \nu a \) corresponds with \( K \) in many theories. Thus eq. (61), which made no assumption about \( (\partial U)_{\gamma_0, a} \), differs from eq. (56) through the inclusion of the term \( \left( \frac{\rho a}{3} \right) \). \( \rho a \) is insensitive to temperature, being determined only by the macroscopic volume of the particular sample. \( \rho a \) is the mean-square displacement length of the unperturbed chains and, as discussed earlier, it varies with temperature as the potentials hindering free rotation are overcome. Since the mean chain lengths are proportional to the cube root of the volume then, for unit volume of the unstrained network,

$$\frac{\rho a^3}{\rho a_0^3} = \frac{1}{\rho a_0^3}$$

(62)

where \( V_0 \) is the volume which the same set of chains would occupy in the noncross-linked and unperturbed state. According to eq. (33)

$$V_0 \propto \eta_b$$

where \( \eta_b \) is the intrinsic viscosity in a \( \theta \)-solvent of a noncross-linked polymer with the same average molecular weight as the cross-linked sub-chains. This factor is important in connection with the thermo-elastic behaviour of elastomers.

---

![Network structures](image.png)

**Fig. 7.6** Network structures
- (a) cross-links
- (b) chain end groups
- (c) active sub-chains
- (d) inactive rings
- (e) inactive loose ends
III. Practical aspects of elasticity theory

1. Testing the stress/strain equation

Eq. 69 indicates that the stress is a function of temperature, strain, molecular weight, degree of crosslinking, et al.
of all these predictions will now be described. By considering only experimental data obtained at extension ratios less than four, the deviations from the Gaussian distributions are small enough to be ignored.

Since the theory of elasticity is thermodynamic in origin it is essential to perform the stress and strain measurements under conditions of true equilibrium. To this end, experiments on crystallizable elastomers have to be carried out at temperatures above the melting points of the crystallites in the stretched state. In addition great care is needed to ensure that the tension established at each deformation represents a true equilibrium state. Experimentally equilibrium has been unexpectedly difficult to achieve, and the problem is accentuated by the lack of a critical test for showing when equilibrium has been reached. The full extent of this practical difficulty was not appreciated by the earliest workers and consequently their results have no absolute significance although they confirmed the trends predicted by the thermodynamic theory.

2. The Thermo-elastic Phenomena

One of the most thoroughly examined aspects of the theory is the connection between tension and temperature at constant pressure [1, 3, 5, 6, 7]. Differentiating eq. (2) for a change of temperature at constant extension ratio and pressure gives

$$\left( \frac{\partial f}{\partial T} \right)_{\gamma, P} = \frac{\nu k}{\gamma L_0} \left( \frac{\gamma}{\gamma^*} \right) \left[ 1 + \frac{\partial \ln \left( \frac{\gamma}{\gamma^*} \right)}{\partial \ln T} \right]$$

(3)

As the second term in the square bracket is certainly small compared with unity, plots of $f$ against $T$ at constant $\gamma$ and pressure should appear to be linear within experimental error and this is observed [1, 3]. Furthermore $\left( \frac{\partial f}{\partial T} \right)_{\gamma, P}$ should decrease as $\gamma$ decreases and tend to zero as $\gamma$ approaches unity. That is to say, there should be no therma-elastic inversion point for which $\left( \frac{\partial f}{\partial T} \right)$ changes sign. This also has been demonstrated [1].

The observed inversion in $\left( \frac{\partial f}{\partial T} \right)_{L, P}$ can readily be understood if eq. (2) is differentiated, remembering that $\gamma$ is equal to $L/L_0$ and neglecting the temperature variation of $\left( \frac{\gamma}{\gamma^*} \right)$. This gives

$$\left( \frac{\partial f}{\partial T} \right)_{L, P} = \frac{\nu k}{\gamma L_0} \left[ \gamma \left( 1 - \frac{2T \gamma^*}{3} \right) - \frac{1}{\gamma^*} \left( 1 + \frac{T \gamma^*}{3} \right) \right]$$

(4)
where $\alpha$ is the coefficient of cubical expansion. It can easily be verified that for
\[
\gamma < \left(\frac{3 + \alpha T}{3 - 2\alpha T}\right)^{\frac{1}{2}}
\]
$(\partial f/\partial T)_{L,P}$ becomes negative. For $T = 300\,^\circ$K and $\alpha = 6.6 \times 10^{-4}$ deg$^{-1}$ this gives $\gamma = 1.07$ as the value below which $(\partial f/\partial T)_{L,P}$ becomes negative. This is in very satisfactory correlation with the results of Anthony, Caston and Guth reproduced in Fig. 6.3. It will also be clear from this figure that although the right hand side of eq. (4) is certainly not independent of temperature the plots of $f$ against $T$ at constant $L$ and $P$ are linear within the accuracy of the experiments. This effect has been amply confirmed by the more recent work of Ciferri [5, 6, 7].

To study the thermo-elastic behaviour more completely it is advantageous to examine the coefficient $[\partial \ln (f/T)/\partial T]_{L,P}$ (see [8]). This may readily be obtained from the experimental data at constant length and pressure since, by straightforward calculus,
\[
\frac{\partial \ln (f/T)}{\partial T}_{L,P} = \frac{1}{f} \frac{\partial f}{\partial T}_{L,P} \frac{1}{T}
\]  

(5)

Equation (2) may be rearranged, after taking logarithms, to give
\[
\ln (f/T) = \ln \eta + \ln \left(\frac{L}{L_0}\right) + \ln \left(\frac{L_0}{L_0 - L}\right) - \ln \eta_0
\]

(6)

Now if $V$ is the volume of the network at the appropriate $T$, $P$ and $f$ then $L_0 \propto V^\frac{2}{3}$ and $\eta_0 \propto V^\frac{2}{3}$.

Hence differentiation of eq. (6) leads to
\[
\frac{\partial \ln (f/T)}{\partial T}_{L,P} = \frac{\partial \ln V^\frac{2}{3}}{\partial T} \left(\frac{\gamma + 2/\gamma^3}{\gamma - 1/\gamma^3}\right) \frac{\partial \ln V^\frac{2}{3}}{\partial T} - \frac{\partial \ln \eta_0^\frac{2}{3}}{\partial T}
\]

and introducing the coefficient of thermal expansion $\alpha$ gives
\[
\frac{\partial \ln (f/T)}{\partial T}_{L,P} = \frac{\alpha}{(\gamma^3 - 1)} \frac{\partial \ln \eta_0^\frac{2}{3}}{\partial T}
\]

(7)

With the aid of eqs. (5) and (7) the experimental curves of $f$ against $T$ at constant $L$ and $P$ permit $(\partial \ln \eta_0^\frac{2}{3}/\partial T)$ to be obtained. This quantity, which measures the temperature variation of the unperturbed chain dimensions, is a function of the internal hindrances to rotation about the chain bonds. It may also be evaluated from viscosity measurements in a series of $\theta$-solvents [9] or, under suitable circumstances, from the temperature coefficient of viscosity in an 'athermal' solvent provided $\eta_0^\frac{2}{3}$ is determined at a single temperature in
one $\theta$-solvent [10]. Some values obtained by the thermoelastic method are
compared, in Table 8.1, with the values available from viscosity measure-

**Table 8.1**

**Variation of unperturbed chain lengths with temperature**

<table>
<thead>
<tr>
<th>Elastomer</th>
<th>$\theta \ln \frac{\delta}{\delta T}$ thermo-elastic (deg$^{-1} \times 10^8$)</th>
<th>$\theta \ln \frac{\delta}{\delta T}$ viscosity (deg$^{-1} \times 10^8$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Polyethylene</td>
<td>-0.97 ± 0.10</td>
<td>-1.2 ± 0.2</td>
</tr>
<tr>
<td>Polyisobutylene</td>
<td>-0.08 ± 0.06</td>
<td>-1.1 ± 0.5*</td>
</tr>
<tr>
<td>Natural rubber</td>
<td>+0.41 ± 0.04</td>
<td>—</td>
</tr>
<tr>
<td>Polydimethyl siloxane</td>
<td>+0.44 ± 0.12</td>
<td>+0.33 ± 0.05</td>
</tr>
<tr>
<td>GR-S</td>
<td>-0.42 ± 0.2</td>
<td>—</td>
</tr>
</tbody>
</table>

* older data of uncertain accuracy.

3. **The Ratio of Stress to Strain**

The difficulty of achieving absolute equilibrium has been nowhere more
evident than in attempts to test the ratio of stress to strain for deformation

![Figure 8.1](image_url)  

**Fig. 8.1** Stress versus extension ratio $\gamma$ for compression and extension of natural rubber with 8% combined sulphur at 20°C. The points are experimental and the solid line theoretical. (Courtesy of L. R. G. Treloar, *Transactions of the Faraday Society* [13].)
Flory [15]. Earlier it had been found that experimental data could be successfully represented by a two constant equation, often called the Mooney equation,

\[ f = 2(C_1 + C_2) \left( \frac{1}{\gamma} - \frac{1}{\gamma^2} \right) \]  

(9)

The constant \( C_1 \) corresponds with the first two terms on the right hand side of eq. (2) but the constant \( C_2 \) is a purely empirical necessity.

Ciferrì and Flory have shown that \( C_2 \) is affected by the rate of stress relaxation in the elastomer and is therefore connected with the rate of approach to equilibrium as well as with the equilibrium state itself. \( C_2 \) is much smaller for swollen elastomers than for unswollen ones. For a variety of unswollen elastomers \( C_2 \) varies considerably, being relatively large for natural rubber and least for silicone rubbers which, as mentioned before, possess a high internal mobility. Furthermore, Gee's method [3] of establishing equilibrium tensions, by alternately swelling and deswelling at each length, had the effect of reducing \( C_2 \).
4. The effect of molecular weight

It can be seen that for a particular elastomer at constant $T$, $\gamma$, and $M_c$, a plot of the stress against $1/M$ for a series of samples of varying $M$ should yield a straight line. The problem of preparing a set of samples with constant $M_c$ but varying $M$ was solved by copolymerizing isobutylene with a small but variable proportion of isoprene. This procedure gave three samples of raw butyl rubber containing respectively 0.5, 1.0 and 1.2% of isoprene units distributed at random along the chains and available for vulcanization. Each sample was heterogeneous with regard to molecular weight and was separated into a series of fractions by precipitation from benzene solution with acetone. The molecular weights $M$ of the various fractions were determined from their intrinsic viscosities in di-isobutylene. The fractions were vulcanized using a standard procedure so that all the fractions from a single raw butyl sample (i.e. with a fixed percentage of isoprene) had the same $M_c$ but, of course, retained their characteristic $M$ values.

\[
f = \frac{mRT}{L_oM_c} \left(1 - 2 \frac{M_c}{M} \left(\frac{r}{P_o}\right)^{\gamma - \frac{1}{\gamma^*}} \right) \left(\gamma - \frac{1}{\gamma^*}\right)
\]

![Fig. 8.3 Tension $f$ versus reciprocal of original molecular weight $M$ for three samples of butyl rubber with different $M_c$ at constant extension ratio $\gamma = 4.6$. (Courtesy of P. J. Flory, Industrial and Engineering Chemistry [196])](image-url)
4. Behavior of elastomers at large deformations

Corrections to the simple stress/stain equation, proposed by Mooney [26], permit an accurate representation of a wide range of experimental data with very few empirical constants. Rivlin [27] has shown that for an isotropic substance the stored energy function, eq. (59) of Chapter 7, can be generalized. The free energy of any homogeneous strain at constant volume is given by

\[ \Delta F_d = \frac{\nu k T}{2} \left( \frac{1}{\gamma_0^2} \gamma^2 + \frac{1}{\gamma_0^3} \gamma^3 + \frac{1}{\gamma_0^4} \gamma^4 - 3 \right) + C \left( \frac{1}{\gamma_0^2} + \frac{1}{\gamma_0^3} + \frac{1}{\gamma_0^4} - 3 \right) \]  

(13)

The value of the empirical constant \( C \) cannot be predicted by a molecular theory and, like \( C_2 \) of eq. (9), it may be connected with some form of slow relaxation process. Equation (13) has been thoroughly tested by Rivlin and Saunders [28] who have found that it can be used to correlate data for different types of homogeneous strain using a single value of \( C \) for each material. In the case of simple elongation, differentiation of eq. (13) gives an equation which corresponds exactly with the Mooney equation (eq. (9)).

6. The effect of crystallization

![Graph showing the effect of crystallization on Young's modulus](image)

*Fig. 8.7 Increase in Young’s modulus of natural rubber as a function of crystallinity. (1% increase in density is approximately equivalent to 10% crystallinity.) (Courtesy of M. Leitner, Transactions of the Faraday Society [32].)*
An approximate theory which combines the thermodynamic treatment of crystallization with the Gaussian network theory has been given by Flory [34] and subsequently extended by him to highly crystalline fibrous polymers. Flory dealt with the case in which all the crystallites were formed after stretching the amorphous elastomer and were perfectly oriented in the direction of stretching. He replaced the equation for a completely amorphous material by an equation which amounts, in the present notation, to

\[ f = \frac{\nu_k T}{L_0(1 - \nu_e)} \left[ \frac{\gamma - 1}{\gamma^2} - \nu_e \left( \frac{6n}{\pi} \right)^{1/2} \right] \]  

(14)

where \( \nu_e \) is the volume fraction of the crystalline material at equilibrium at the extension ratio \( \gamma \). \( n \) is the number of links in a freely jointed chain statistically equivalent to an actual sub-chain of the network. The term \( 1/(1 - \nu_e) \) allows for the reduction in the volume of deformable material. It will be seen that the second term in the square brackets of eq. (14) has the effect of reducing the stress below the value for a fully amorphous elastomer. When the crystallites are oriented in the stretching direction the chain segments in the crystallites are fully extended in this direction. Consequently the amorphous segments connecting them are not so highly elongated as they would be in the absence of oriented crystallization.

---

**Fig. 8.8** Stress versus strain for elongation of latex rubber at 50°C showing effect of crystallization at large extensions.

Curve (a): experimental for latex rubber lightly vulcanized, \( M_e = 4100 \)

Curve (b): theoretical from curve (b) of Fig. 8.6.

A random network of sub-chains with 100 links corresponds with natural rubber of \( M_e = 4800 \).

(Data from L. R. G. Treadgold, *Transactions of the Faraday Society* [13, 30]).
7. Fillers

Powders of certain inorganic substances consisting of particles of colloidal dimensions are frequently incorporated into elastomers prior to vulcanizing. Substances such as the alkaline earth carbonates and oxides and, especially, carbon black and silica are used in this way. They are called fillers and have the effect of increasing the tensile strength and also the elastic modulus of the material. For those cases in which the fillers do not combine chemically with the rubber a theoretical treatment of their effect on the elasticity has been given by Guth [40]. He has used Einstein’s equation for the viscosity of a suspension of spherical particles in a continuous medium to estimate the change in the internal freedom of an idealized network containing spherical filler particles. His conclusions can be simply expressed by eq. (16), where \( \nu_r \) is the volume fraction of filler incorporated into the elastomer.

\[
f = f_0(1 + 2.5\nu_r + 14.1\nu_r^2)
\]

(16)

\( f \) and \( f_0 \) are respectively the actual stress and the stress which would be found when using an unfilled sample maintained at the same extension ratio. The equation has been found to apply fairly well in practice for values of \( \gamma \) up to about 2. It predicts that for 20% filler by volume the elastic modulus for simple extension will be increased by more than 50%.

By far the most important effect of a filler is to increase the tensile strength of an elastomer. In the synthetic elastomers this increase may reach tenfold. When the filler is carbon black and any form of sulphur vulcanization is used the carbon particles become bonded chemically to the rubber. This has the same effect on the elasticity as increasing the degree of cross-linking, and it is now believed that the main effect of fillers is to promote polymer-particle attachments of this kind [41].