

Chapter 6. The Nature of Viscoelasticity

I. Classification of the mechanical states of polymers

1. Creep experiment: At constant stress, the strain of the specimen was recorded as a function of time.
2. Relaxation experiment: At constant strain, the applied stress was recorded as a function of time.

II. Model of viscoelastic behavior

1. Creep experiments

(a) $\frac{1}{E}$ (spring)
 (Glassy state)
 $\epsilon = \frac{\sigma_0}{E}$

(d) Viscous state

$\frac{1}{\eta}$ (dash pot)
 $\eta \frac{d\epsilon}{dt} = \sigma$
 $\epsilon = \frac{\sigma_0 t}{\eta}$

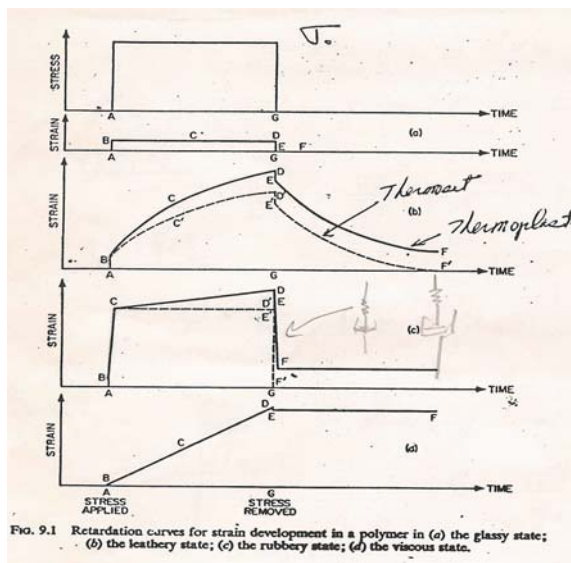
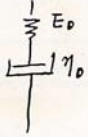
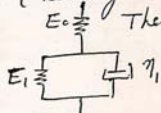
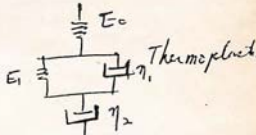


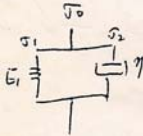
FIG. 9.1 Retardation curves for strain development in a polymer in (a) the glassy state; (b) the leathery state; (c) the rubbery state; (d) the viscous state.

(c) Rubbery State


 (Rubbery state)

$$\epsilon = \frac{\sigma_0 t}{\eta_0} + \frac{\sigma_0}{E_0}$$
 Maxwell model.
 (For Thermoplastic.)

(b) (Leaky state)

 Thermoplastic
 (Three-element Model)

 Thermoplastic
 (Four-element Model for creep)


 Voigt Model

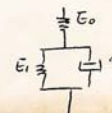
$$\sigma_0 = \sigma_1 + \sigma_2$$

$$= E_1 \epsilon + \eta_1 \frac{d\epsilon}{dt}$$

$$\epsilon = \frac{\sigma_0}{E_1} (1 - e^{-t/\tau_1})$$

$$\tau_1 = \frac{\eta_1}{E_1}$$

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For Three-element Model for creep.
 (拉伸时)
$$\epsilon = \frac{\sigma_0}{E_0} + \frac{\sigma_0}{E_1} (1 - e^{-t/\tau_1})$$


当力层纹掉时.

$$\sigma_1 + \sigma_2 = 0$$

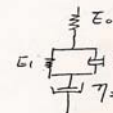
$$E_1 \epsilon + \eta_1 \frac{d\epsilon}{dt} = 0$$

$$\epsilon = \epsilon(t_1) e^{-(t-t_1)/\tau_1}$$

$$= \frac{\sigma_0}{E_1} (1 - e^{-t/\tau_1}) e^{-(t-t_1)/\tau_1}$$

For Four-element Model for creep.

拉伸时

$$\epsilon = \frac{\sigma_0}{E_0} + \frac{\sigma_0}{E_1} (1 - e^{-t/\tau_1}) + \frac{\sigma_0 t}{\eta_2}$$


纹掉时.

$$\epsilon = \frac{\sigma_0}{E_1} (1 - e^{-t/\tau_1}) e^{-(t-t_1)/\tau_1} + \frac{\sigma_0 t_1}{\eta_2}$$

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Because polymer chains have a distribution of relaxation time,

$$\frac{\varepsilon(t)}{\sigma_0} = \sum_n \frac{1}{E_n} (1 - e^{-t/\tau_n})$$

where $n=1,3,5\dots N$.

$$\varepsilon(t) = \sigma_0 \int_{-\infty}^{\infty} \bar{J}(\log \tau) (1 - e^{-t/\tau}) d \log \tau$$

where $J=1/E$ is the elastic compliance and $\bar{J} = \tau / E$ is the retardation distribution function.

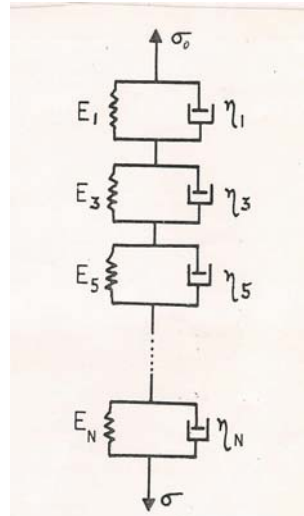


Figure 37. A multiple Voigt-Kelvin model.

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2. Relaxation experiments

(a) (Glassy state)

(b) (Leathery state)

(i) Thermoplastic.

Maxwell model

(c) (Rubbery state)

(d) (Viscous state)

$$\sigma = E_0 \varepsilon_0 = \eta_1 \frac{d\varepsilon_1}{dt}$$

$$(\sigma - E_1 \varepsilon_1) E_1 = \eta_1 \frac{d\varepsilon_1}{dt}$$

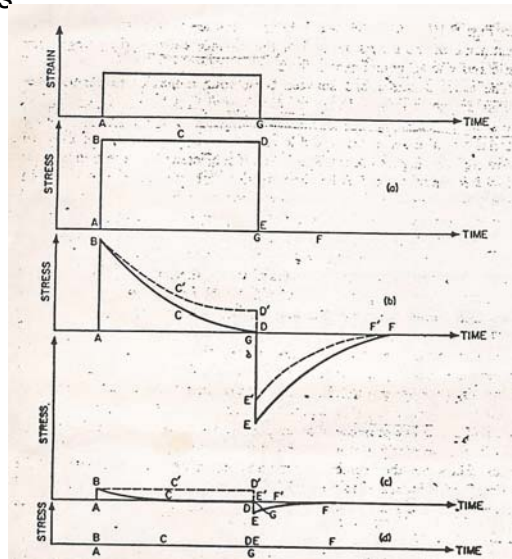
$$= -\eta_1 \frac{d(\varepsilon_0 - \varepsilon_1)}{dt}$$


FIG. 9.2. Relaxation curves for stress decay in a polymer in (a) the glassy state; (b) the leathery state; (c) the rubbery state; (d) the viscous state.

$$\therefore \varepsilon_0 - \varepsilon_{\eta_1} = c e^{-t/\tau_1}$$

$$\varepsilon_{E_1} = \varepsilon_0 e^{-t/\tau_1}$$

$$\frac{\sigma_1}{E_1} = \varepsilon_0 e^{-t/\tau_1}$$

$$\sigma_1 = E_1 \varepsilon_0 e^{-t/\tau_1}$$

$$\therefore \sigma = \sigma_1 + \sigma_2 = \varepsilon_0 (E_1 e^{-t/\tau_1} + E_2 e^{-t/\tau_2})$$

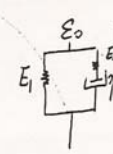
(其中 $\tau_1 = \frac{\eta_1}{E_1}$, $\tau_2 = \frac{\eta_2}{E_2}$)

(取回至或压回至时)

$$\sigma = \varepsilon_0 (E_1 e^{-t/\tau_1} + E_2 e^{-t/\tau_2}) - \varepsilon_0 (E_1 e^{-(t-t_0)/\tau_1} + E_2 e^{-(t-t_0)/\tau_2})$$

(ii) Thermoact

(拉伸时)



$$\sigma = \sigma_1 + \sigma_2$$

$$= \varepsilon_0 E_1 + \varepsilon_0 E_2 e^{-t/\tau_2}$$

$$= \varepsilon_0 (E_1 + E_2 e^{-t/\tau_2})$$

(压回时)

$$\sigma = \varepsilon_0 (E_1 + E_2 e^{-t/\tau_2}) - \varepsilon_0 (E_1 + E_2 e^{-(t-t_0)/\tau_2})$$

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III. Molecular interpretation of stress/strain behavior

The atoms or molecules in a condensed phase at equilibrium occupy states of minimum free energy by vibrating about certain mean positions in the potential energy fields which are created by their interactions with neighbouring molecules. In an unstressed material these mean positions are also minima in the potential energy fields. Speaking generally, equivalent or almost equivalent potential energy minima are distributed in a fairly regular way throughout the substance. In a crystal this regularity extends over great distances on the molecular scale and is more complete than in a liquid or amorphous substance. When a stress is applied the mean positions of the molecular vibrations are moved instantly to new equilibrium positions which are somewhat displaced from the potential energy minima. Thus work is done, elastic energy is stored in the substance and is recovered when the stress is removed. The new equilibrium positions are still free-energy minima but their height below the free-energy maxima separating the equilibrium positions is reduced by an amount related to the stored energy.

If all the equilibrium positions were occupied by atoms or molecules the stress which would be required to move all the atoms in a crystal plane simultaneously over the intervening maxima in order to produce a shearing motion between two planes would be truly enormous. Normally stresses produce only very small displacements from the potential energy minima and it is this fact which accounts for the almost linear stress/strain behaviour so commonly observed and which is described by Hooke's law. It is always found that even the most perfect crystals which can be obtained will rupture in shear under stresses several orders of magnitude less than would be required theoretically to raise all the atoms in a crystal plane to the maxima of their free-energy curves.

This observation is explained by the fact that no substances have structures so perfect that all the free-energy minima are occupied. There are always some vacant minima and also some atoms situated in between minima in what are called *dislocations*. The number of vacant minima in a crystal is usually relatively small but they are more numerous in amorphous solids and liquids. Their number increases with decreasing density of the material, whether this is brought about by decreasing the pressure or increasing the temperature. It is the atoms in dislocations which are mainly

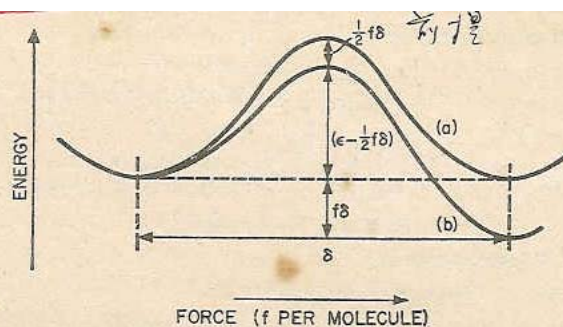


FIG. 9.3 Energy profiles between potential minima for molecules in a liquid (a) unstressed and (b) with shear stress.

In an unstressed material, although molecules are constantly jumping from one equilibrium position to another, no direction of motion is preferred. Consequently there is no net movement of the centre of mass when averaged over the many molecules constituting a macroscopic sample. Individual molecules do move around in the material following paths which consist of a sequence of random jumps and which correspond mathematically with the statistical configurations of a freely jointed chain (cf. Chapter 7). However no macroscopic flow or deformation of the sample takes place.

When a stress is applied each molecule is subjected to a tiny average force f in the direction of stress. Let the average length of a molecular jump be δ and, for simplicity, only jumps parallel to the applied stress be considered. When a jump is made in the stress direction the force does work $f\delta$ on the molecule whereas a jump in the reverse direction needs work $f\delta$ to be done against the force.

If ε is the height of the energy barrier midway between adjacent equilibrium positions, then in the stressed state a molecule has to acquire thermally a minimum energy $(\varepsilon - \frac{1}{2}f\delta)$ in order to jump forwards. The energy decrement $\frac{1}{2}f\delta$ enters because this amount of work is done by the applied force when the molecule moves from its equilibrium position up to the highest point of the barrier. Similarly to jump backwards the thermal activation energy required is $(\varepsilon + \frac{1}{2}f\delta)$. The effective internal energy profiles in the unstressed and stressed conditions are illustrated in Fig. 9.3. The effect of an applied stress is therefore to lower the free energy of activation for a molecule to jump into a neighbouring hole in the stress or forward direction and, at the same time, to raise it for a jump in the opposite or backward direction. The chance of a molecule jumping forwards into a hole under stress is thus greater than the chance of one jumping back and so a net movement occurs in the stress direction.

Eyring and his collaborators by using the theory of absolute reaction rates to give a unified theory of molecular motion in liquids [4]. If the number of times per second that a molecule jumps from one equilibrium position to another is denoted by p_0 in the unstressed state, then

$$p_0 = \left[\frac{kT v_\phi^{-1}}{(2\pi mkT)^{\frac{1}{2}}} \right] \exp(-\varepsilon/kT) \quad (1)$$

where ε is the height of the energy barrier in Fig. 9.3, m is the mass per molecule, and v_ϕ the free volume per molecule. v_ϕ may be defined by reference to the partition function of the liquid when that function is based on the smoothed potential approximation of the cell model. In general terms v_ϕ is the volume in which each molecule in the liquid is apparently quite free to move without interference from other molecules.

Under an applied shear giving a force f per molecule, which tends to displace it laterally with respect to its neighbours, the rate of jumping in the forward direction p_f becomes

$$\begin{aligned} p_f &= \left[\frac{kT v_\phi^{-1}}{(2\pi mkT)^{\frac{1}{2}}} \right] \exp[-(\varepsilon - \frac{1}{2}f\delta)/kT] \\ &= p_0 \exp(f\delta/2kT) \end{aligned} \quad (2)$$

Similarly jumps in the opposite direction take place at a rate

$$p_b = p_0 \exp(-f\delta/2kT) \quad (3)$$

The ratio of these two rates is

$$p_f/p_b = \exp(f\delta/kT) \quad (4)$$

It is dependent on the nature of the liquid only through δ which ordinarily will be comparable with the molecular diameter. The net rate of movement of a molecule in the forward direction u is given by

$$u = \delta(p_f - p_b) = \delta p_0 [\exp(f\delta/2kT) - \exp(-f\delta/2kT)] \quad (5)$$

i.e.
$$u = 2\delta p_0 \sinh(f\delta/2kT) \quad (6)$$

In most practical circumstances $f\delta \ll kT$ so that the exponentials may be expanded and only the first order terms retained. Thus eq. (5) becomes

$$u = \frac{p_0 \delta^2 f}{kT} = \left[\frac{\delta^2 f v_\phi^{-1}}{(2\pi mkT)^{1/2}} \right] \exp(-\varepsilon/kT) \quad (7)$$

The activation energy ε is made up from two contributions, the work required to make a hole for the molecule to jump into, ε_h , and the work required to free the molecule from its immediate environment to enable it to jump, ε_f . Usually $\varepsilon_h > \varepsilon_f$ for simple and relatively non-polar liquids. Also ε_h is related to the energy of vaporization per molecule, ε_{vap} . Powell, Roseveare and Eyring [5] have produced convincing experimental evidence to support this molecular mechanism for flow by showing that for a wide range of normal liquids the energy of vaporization bears an almost constant ratio, between 3 and 4, to the energy of activation for viscous flow.

other considerations show that, if the flow of polymers were to take place by the jumping of whole molecules into neighbouring holes, the viscosities of polymers would be many orders of magnitude larger than are actually observed. It must be concluded that the flowing units are not whole molecules but molecular segments consisting of a small number, frequently between five and ten, monomer units. Since the polymer molecule is flexible and kinked, all these molecular segments do not have to jump simultaneously. Provided the jumps of separate segments preponderate in the direction of stress the centre of mass of the molecule moves progressively forward. It must be appreciated that in the unstressed material segments are constantly jumping from occupied sites into holes which appear nearby but no direction of jumping is preferred so that on an average no bulk movement takes place. In this way all the random-walk configurations may be explored by each chain molecule.

When a stress is applied, a small preference is introduced in favour of jumps in the stress direction. However the number of forward jumps in excess of the backward jumps is usually small compared with the total number. Thus the randomness of the molecular configuration is scarcely disturbed by the net movement of the centre of mass of the molecule.

Three types of deformation may therefore follow the application of stress to a polymer sample. These are

- (a) an instantaneous shift of the segments from their potential energy minima
- (b) a diffusion of the relatively free chain segments by a preponderance of micro-Brownian jumps in the stress direction
- (c) a breaking down of the chain entanglements under stress and the formation of new ones in unstressed situations.

The four phases of mechanical behaviour differ in the relative rates and magnitudes of these three responses.

In the glassy state the free volume is very low and all segmental motions are very slow indeed so that (b) and (c) may be disregarded and only the instantaneous shift (a) need be considered.

In the leathery state the diffusional motions are very slow compared with (a) though rapid compared with the breakdown of entanglements. In addition the net movement due to (b) is appreciable during the time scale of the observations.

IV. The dynamic of network response, creep

1. The sping-bead model

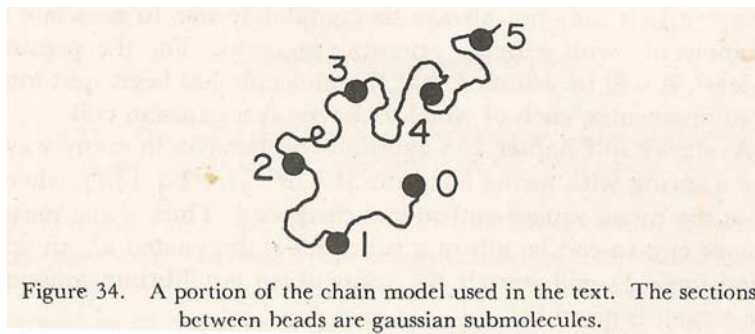


Figure 34. A portion of the chain model used in the text. The sections between beads are gaussian submolecules.

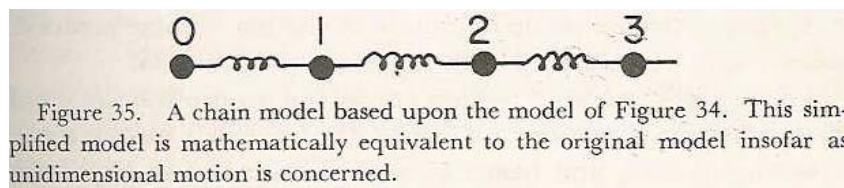


Figure 35. A chain model based upon the model of Figure 34. This simplified model is mathematically equivalent to the original model insofar as unidimensional motion is concerned.

As shown in Chapter 2, a gaussian coil behaves in many ways like a spring with spring constant $3kT/R^2$. [See Eq. (2.7), where R^2 is the mean square end-to-end distance.] Thus, if the mean square end-to-end length of a subchain is designated a^2 , an applied force F_x will stretch the segment an equilibrium amount Δx , which is given by

$$F_x = (3kT/a^2) \Delta x \quad (6.4)$$

Looking now at the i 'th bead, one sees that the total x -directed force on it will be the difference between the x -component tensions in the i and $(i + 1)$ segments. Therefore the following expresses the net x -directed force on the i 'th bead:

$$F_{xi} = e(x_{i+1} - x_i) - e(x_i - x_{i-1})$$

or

$$F_{xi} = ex_{i+1} - 2ex_i + ex_{i-1} \quad (6.5)$$

with $e = 3kT/a^2$.

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in the absence of friction forces, the force in Eq. (6.5) is simply equated to the mass times the x component of the acceleration:

$$m\ddot{x}_i = e(x_{i+1} - 2x_i + x_{i-1}) \quad (A9.1)$$

There are N equations similar to, Eq. (A9.1) for the total N beads of the chain. The beads on the two chain ends have slightly different equations of motion, since they are not constrained on one side:

$$m\ddot{x}_0 = e(x_1 - x_0)$$

and

$$m\ddot{x}_N = e(x_N - x_{N-1})$$

The solutions of these equations are of form

$$x_{in} = \exp(j\omega_n t) \cos(ik_n) \quad (A9.3)$$

with

$$e = 3kT/a^2$$

and

$$\omega_n^2 = 2e(1 - \cos k_n)/m \quad k_n = n\pi/N$$

The quantity j is $\sqrt{-1}$, and n takes on all the integer values from zero to N .

$$\begin{aligned} m\ddot{x}_1 &= e(x_2 - 2x_1 + x_0) \\ m\ddot{x}_0 &= e(x_1 - x_0) \\ &\vdots \\ m\ddot{x}_N &= e(x_N - x_{N-1}) \\ \chi_{in} &= e^{\chi} \end{aligned}$$

The simplest mode of motion consists of a pure translation of the bar in the x direction. Of course, the frequency for this mode of motion is zero, and hence $\omega_0 = 0$. This is not an important mode of motion in the present instance, since the molecule will

$$\text{As } 0 < n < N \quad \omega_n^2 = 2e \left(1 - \cos \frac{n\pi}{N} \right) / m = \left(\frac{6KT}{a^2} \right) \left(2 \sin^2 \left(\frac{n\pi}{2N} \right) \right) / m$$

$$= \frac{3KT}{a^2} \left(n^2 \pi^2 / N^2 \right) / m$$

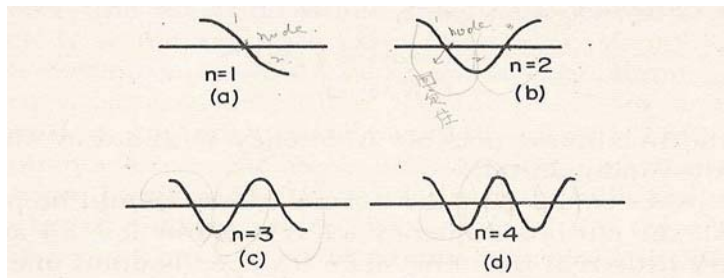


Figure 36. Various resonant modes of motion of a chain.

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$$\text{So, } x_i = \sum_{n=0}^N x_{i,n} = \sum_{n=0}^N \exp \left[j \left(\frac{n\pi}{Na} \right) \left(\frac{3KT}{m} \right)^{1/2} t \right] \cos ik_n$$

The above equation does not consider the intermolecular interactions, such as the viscous force.

Even if friction forces act upon the beads, the above equations can be handled in a straightforward way to obtain the motion of the system. This is most easily done by the method of normal coordinates. Mathematically the present problem is nearly identical to the problem of the vibration of N equal masses suspended at equal distances on a string in a viscous medium. Although the solution to this problem is well known, it is a rather lengthy and involved computation. For this reason, only the result will be given here.

In terms of the normal coordinates q_n , the displacement of the i 'th particle is given by

$$x_i = \sum_{n=1}^N [2q_n / (2mN)^{1/2}] \cos (ik_n) \quad (\text{A9.4})$$

The normal coordinates are to be determined from the differential equation

$$\ddot{q}_n + (f_0/m)\dot{q}_n + \omega_n^2 q_n = F_n \quad (\text{A9.5})$$

- What are the normal coordinates?

$$m[\ddot{x}] + f_o[\dot{x}] + e[A][x] = [F]$$

where

$$[\ddot{x}] = \begin{bmatrix} \ddot{x}_0 \\ \ddot{x}_1 \\ \vdots \\ \ddot{x}_N \end{bmatrix}, \quad [\dot{x}] = \begin{bmatrix} \dot{x}_0 \\ \dot{x}_1 \\ \vdots \\ \dot{x}_N \end{bmatrix}, \quad [x] = \begin{bmatrix} x_0 \\ x_1 \\ \vdots \\ x_N \end{bmatrix}, \quad [A] = \begin{bmatrix} 1 & -1 & 0 & \dots & \dots & \dots & \dots \\ -1 & 2 & -1 & 0 & \dots & \dots & \dots \\ 0 & -1 & 2 & -1 & 0 & \dots & \dots \\ \vdots & \vdots & \vdots & \vdots & \vdots & \vdots & \vdots \\ 0 & 0 & 0 & \dots & \dots & -1 & 2 & -1 \\ 0 & 0 & 0 & 0 & \dots & \dots & -1 & 1 \end{bmatrix}_{N+1, N+1}, \quad [F] = \begin{bmatrix} F_0 \\ F_1 \\ \vdots \\ F_N \end{bmatrix}$$

Let,

$$m[\ddot{x}] + f_o[\dot{x}] + e[c^T][c][x] = [F]$$

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this, note that

$$[A] = [C^T][C]$$

where $[C]$ is also a matrix of order $z \times (z + 1)$ and has the form

$$[C] = \begin{bmatrix} 1 & -1 & 0 & 0 & \dots & \dots & \dots \\ 0 & 1 & -1 & 0 & \dots & \dots & \dots \\ 0 & 0 & 1 & -1 & \dots & \dots & \dots \\ \vdots & \vdots & \vdots & \vdots & \vdots & \vdots & \vdots \\ \dots & \dots & \dots & \dots & \dots & 1 & -1 & 0 \\ \dots & \dots & \dots & \dots & \dots & 0 & 1 & -1 \end{bmatrix}_{N, N+1}$$

and

$$[C^T] = \begin{bmatrix} 1 & 0 & 0 & 0 & \dots & \dots & \dots \\ -1 & 1 & 0 & 0 & \dots & \dots & \dots \\ 0 & -1 & 1 & 0 & \dots & \dots & \dots \\ \vdots & \vdots & \vdots & \vdots & \vdots & \vdots & \vdots \\ \dots & \dots & \dots & \dots & \dots & -1 & 1 \\ \dots & \dots & \dots & \dots & \dots & 0 & -1 \end{bmatrix}_{N+1, N}$$

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$$m[c][\ddot{x}] + f_o[c][\dot{x}]z + e[c][c^T][c][x] = [c][F]$$

$$m[c][\ddot{x}] + f_o[c][\dot{x}]z + e[R][c][x] = [c][F]$$

where $[R] = [c][c^T]$ is called Rouse matrix

$$[R] = \begin{bmatrix} 2 & -1 & 0 & 0 & \dots & \dots & \dots \\ -1 & 2 & -1 & 0 & \dots & \dots & \dots \\ 0 & -1 & 2 & -1 & \dots & \dots & \dots \\ \dots & \dots & \dots & \dots & \dots & \dots & \dots \\ \dots & \dots & \dots & \dots & -1 & 2 & -1 & 0 \\ \dots & \dots & \dots & \dots & 0 & -1 & 2 & -1 \\ \dots & \dots & \dots & \dots & 0 & 0 & -1 & 2 \end{bmatrix}_{N,N}$$

There exists the marix [Q] as that

$$[\varphi^{-1}][R][\varphi] = [\Lambda], \quad [\varphi^{-1}][\varphi] = [I]$$

where

$$[\Lambda] = \begin{bmatrix} \lambda_1 & 0 & 0 & \cdot & \cdot & \cdot \\ 0 & \lambda_2 & 0 & \cdot & \cdot & \cdot \\ 0 & 0 & \lambda_3 & \cdot & \cdot & \cdot \\ \cdot & \cdot & \cdot & \cdot & \cdot & \cdot \\ 0 & 0 & 0 & 0 & \lambda_{N-1} & 0 \\ 0 & 0 & 0 & 0 & 0 & \lambda_N \end{bmatrix}_{N,N}$$

$$m[\varphi^{-1}][c][\ddot{x}] + f_o[\varphi^{-1}][c][\dot{x}] + e[\varphi^{-1}][R][c][x] = [\varphi^{-1}][c][F]$$

$$m[\varphi^{-1}][c][\ddot{x}] + f_o[\varphi^{-1}][c][\dot{x}] + e[\Lambda][\varphi^{-1}][c][x] = [\varphi^{-1}][c][F]$$

Let, $[\ddot{q}] = [\varphi^{-1}][c][\ddot{x}]$, $[\dot{q}] = [\varphi^{-1}][c][\dot{x}]$, $[q] = [\varphi^{-1}][c][x]$

$$[\mathfrak{F}] = [\varphi^{-1}][c][F]$$

So, $m[\ddot{q}] + f_o[\dot{q}] + e[\Lambda][q] = [\mathfrak{F}]$

Since $[\varphi^{-1}][R][\varphi] = [\Lambda]$, $[\varphi][\varphi^{-1}][R][\varphi] = [\varphi][\Lambda] = [\Lambda][\varphi]$
 $[R][\varphi] = [\Lambda][\varphi]$, $([R] - [\Lambda])[\varphi] = 0$

Thus,

$$\begin{aligned} (2 - \lambda)\varphi_{11} - \varphi_{12} &= 0 \\ -\varphi_{21} + (2 - \lambda)\varphi_{22} - \varphi_{23} &= 0 \\ -\varphi_{32} + (2 - \lambda)\varphi_{33} - \varphi_{34} &= 0 \\ \dots\dots\dots & \\ -\varphi_{n,n-1} + (2 - \lambda)\varphi_{nn} &= 0 \end{aligned} \tag{h}$$

where φ_{ij} is the ij th term in $[\varphi]$.

In order to solve the set of equations given above, note that they all have the same form:

fix $-\varphi_{m-1} + (2 - \lambda)\varphi_m - \varphi_{m+1} = 0$ (i)

with the condition that

$$\varphi_0 = \varphi_{n+1} = 0 \tag{j}$$

Equation (i) can be treated and solved as a difference equation. In operator notation it is just

$$[-E^{-1} + (2 - \lambda) - E]\varphi_m = 0 \tag{k}$$

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where the operator E displaces a function in the positive direction and E^{-1} in the negative direction, i.e.,

$$\begin{aligned} E\varphi_m &= \varphi_{m+1} \\ E^{-1}\varphi_m &= \varphi_{m-1} \end{aligned}$$

Now to solve equation (k), assume that the solution has the following form:

$$\varphi_m = \beta e^{m\alpha} \tag{l}$$

where β is a constant and α is a function to be determined. Insertion of equation (l) into equation (k) results in

$$\beta e^{m\alpha} [-e^{-\alpha} + (2 - \lambda) - e^{\alpha}] = 0 \tag{m}$$

*$E^{-1} = e^{-\alpha}$
 $E = e^{\alpha}$*

In order for equation (m) to yield nontrivial results, it is necessary that

$$-e^{-\alpha} + (2 - \lambda) - e^{\alpha} = 0$$

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or

$$\frac{2 - \lambda}{2} = \frac{e^\alpha + e^{-\alpha}}{2} = \cosh \alpha \quad (n)$$

Equation (n) is satisfied by two values of α , namely $+\alpha$ and $-\alpha$, since $\cosh(+\alpha) = \cosh(-\alpha)$. Thus, the solution to the difference equation also must be satisfied by two functions (i.e., $\beta e^{+\alpha x}$ and $\beta e^{-\alpha x}$). The general solution is then just

$$\varphi_m = P_1 \beta e^{m\alpha} + P_2 \beta e^{-m\alpha} \quad (o)$$

where the P 's are constants. Since

$$\sinh x = (e^x - e^{-x})/2$$

and

$$\cosh x = (e^x + e^{-x})/2$$

we can have the following equivalent general solution:

$$\varphi_m = M_1 \sinh(m\alpha) + M_2 \cosh(m\alpha) \quad (p)$$

where the M 's are constants. For $m = 0$, equation (j), the boundary condition, demands

$$\varphi_0 = 0 = M_2 \quad (q)$$

and

$$\varphi_{N+1} = 0 = \sinh[(N+1)\alpha] \quad (r)$$

since M_1 is a constant. But the value of the hyperbolic sine is zero if the argument is an integral multiple of $(i\pi)$, where $i = \sqrt{-1}$. Therefore,

$$\alpha = ip\pi/(N+1), \quad p = 1, 2, 3, \dots, N \quad (s)$$

Combination of equations (s) and (n) finally gives the desired result:

$$\begin{aligned} \lambda_p &= 2 - 2 \cosh[ip\pi/(N+1)] \\ &= 2\{1 - \cos[p\pi/(N+1)]\} \\ &= 4 \sin^2[p\pi/2(N+1)] \end{aligned} \quad (7-53)$$

where $p = 1, 2, 3, \dots, N$.

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So,

$$m[\ddot{q}_n] + f_o[\dot{q}_n] + e \left[2 \left(1 - \cos \frac{n\pi}{N+1} \right) \right] [q_n] = [\mathfrak{F}_n]$$

$$[\ddot{q}_n] + \frac{f_o}{m} [\dot{q}_n] + \left[\frac{2e}{m} (1 - \cos k_n) \right] [q_n] = [\mathfrak{F}_n]$$

$$[\ddot{q}_n] + \frac{f_o}{m} [\dot{q}_n] + \omega_n^2 [q_n] = [\mathfrak{F}_n] \dots\dots\dots(1)$$

It should be noted that

$$x_i = \sum_{n=1}^N \left[2q_n / (2mN)^{1/2} \right] \cos(ik_n) \dots\dots\dots(2)$$

$$\mathfrak{F}_n = \sum_{i=0}^N \left[2F(i,t) / (2mN)^{1/2} \right] \cos(ik_n) \dots\dots\dots(3)$$

As a simple example of the use of these equations, consider the response of the chain to a force f applied at each end of the chain so as to stretch it:

$$F(0,t) = -f, \quad F(N,t) = +f, \quad \text{all the other values of } F \text{ are zero.}$$

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Substitution of these values into eq 3 yields

$$\mathfrak{F}_n = 0 \quad \text{for } n \text{ even,} \quad \mathfrak{F}_n = -4f / (2mN)^{1/2} \quad \text{for } n \text{ odd.}$$

Since the viscous forces will be assumed large enough so that all inertial effects will be negligible, the solution of eq 1 is simply

$$q_n = (\mathfrak{F}_n / \omega_n^2) (1 - \exp(-t / \tau_n))$$

with

$$\tau_n = f_o / \omega_n^2 m, \quad \omega_n^2 = \frac{3KT}{a^2} (n^2 \pi^2 / N^2) / m$$

Substitution to eq 2 yields the following expression,

$$x_o = \sum_{n=0}^N \left[2 / (2mN)^{1/2} \right] \left\{ \mathfrak{F}_n / \omega_n^2 \right\} [1 - \exp(-t / \tau_n)]$$

and

$$x_N = - \sum_{n=0}^N \left[2 / (2mN)^{1/2} \right] \left\{ \mathfrak{F}_n / \omega_n^2 \right\} [1 - \exp(-t / \tau_n)]$$

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$$x_N - x_0 = (fNa^2/3kT)(8/\pi^2) \sum (1/n^2)[1 - \exp(-t/\tau_n)]$$

$$n = 1, 3, 5, \dots, N \quad (6.8)$$

where

$$\tau_n = f_0N^2a^2/3\pi^2kTn^2$$

The meaning of this equation is as follows. When the tensile force f is applied to the ends of the molecule, all odd-numbered modes of vibration of the molecule are excited. These are the modes for which the chain ends move in opposite directions, as can be seen from Figure 36a and c. Since the applied force is *not* trying to move both ends of the molecule in the same direction, the even-numbered modes are not excited.

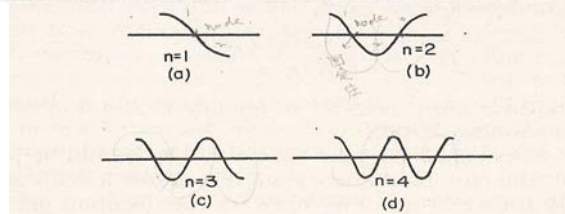


Figure 36. Various resonant modes of motion of a chain.

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After a long time, the molecule will have reached an equilibrium elongation, and the exponentials in Eq. (6.8) will be zero. Each mode of response of the molecule will have contributed an amount proportional to $1/n^2$ to the elongation; hence it is clear that the first few modes of motion are by far the most important for this type of chain motion. For example, the fifth mode will contribute less than 4 per cent of the total elongation.

Another interesting fact brought out by Eq. (6.8) is that the response or retardation times (τ_n) for the various modes of motion are not at all uniform. In general, the higher modes of motion show the shorter retardation times. This characteristic is represented by the relation

$$\tau_n = (1/n^2)\tau_1 \quad (6.9)$$

which means that the initial response of the chain just after the load has been applied will be chiefly the result of the response of the very high modes of motion. Notice also, from the definition of τ_1 in Eq. (6.8), that the retardation time is proportional to f_0N^2 . Consequently, the retardation times will be large for long chains in highly viscous surroundings.

Since the gross rubber sample must elongate in proportion to the individual chains, the final result is that

$$(\Delta L/L) = (\sigma/3\nu kT) \sum_{n=1,3,5,\dots,N} (8/\pi^2 n^2) [1 - \exp(-t/\tau_n)] \quad (6.10)$$

where σ is the force per unit area and ν is the number of network chain in unit volume.

since the tensile compliance of the material $D(t)$ is merely $(\Delta L/L)/\sigma$,

$$3\nu kTD(t) = (8/\pi^2) \sum_{n=1,3,5,\dots,N} n^{-2} [1 - \exp(-t/\tau_n)] \quad (6.11)$$

Equation (6.11) differs from the result obtained for the Kelvin spring-dashpot model in an easily visualized way. The result for the Kelvin model given by Eq. (6.3) is just a single term of Eq. (6.11). This means that the actual freely orienting chain does not behave like a single Kelvin element; instead, the chain

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Elongates like a series of many spring-dashpot elements. This can be seen to be true from a consideration of the series of Kelvin model shown in Figure 37.

The model system in Figure 37 will elongate in the following way, since each element is subject to the same stress and the elongations are additive.

$$y/\sigma = \sum_{n=1,3,5,\dots,N} E_n^{-1} [1 - \exp(-t/\tau_n)]$$

$$n=1, 3, 5, \dots, N$$

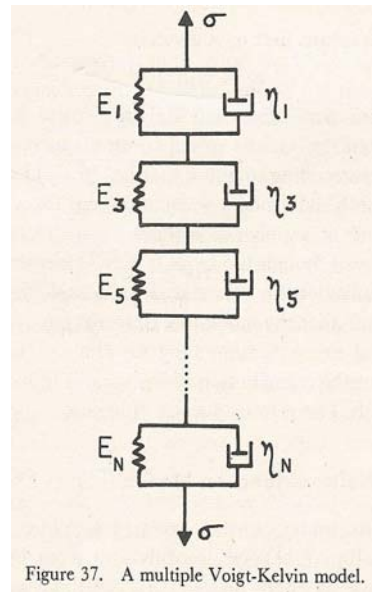


Figure 37. A multiple Voigt-Kelvin model.

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with $\tau_n = \eta_n/E_n$. This equation for the compliance (y/σ) of the series of Kelvin models can be put in exactly the same form as Eq. (6.11) for the freely orienting chain model if the following replacements are made:

$$\eta_n/E_n = (1/n^2)(f_0 N^2 a^2 / 3\pi^2 k T) \quad (6.13a)$$

and

$$1/E_n = (1/n^2)(8/3\pi^2 \nu k T) \quad (6.13b)$$

which in turn means that η_n is given by

$$\eta_n = \nu f_0 N^2 a^2 / 8 \quad (6.13c)$$

These relations show that each Kelvin element has the same value for η , but the various spring constants increase as n^2 . In addition, it is interesting to notice that Eq. (6.13c) for the viscous element in the Kelvin model is equal, except for a factor of $1/2$, to the viscosity of a polymer without entanglements given in Eq. (3.16). Even though the series of Kelvin elements shown in Figure 37 duplicates the behavior of an actual freely orienting chain, it is clear that the individual elements have little relation to the physical elements composing the chain. They do, however, represent the contribution of the various individual modes of motion of the chain to its over-all elongation.

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- From the free draining model, the viscosity of polymer melt or concentrated polymer solution can be expressed as

$$\eta = \left(\frac{\rho \aleph}{36} \right) \left(\frac{r_o}{M} \right)^{-2} N f_o = \frac{1}{36} \left(\frac{\rho \aleph}{M} \right)^{-2} N f_o = \frac{1}{36} \nu a^2 N^2 f_o$$

or

$$\eta - \eta_o = \left(\frac{c \aleph}{36} \right) \left(\frac{r_o}{M} \right)^{-2} N f_o = \frac{1}{36} \left(\frac{c \aleph}{M} \right)^{-2} N f_o = \frac{1}{36} \zeta a^2 N^2 f_o$$

Where ρ is the density, \aleph is the Avogadro number, ν is the number of polymer chains per unit volume, η_o is the viscosity of solvent, c is the concentration, and ζ is the number of polymer chains per unit volume in solution.

So,

$$\frac{\eta_n}{\eta} = \frac{36}{8} = \frac{9}{2}$$

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2. Comparison with the experimental data

It is now of interest to compare the response of the simple Voigt-Kelvin model as given by Eq. (6.3) with the observed elongation curve for the rubber shown in Figure 30. This comparison is made in Figure 33, where the value of τ has been

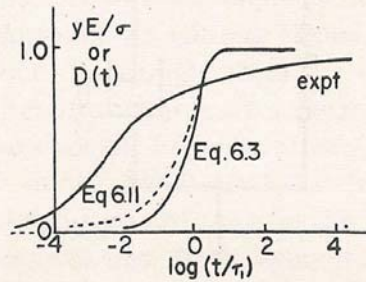


Figure 33. The compliance curve for the rubber of Figure 30 (expt) compared with the response predicted from Eqs. (6.3) and (6.11).

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- Two sources of the error present in Rouse model
 1. The assumption of freely-jointed segment between two adjacent beads is rather crude.
 2. The assumption of affine deformation of the network to derive the eq 6.11 is unrealistic, i.e., the sample as a whole elongated in the same way as the individual chains elongated.

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3. The motion of network junction

$$3\nu KTD(t) = [1 - \exp(-t/\tau_1)] + \sum_{n=1}^{\infty} \beta^{-n} (1 - \exp(-t/\tau_1 \beta^{2n}))$$

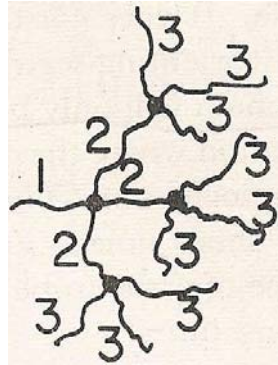
$$D(t) = D_o(t) + \frac{1}{3\nu KT} \sum_{n=1}^{\infty} \beta^{-n} (1 - \exp(-t/\tau_1 \beta^{2n}))$$

where

$$D_o(t) = \frac{1}{3\nu KT} (1 - \exp(-t/\tau_1))$$

$$\tau_1 = \frac{f_o N^2 a^2}{3\pi^2 KT}$$

$$n=1, 2, \dots, \infty$$



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values of β are shown in Figure 39. The cases of $\beta = 10$ and $\beta \rightarrow \infty$ are unrealistic, since a tetrahedral crosslink can at most have $\beta = 3$. However, the $\beta \rightarrow \infty$ case is included, since this is equivalent to the result given in Eq. (6.11). If β is infinitely large, no motion of the crosslink will occur, since chain 1 in Figure 38 would have to pull an infinite number of chains along with it if the junction were to move.

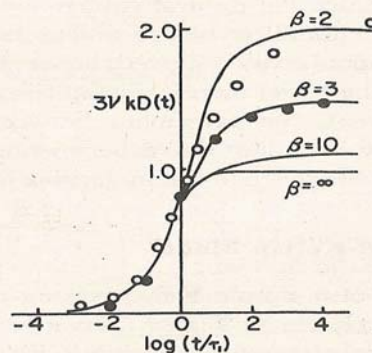


Figure 39. The lines represent compliance curves predicted by Eq. (6.14), using the values of β indicated. Data for the natural rubber of Figures 30 and 33 are shown (○) together with data for crosslinked polyethyl methacrylate (●) (75).

4. The reptation model to correct the entanglement effect

We may start by considering a coiled chain trapped in a network. This is a simpler case than the case of a thermoplastic melt since non-trivial entanglement effects are avoided. We may think about the system in only two dimensions (Fig. 6.15), with a coiled (C) chain and a great number of surrounding network chain segments which are obstacles, denoted O_i . The C chain is not allowed to cross any of the obstacles. It can, however, move in a worm-like fashion along its own axis. This motion was given the name **reptation** by its inventor Pierre Gilles de Gennes (1971). It is convenient to think that the C chain is trapped within a tube. This commonly used term¹¹

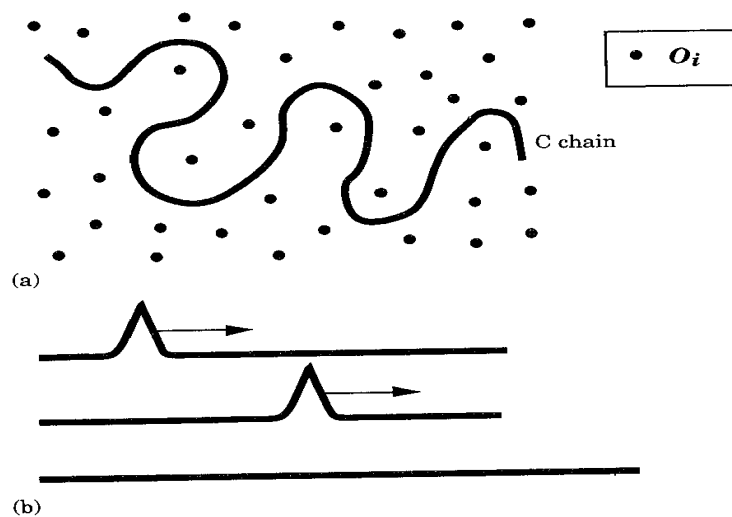


Figure 6.15 (a) Schematic description of the reptation process considering a single chain (C chain) surrounded by numerous obstacles (O_i). The C chain cannot move much laterally due to the obstacles. (b) Fundamental reptation process with the translative motion of a defect along the chain leading to a longitudinal shift of the reptating chain.

mass. A similar equation can be derived for the tube diffusion coefficient (D_{tube}):

$$D_{\text{tube}} = \frac{D_0}{M} \quad (6.45)$$

where D_0 is a constant which is independent of molar mass. The time for the tube renewal process (τ_{ren}) can then be derived from the diffusion distance which is equal to the chain length (L):

$$\tau_{\text{ren}} = \frac{L^2}{D_{\text{tube}}} = \frac{L^2 M}{D_0} \quad (6.46)$$

The chain length is proportional to the molar mass, i.e.:

$$\tau_{\text{ren}} = \tau_{\text{ren}}^0 \cdot M^3 \quad (6.47)$$

where τ_{ren}^0 is a constant.

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of a step strain. The subsequent relaxation of stress was then calculated under the assumption that reptation was the only mechanism for stress release. This led to an equation for the shear relaxation modulus, $G(t)$, in the terminal region. From $G(t)$, the following expressions for the plateau modulus, the zero-shear-rate viscosity and the steady-state recoverable compliance are obtained:

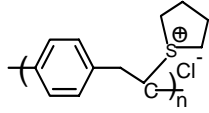
$$G_p \propto M^0 \quad (6.48)$$

$$\eta_0 \propto M^3 \quad (6.49)$$

$$J_e^0 \propto M^0 \quad (6.50)$$

Experimental data indicate that η_0 increases more strongly with M , $\eta_0 \propto M^{3.4}$ (Fig. 6.13) and the predicted viscosity values are in fact greater than the experimental. The predicted values for J_e^0 are lower than the experimental values. As pointed out by, for ⁴⁴

Chain Conformation of PXT in Semidilute Solution



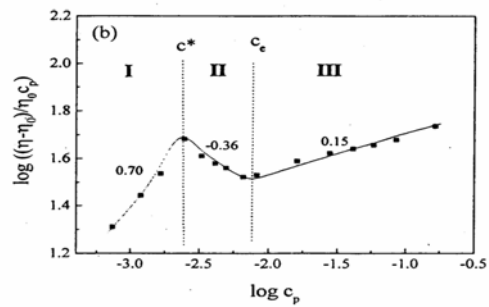
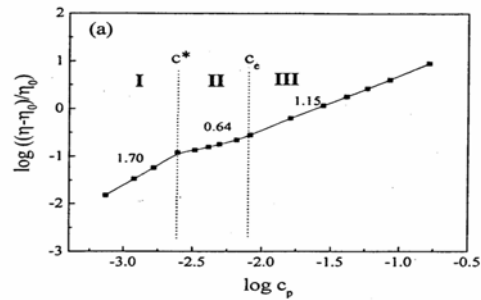
Poly(xylylene tetrahydrothiophenium chloride)

Fuoss proposed (1949)

$$\frac{\eta_{sp}}{c} = \frac{A}{1 + B\sqrt{c}}$$

De Gennes proposed (1976)

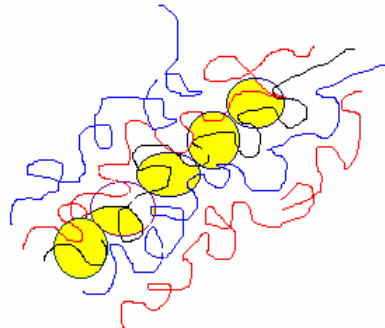
$$\eta_{red} \approx c^{-1/2}$$



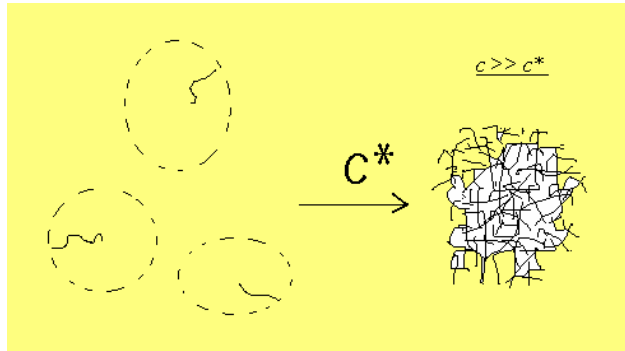
Theoretical Model to Predict the Chain Conformations of PPV Precursor and c_p^*

Assumption:

1. The chains were treated as a succession of blobs, which carry a g -number of monomers;
2. The blob size ξ is equal to the mesh size of the solutions in the semidilute regime;
3. $\xi \ll R$



Chain overlapping started at $c_p^* = N/R^3$, where N is the number of monomers in a chain, and R is the end to end distance of the chains.



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Modified deGennes' Scaling Arguments

From Rouse equation,

$$\eta - \eta_0 = \frac{1}{36} \rho r_0^{-2} N^* f_0$$

where η_0 is the viscosity of solvent,

ρ = moles of polymer chains/volume $\sim c_p/N$,

$N^* = N/g$ is the number of blobs per chain,

$$f_0 = 3\pi\eta_0\xi$$

$$g \approx c_p \xi^3$$

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Modified deGennes' Scaling Arguments

The rewritten Rouse equation,

$$\eta_{red} = \frac{\eta - \eta_0}{c_p} \approx \frac{N}{c_p \xi^3}$$

$$(c_p \gg c_p^*)$$

$$\xi = R \left(\frac{c_p^*}{c_p} \right)^m$$

where ξ is the molecular weight independence.

For rodlike chains, $R=Na$. We obtained

For ideal Gaussian chains, $R=N^{1/2}a$. We obtained

$$\eta_{red} \approx Nc_p$$

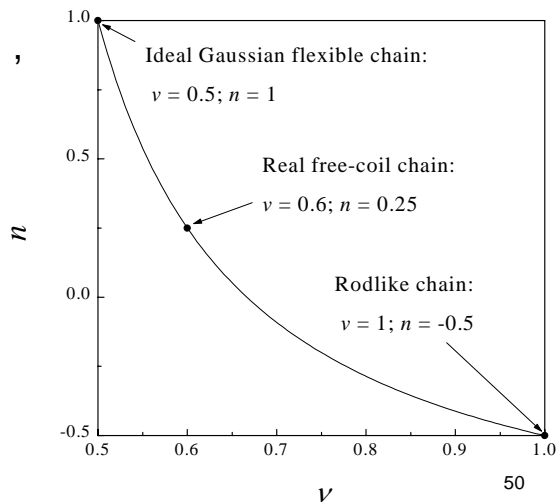
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Modified deGennes' Scaling Arguments

By assuming $R = N^\nu a$,

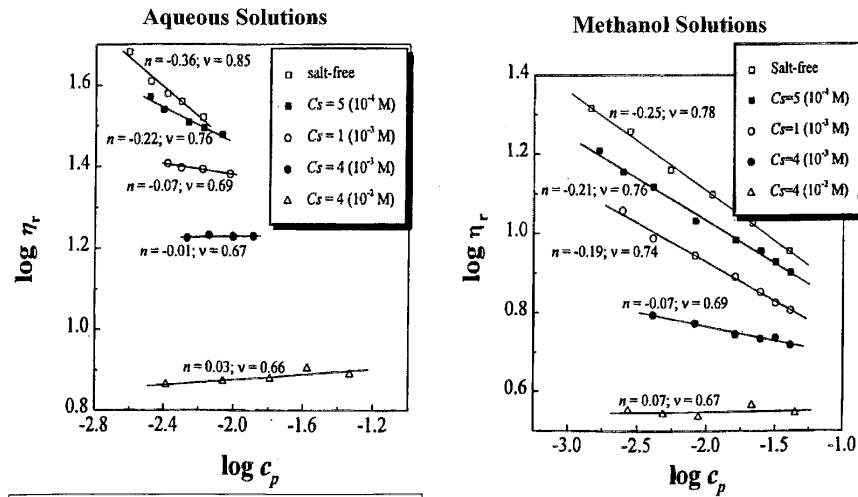
$$\eta_{red} \approx Nc_p^n \approx Nc_p^{-\left(\frac{3\nu-2}{3\nu-1}\right)}$$

$$\text{or } \nu = \frac{n+2}{3n+3}$$



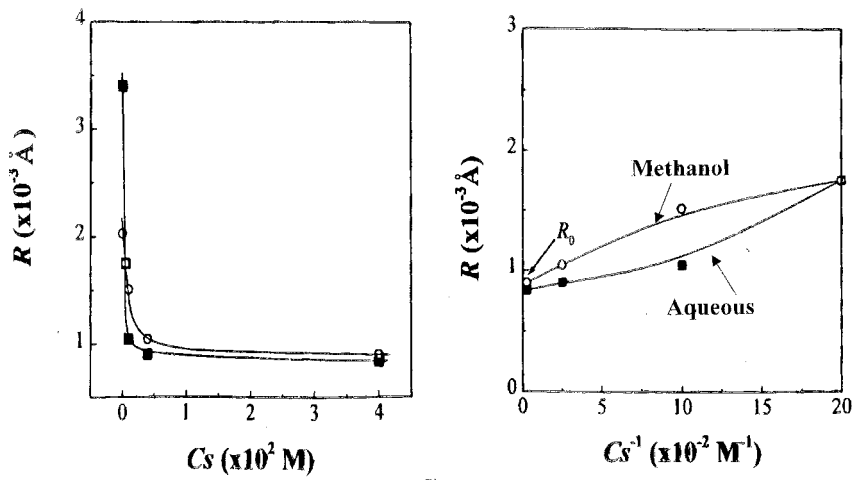
50

Chain Conformation of PXT in Solutions with NaCl Salts



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Chain Conformation of PXT in Solutions with NaCl Salts



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V. Time-temperature superposition principles

Since
$$D(t) = D_o(t) + \frac{1}{3\nu KT} \sum_{n=1}^{\infty} \beta^{-n} (1 - \exp(-t/\tau_1 \beta^{2n}))$$

It shows that
$$3\nu kTD(t) = \psi(t/\tau_1) \quad (6.15)$$

The function on the right-hand side of Eq. (6.15) involves no quantities other than β and t/τ_1 . Since β is a constant of the network system, it is apparent that $TD(t)$ is a function of only one variable, t/τ_1 .

Moreover,
$$\tau_1 = \frac{f_o N^2 a^2}{3\pi^2 KT} = \left(\frac{N^2 a^2}{3\pi^2 K} \right) \frac{f_o}{T}$$

When temperature was increased from T to T' , $\tau_1' = a_T \tau_1$

where $a_T < 1$, is known as the shifting factor.

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Since $f_o = \frac{KT}{D}$ and $D = \frac{\phi \delta^2}{6}$, $f_o = \frac{6KT}{\phi \delta^2}$

From the last section, a_T is by definition the ratio of the response time τ_1' at temperature T' to the response time τ_1 at temperature T . If T is arbitrarily selected as the glass temperature T_g ,

$$a_T = \tau_1' / \tau_{1g} \quad (6.17)$$

But from the definition of τ_1 ,

$$a_T = f_o' T_g / f_{og} T' \quad (6.18)$$

In addition, making use of the relation between jump frequency ϕ and f_o given by Eq. (3.8), one finds

$$\begin{aligned} a_T &= \phi_g / \phi' \\ &= \exp \{ \beta^* \nu^* [(1/\nu_f') - (1/\nu_{fg})] \} \end{aligned} \quad (6.19)$$

So,

$$\ln a_{Tg} = \frac{\beta^* \nu^*}{\nu_{fg}} \left(\frac{\nu_{fg} - \nu_f'}{\nu_f'} \right) = \frac{-\beta^* \nu^*}{\nu_{fg}} \left[\frac{\alpha \nu_g (T' - Tg)}{\nu_{fg} + \alpha \nu_g (T' - Tg)} \right]_{54}$$

$$\ln a_{T_g} = \frac{-\beta^* \nu^* (T' - T_g)}{\frac{\nu_{fg}}{\alpha \nu_g} + T' - T_g}$$

which is an alternate form of the WLF equation by using T_g as the reference temperature,

$$\ln a_{T_g} = \frac{-40(T' - T_g)}{52 + T' - T_g}$$

If the reference temperature is above T_g , such as $T_g + 50^\circ\text{C}$,

$$\ln a_{T_{ref}} = \frac{-C_1(T' - T_{ref})}{C_2 + T' - T_{ref}}$$

What are C_1 and C_2 ?

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$$3\nu KTD(t) = \psi(\ln(t / \tau_1))$$

When temperature was shifted to reference temperature, the equation can be modified as

$$3\nu K T_{ref} D(t) = \psi(\ln(t / a_{T_{ref}} \tau_1)) = \psi(\ln(t / \tau_1) - \ln a_{T_{ref}})$$

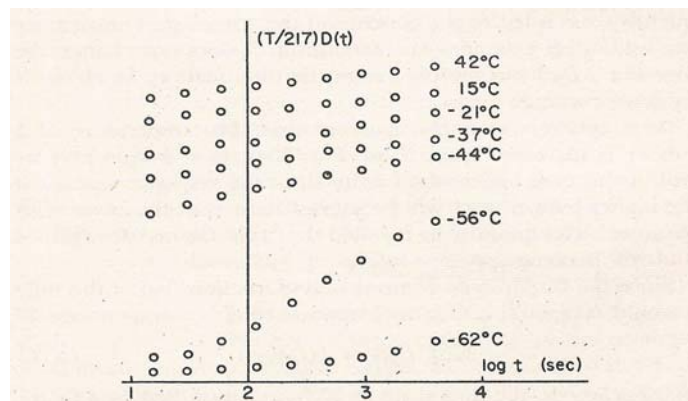


Figure 40. Compliance curves obtained for a vulcanized rubber at several temperatures.

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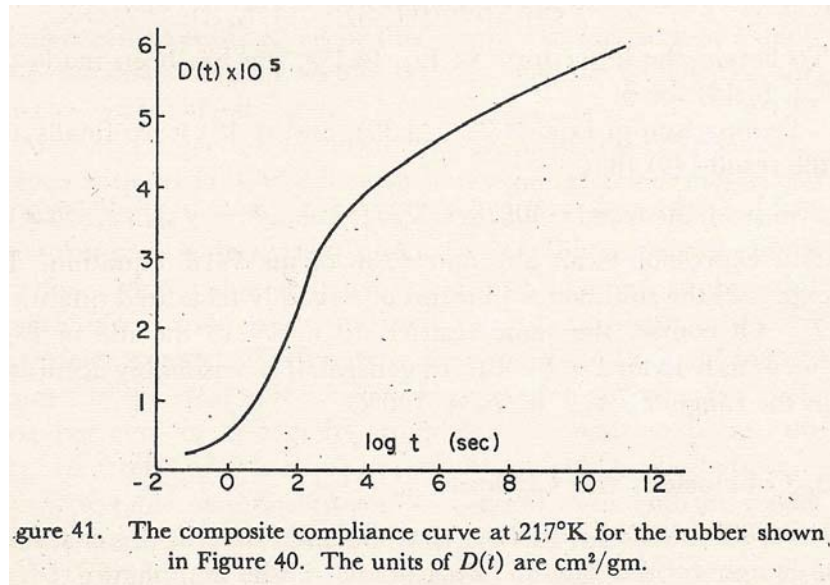


Figure 41. The composite compliance curve at 21.7°K for the rubber shown in Figure 40. The units of $D(t)$ are cm^2/gm .

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VI. Boltzman superposition principle

The Boltzmann superposition principle is one of the simplest but most powerful principles of polymer physics.¹⁰ We have previously defined the shear creep compliance as relating the stress and strain in a creep experiment.*

$$\gamma(t) = \sigma_0 J(t) \quad (2-23)$$

The stress σ_0 is applied instantaneously at time equal to zero. One might, however, imagine an experiment where the stress σ_1 is applied, not at $t = 0$, but at some other arbitrary time, perhaps u_1 . Then equation (2-23) would become

$$\gamma(t) = \sigma_1 J(t - u_1) \quad (2-24)$$

Consider now the application of two stresses σ_0 and σ_1 at the times $t = 0$ and $t = u_1$ respectively. The Boltzmann superposition principle asserts that the two stresses act independently and the resultant strains add linearly. This situation is shown in Figure 2-9. Thus

$$\gamma(t) = \sigma_0 J(t) + \sigma_1 J(t - u_1) \quad (2-25) \quad 58$$

or for a more general experiment consisting of discrete stresses $\sigma_1, \sigma_2, \dots, \sigma_n$ applied at times $t = u_1, u_2, \dots, u_n$

$$\gamma(t) = \sum_{i=1}^n \sigma_i J(t - u_i) \quad (2-26)$$

The summation of the individual σ_i 's would represent the total stress so that in considering a continuous stress application, $\sigma(t)$, the increment of applied stress is just the derivative of $\sigma(t)$. Replacing the summation by an integration and remembering that u is the variable results in

$$\gamma(t) = \int_{-\infty}^t \frac{\partial \sigma(u)}{\partial u} J(t - u) du \quad (2-27)$$

The limits of integration are taken as $-\infty$ since the complete stress history contributes to the observed strain and t since it is obvious that stresses applied after t , the time of observation of the strain, can have no effect on the observed strain.

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In a completely analogous manner one may derive an expression relating the stress $\sigma(t)$ to the strain in a sample which has experienced some continuous strain history given by the function $\gamma(t)$

$$\sigma(t) = \int_{-\infty}^t \frac{\partial \gamma(u)}{\partial u} G(t - u) du \quad (2-28)$$

Equations (2-27) and (2-28) are often given in an alternative form which we will now derive. Integrating equation (2-27) by parts

$$\int w dv = - \int v dw + \int d(wv) \quad (2-29)$$

where

$$dv = \left(\frac{\partial \sigma(u)}{\partial u} \right) du \quad w = J(t - u)$$

one obtains

$$\gamma(t) = J(t - u)\sigma(u) \Big|_{-\infty}^t - \int_{-\infty}^t \sigma(u) \frac{\partial J(t - u)}{\partial u} du \quad (2-30)$$

We assume that $\sigma(-\infty)$ is equal to zero. Setting $t - u$ equal to a , a new variable, and observing new limits of integration due to this variable change gives

$$\gamma(t) = J(0)\sigma(t) + \int_0^t \sigma(t-a) \frac{\partial J(a)}{\partial a} da \quad (2-31)$$

In an analogous manner, equation (2-28) becomes

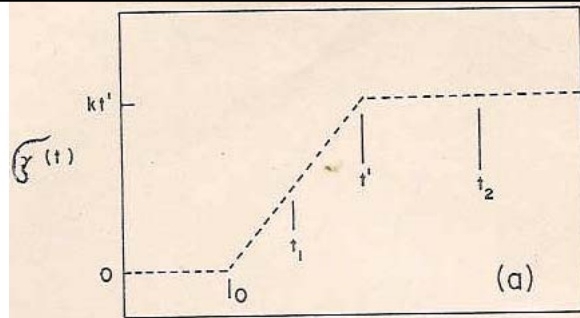
$$\sigma(t) = G(0)\gamma(t) + \int_0^t \gamma(t-a) \frac{\partial G(a)}{\partial a} da \quad (2-32)$$

Ex.

As a specific example of the use of the Boltzmann principle, consider a material with a creep compliance given by the function

$$J(t) = J_r + t/\eta \quad (a)$$

where J_r represents the recoverable deformation and η is the viscosity. Let us calculate the strain $\gamma(t)$ when this body is subjected to the linear stress function $\sigma(t)$ shown in part (a) of Figure 2-10; (i) at the time t_1 during the loading and (ii) at the time t_2 after the loading has ceased.



i The stress can be written as

$$\begin{aligned} -\infty \leq t \leq 0 & \quad \sigma(t) = 0 \\ 0 \leq t \leq t_1 & \quad \sigma(t) = kt \end{aligned}$$

Making use of equation (2-27) one has

$$\gamma(t_1) = \int_0^{t_1} k \left[J_r + \frac{t_1}{\eta} - \frac{u}{\eta} \right] du$$

and carrying out this simple integration leads to

$$\gamma(t_1) = kt_1 J_r + \frac{kt_1^2}{2\eta} \quad (c)$$

Remembering that kt_1 is just the total applied stress at the time t_1 yields

$$\gamma(t_1) = \sigma(t_1) \left[J_r + \frac{t_1}{2\eta} \right] \quad (d)$$

Equation (d) then gives an expression for the strain at time t_1 in a body whose creep compliance is given by equation (a) when it is subjected to a linear loading pattern starting at time zero. Note that t_1 must occur during the stressing period.

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ii We will now calculate the strain after the stress addition has stopped. Again we can summarize the stressing history

$$\begin{aligned} -\infty \leq t \leq 0 & \quad \sigma(t) = 0 \\ 0 \leq t \leq t' & \quad \sigma(t) = kt \\ t' \leq t \leq t_2 & \quad \sigma(t) = kt' \end{aligned}$$

Now equation (2-27) becomes

$$\gamma(t_2) = \int_0^{t'} k \left[J_r + \frac{t_2 - u}{\eta} \right] du \quad (e)$$

Again, this is a simple integration which gives the result that

$$\gamma(t_2) = \sigma(t') \left[J_r + \frac{t_2}{\eta} - \frac{t'}{2\eta} \right] \quad (f)$$

It is interesting to carry out part (ii) of this example using the more widely used equation (2-31) instead of equation (2-27). One must use the new variable in the integral so that the strain history must be introduced in terms of this transformed variable rather than in terms of the normal laboratory time. Writing equation (2-31) for part (ii) of the example gives

$$\gamma(t_2) = J(0)\sigma(t_2) + \int_0^\infty \sigma(t_2 - a) \frac{\partial J(a)}{\partial a} da \quad (g)$$

In laboratory time, there was no stress imposed between the time $t = -\infty$ and $t = 0$. In terms of the variable a , however this corresponds to $a = \infty$ and $a = t_2$ for when $a = \infty$, $t_2 - a = -\infty$ and when $a = t_2$, $t_2 - a = 0$. This is a consequence of the variable change used to derive equation (2-31). Application of this equation without changing variables will necessarily lead to an incorrect result. Completing the stress summary in the usual way

(Because $t_2 - u = a$)

$-\infty \leq t \leq 0$	$\sigma(t) = 0$	$\infty \geq a \geq t_2$
$0 \leq t \leq t'$	$\sigma(t) = kt$	$t_2 \geq a \geq t_2 - t'$
$t' \leq t \leq t_2$	$\sigma(t) = kt'$	$t_2 - t' \geq a \geq 0$

From equation (a)

$$\frac{\partial J(a)}{\partial a} = \frac{1}{\eta} \quad (h)$$

Substituting equation (h) and the strain history into equation (g) yields

$$\gamma(t_2) = J_r \sigma(t') + \int_0^{t_2-t'} \frac{k(t')}{\eta} da + \int_{t_2-t'}^{t_2} \frac{k}{\eta} (t_2 - a) da \quad (i)$$

Integration and cancellation gives (f) as indeed it must.

VII. Relationship between the creep compliance and the stress relaxation modulus

First consider the calculation of the LaPlace transform of the function

$$F(t) = at \quad (2-34)$$

where a is a constant.

Substitution into equation (2-33) gives

$$L(at) = \int_0^\infty e^{-pt} at dt \quad (2-35)$$

which upon integration yields

$$L(at) = \frac{a}{p^2} \quad (2-36)$$

Thus it is clear

$$L(t) = \frac{1}{p^2} \quad L(aF(t)) = aL(F(t)) \quad (2-37)$$

Next consider the LaPlace transform of the function $F(t - a)$, where $F(x) = 0$ for $x < 0$. Again, substitution into equation (2-23) gives

$$L(F(t - a)) = \int_0^\infty e^{-pt} F(t - a) dt \quad (2-38)$$

Now letting $t - a = x$, one has

$$L(F(t - a)) = e^{-ap} \int_0^\infty e^{-xp} F(x) dx = e^{-ap} L(F(t)) \quad (2-39)$$

Lastly consider the transform of $F'(t)$. Proceeding as above

$$L(F'(t)) = \int_0^\infty e^{-pt} F'(t) dt \quad (2-40)$$

Integration by parts yields

$$L(F'(t)) = e^{-pt} F(t) \Big|_0^\infty + p \int_0^\infty e^{-pt} F(t) dt \quad (2-41)$$

The second term is just the definition of the LaPlace transform of $F(t)$; evaluation of the first term at the limits of integration gives

$$L(F'(t)) = -F(0) + pL(F(t)) \quad (2-42)$$

One additional result will be needed which will be derived in Appendix 2 of this chapter. This is Borel's theorem which states

$$L\left(\int_0^t F_1(t-\tau) F_2(\tau) d\tau\right) = L(F_1(t)) L(F_2(t)) \quad (2-43)$$

Using these results we can now derive the relationship between the creep compliance and the stress relaxation modulus.

The LaPlace transform of equation (2-31) yields

$$L(\gamma(t)) = J(0) L(\sigma(t)) + \int_0^\infty e^{-pt} \int_0^\infty \sigma(t-a) \frac{\partial J(a)}{\partial a} da dt \quad (2-44)$$

or

$$L(\gamma(t)) = J(0) L(\sigma(t)) + \int_0^\infty \frac{\partial J(a)}{\partial a} \int_0^\infty e^{-pt} \sigma(t-a) dt da \quad (2-45)$$

Making use of the result derived in equation (2-43) gives

$$L(\gamma(t)) = J(0) L(\sigma(t)) + \left[\int_0^\infty e^{-ap} \frac{\partial J(a)}{\partial a} da \right] L(\sigma(t)) \quad (2-46)$$

The term enclosed in brackets, however, is nothing except the LaPlace transform of the derivative of $J(t)$. Thus we may apply the result obtained in equation (2-45) to get

$$L(\gamma(t)) = J(0) L(\sigma(t)) + L(\sigma(t)) [pL(J(t)) - J(0)] = \frac{pL(\sigma(t)) L(J(t))}{\quad} \quad (2-47)$$

Next, transform equation (2-32) into LaPlace space in the same manner to obtain

$$L(\sigma(t)) = G(0) L(\gamma(t)) + L(\gamma(t)) [pL(G(t)) - G(0)] = \frac{pL(\gamma(t)) L(G(t))}{\quad} \quad (2-48)$$

Equations (2-47) and (2-48) give

$$\frac{1}{p^2} = L[G(t)]L[J(t)] \quad (2-49)$$

This is the solution of the problem in transform space. We have a direct relationship between the transforms of the compliance and the modulus. This solution must now be returned to real space. Making use of Borel's theorem, equation (2-43) and the result derived in equation (2-33) gives the final result

$$t = \int_0^t G(\tau) J(t - \tau) d\tau \quad (2-50)$$

This is the convolution integral which is the relationship between the creep compliance and the stress relaxation modulus. It is exact and depends only on the applicability of the Boltzmann superposition principle.

VIII. Retardation and relaxation time spectra

For a large number of Voigt elements in series the response would be

$$D(t) = \gamma / \sigma_0 = \sum (1/E_n) [1 - \exp(-t/\tau_n)] \quad (7.22)$$

Notice that the contribution of each Voigt element to the equilibrium compliance is merely $1/E_n$; in other words, each retardation time τ_n is associated with a compliance $1/E_n$. One is therefore led to adopt a terminology in which one speaks of a spectrum of retardation times, each of strength $1/E_n$.

It frequently happens that the retardation times become so closely spaced and so numerous that the sum of Eq. (7.22) can be replaced by an integral. Then,

$$D(t) = \int (1/E) [1 - \exp(-t/\tau)] d\tau \quad (7.23)$$

Usually data are plotted as a function of $\log(t/\tau)$, and it is therefore more convenient to express the integral in terms of $\ln \tau$. Since

$$d(\ln \tau) = \tau^{-1} d\tau$$

then

$$D(t) = \int (\tau/E) [1 - \exp(-t/\tau)] d(\ln \tau) \quad (7.24)$$

where it is understood that all values of τ are to be covered by the integral.

The quantity τ/E in Eq. (7.24) is the contribution of retardation times in the range $d(\ln \tau)$ to the creep compliance. It is often referred to as the “retardation spectrum” and is represented by the symbolism $L(\tau)$. If this terminology is used,

$$D(t) = \int L(\tau)[1 - \exp(-t/\tau)] d(\ln \tau) \quad (7.25)$$

It is also common to define $L(\tau)$ by an equation similar to Eq. (7.25), but with $D(t)$ replaced by the shear compliance $J(t)$. Since $J(t) = 3D(t)$ for rubbers, the two definitions differ by a factor of 3. The definition used will usually be clear from the context.

By the same token

$$E(t) = \int H(\tau) \exp(-t/\tau) d(\ln \tau) \quad (7.38)$$

where $H(\tau) = \tau E(\tau)$. The quantity $H(\tau)$ is called the “relaxation-time distribution function,” or the “relaxation spectrum.”