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The Modulus of a Cross Linked Melt

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History

The problem of permanent cross links (see figure 1), where $\mathbf{r}(s_b^a) = \mathbf{r}(s_a^b)$, and that of entanglements, where $I_{ab}([\mathbf{r}_a][\mathbf{r}_b]) = I_{ab}([\mathbf{r}_a^{-1}][\mathbf{r}_b^{-1}])$, is how to determine the modulus, G:

$$G = G' + iG''$$

$$G = G(\omega, c_x, c_e) \tag{1}$$

where $c_x = \frac{N_x}{V}$ and $c_e = \frac{\sum I}{V}$.

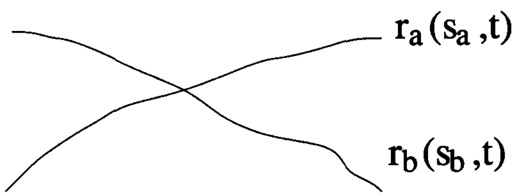

Figure 1:

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The problem is that we need to obtain F_{expt}, where

$$\begin{aligned} F_{expt} &= \langle F([s^{\mathrm{a}}_{\mathrm{b}}], I_{\mathrm{ab}})\rangle & (2) \\ &= \left\langle kT \log \int \exp(-H/kT) \prod \begin{bmatrix} \delta(r^{\mathrm{b}}_{\mathrm{a}} - r^{\mathrm{a}}_{\mathrm{b}}) \\ \delta(I - J) \end{bmatrix} \right\rangle & (3) \end{aligned}$$

i.e.

$$\begin{aligned} F_{expt} &= \langle \log Z \rangle & (4) \\ &\neq \log \langle Z \rangle & (5) \end{aligned}$$

If $F(n) = \langle Z^n \rangle$, then

$$\left.\frac{\partial F}{\partial n}\right|_{n=o} = \langle F \rangle \quad (6)$$

This is the extension of the Gibbs method (equivalent to the replica method). It *cannot* give G. We therefore need a dynamical solution. The dynamical problem needs extensions of the Boltzmann (Smoluchowski, Langevin, Fokker-Planck) equation.

Method

The method is to use the Rayleighan (or Rayleighs friction function).

$$\mathcal{R}_0 = L + M + \sum \lambda C \quad (7)$$

where L is the Lagrangian, M is the friction function, λ are the Lagrange multipliers, and C are the associated constraints. Rayleigh showed that:

$$\frac{\delta L}{\delta r} + \frac{\delta M}{\delta u} + \sum \lambda \frac{\delta C}{\delta r} = 0 \quad (8)$$

where $u = \dot{r}$, but is only identified at the end.

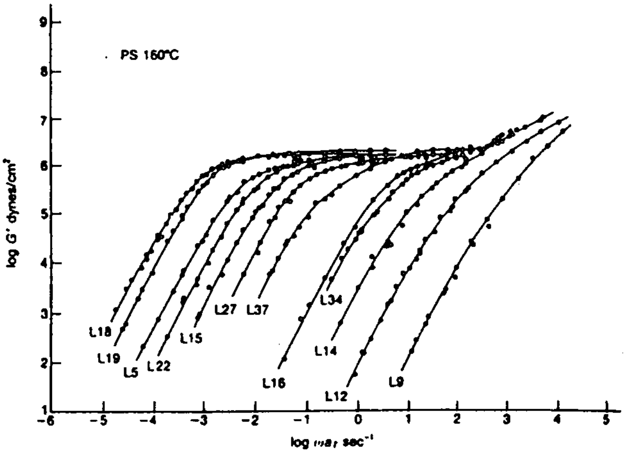

Figure 2: Experimental data from Onogi, Masuda and Kitagawa, *Macromolecules*, **3**, 109 (1970)

Problem

The problem is to predict the experimental curve

$$G'(c_e) > G'(c_e = 0) \tag{9}$$

A simple qualitative explanation can be seen in figure 4.

Model

$n = n(s)$. The axis of the tube, the primitive path, is described by $\mathbf{R}(\mathrm{n}(\mathrm{s}), \mathrm{t})$. The Rayleighan involves $\mathbf{r}, \dot{\mathbf{r}}, \mathbf{R}, \dot{\mathbf{R}}$.

The potential function is given by:

$$U = \frac{3kT}{2L}\int_0^L \left[\left(\frac{\partial \mathbf{r}}{\partial s}\right)^2 + q_1^2 (\mathbf{r} - \mathbf{R})^2\right] \tag{10}$$

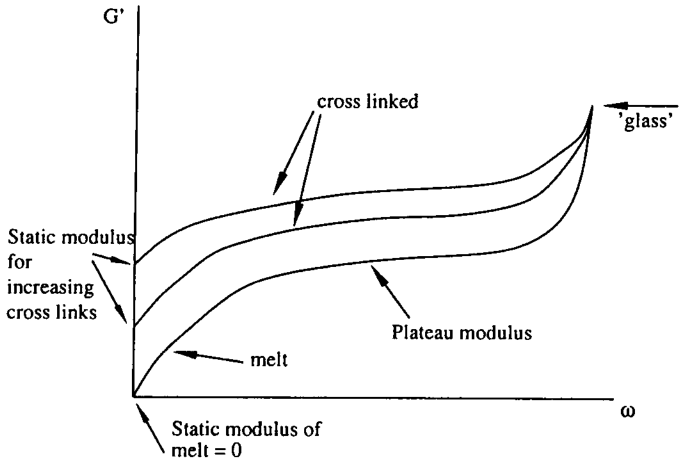

Figure 3:

and the constraint

$$\int_0^L \frac{\partial n}{\partial s} ds = N \tag{11}$$

where aN is the length of the tube.

The relative velocities are given by:

$$\left(\frac{d\mathbf{r}}{dt} - \frac{d\mathbf{R}}{dt}\right)\bigg|_{\text{fixed s}} = \left(\dot{\mathbf{r}} - \frac{\partial \mathbf{R}}{\partial n}\dot{n} - \dot{\mathbf{R}}\right) \tag{12}$$

this velocity $\times\zeta$ gives the friction of a chain segment within its environment.

$$\left(\frac{d\mathbf{R}}{dt}\bigg|_s - \frac{\partial \mathbf{R}}{\partial t}\bigg|_n\right) \rightarrow \frac{\partial \mathbf{R}}{\partial n}\dot{n} \tag{13}$$

Equation 13 is the slip motion along the primitive path, and has friction ν.

Therefore, the Rayleighan becomes:

$$\mathcal{R}_0 = -U - \frac{1}{2}\zeta \int ds \left(\dot{\mathbf{r}} - \mathbf{R}'\dot{n} - \dot{\mathbf{R}}\right)^2 - \frac{1}{2}\nu \int ds \left(\mathbf{R}'\dot{\mathbf{r}}\right)^2 \tag{14}$$

and from Rayleighs equations, we obtain:

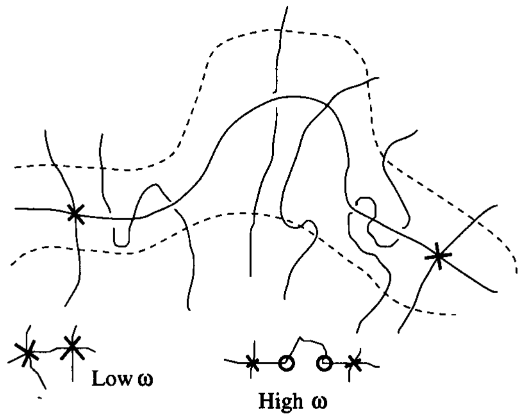

Figure 4:

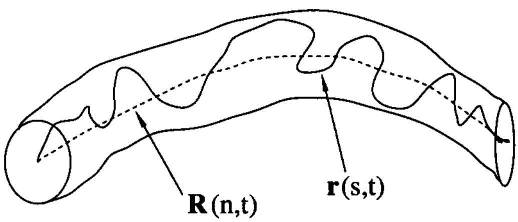

Figure 5:

$$\zeta\left(\dot{\mathbf{r}}-\frac{\partial\mathbf{R}}{\partial n}\dot{n}-\dot{\mathbf{R}}\right)+\frac{3kT}{L}\left(-\frac{\partial^2\mathbf{r}}{\partial s^2}+q_1^2\left(\mathbf{r}-\mathbf{R}\right)\right)=\mathbf{0} \tag{15}$$

$$\nu\left(\frac{\partial\mathbf{R}}{\partial n}\right)^2\dot{n}+\frac{3kT}{L}\frac{\partial\mathbf{R}}{\partial n}\left(-\frac{\partial^2\mathbf{r}}{\partial s^2}\right)=0 \tag{16}$$

Now put $\tilde{\mathbf{r}}(st)=\mathbf{r}(st)-\mathbf{R}(n,t)$, and ignore $\tilde{\mathbf{r}}$, to obtain:

$$\nu\left(\frac{\partial\mathbf{R}}{\partial n}\right)^2\dot{n}+\frac{3kT}{L}\left(\frac{\partial\mathbf{R}}{\partial n}\right)\cdot\left(-\frac{\partial^2\mathbf{R}}{\partial s^2}\right)=0 \tag{17}$$

The static equilibrium solution is:

$$R_0 \sim an\,(s,t)\,, \quad \frac{\partial^2 n}{\partial s^2} = 0 \tag{18}$$

and

$$n_0 = \frac{N}{L} s \tag{19}$$

for uniform progression.

Deformation

The deformation is given by a linear theory:

$$\mathbf{R} = \underline{\underline{E}}\,(t)\,\mathbf{R}_0 \cong \mathbf{R}_0 + \underline{\underline{\varepsilon}} \cdot \mathbf{R}_0 \tag{20}$$

$$n\,(st) = n_0 + n_1 \tag{21}$$

$$\frac{l\nu}{3kT}\left(\frac{\partial n_1}{\partial t}\right) - \frac{\partial^2 n_1}{\partial s^2} = \left(\frac{N}{aL}\right)^2 \frac{\partial \mathbf{R}_0}{\partial n}\left(\varepsilon + \varepsilon^T\right)\frac{\partial \mathbf{R}_0}{\partial n} \tag{22}$$

where the right hand side of the last equation represents the source of n_1 changes.

Stress

We have the usual formula:

$$\sigma_{ij} = c_x \left(\frac{3kT}{l}\right) \int_0^L ds \left\langle \frac{\partial r_i}{\partial s} \frac{\partial r_j}{\partial s} \right\rangle \tag{23}$$

where

$$\mathbf{r}\,(\mathrm{s,t}) \cong \mathbf{R}_0\,(\mathrm{n}_0) + \underline{\underline{\varepsilon}}\mathbf{R}_0 + \left(\frac{\partial \mathbf{R}_0}{\partial \mathrm{n}_0}\right) \mathrm{n}_1\,(\mathrm{s,t}) \tag{24}$$

and

$$\mathbf{r} \cong \mathbf{R}_0 + \underline{\underline{\varepsilon}} \cdot \mathbf{R}_0 + \left(\frac{\partial \mathbf{R}_0}{\partial \mathrm{n}_0}\right) \mathrm{n}_1 \tag{25}$$

where the first term of equation (25) gives *zero* effect from thermodynamic theory and the second term corresponds to the *stress*, $G(\omega \rightarrow 0)$. For a random walk on a primitive path, we have

$$\left\langle \frac{\partial R_{0i}}{\partial s} \frac{\partial R_{0j}}{\partial s} \right\rangle = \left(\frac{N}{L} \right)^2 \frac{a^2}{3} \delta_{ij} \tag{26}$$

and using the fact that $Na^2 = Ll$, we have

$$\underline{\underline{\sigma}} = (c_x N)\, kT \underline{\underline{\varepsilon}}\,(t) \tag{27}$$

The third term of equation 25 corresponds to the relaxation.

$$n_1 = \int_o^L G(ss') \tag{28}$$

with a source term

$$\left(\frac{N}{aL} \right)^2 \frac{\partial R_0}{\partial n} \left(\varepsilon + \varepsilon^T \right) \frac{\partial R_0}{\partial n} \tag{29}$$

and

$$\left(\frac{l\nu}{3kT} i\omega - \frac{\partial^2}{\partial s^2} \right) G = \delta(s - s'). \tag{30}$$

Final Result

Take the case of $\epsilon_{\alpha\beta} = \epsilon^0_{\alpha\beta} Re(\exp(i\omega t))$

$$\sigma = c_x N kT \underline{\underline{\varepsilon}}^0 Re \left[2 - \frac{2}{5} \frac{1}{x} f(x, N) \exp(i\omega t) \right] \tag{31}$$

where

$$x = \exp(i\pi/4) \sqrt{\frac{l\nu\omega}{kT}} \left(\frac{L}{N} \right) \tag{32}$$

and

$$f(x,N) = 1 - \exp(-x) - \frac{2\exp(-nX)}{\sinh(Nx)}\sinh^2\left(\frac{x}{2}\right) - \frac{1}{N}\tanh\left(\frac{x}{2}\right) \tag{33}$$

The diffusion of the primitive path is characterised by the time:

$$\tau = \frac{1}{2}\frac{l\nu}{3kT}\left(\frac{L}{N}\right)^2 \tag{34}$$

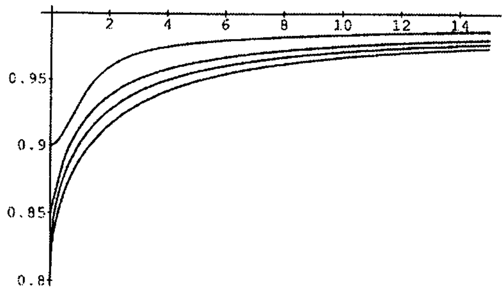

Figure 1: $G'/[2k_BT(c_x + c_e)]$ versus $\tau_{L/N}\omega$.
From top to bottom, $N = 1 + c_e/c_r = 1, 2, 4, 8, \infty$.

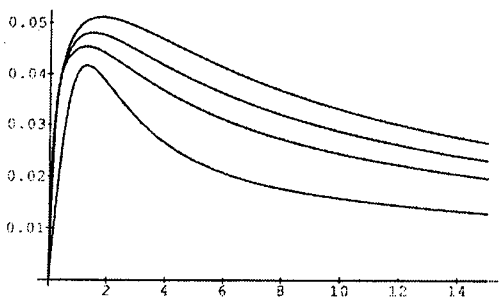

Figure 2: $G''/[2k_BT(c_x + c_e)]$ versus $\tau_{L/N}\omega$.
From bottom to top, $N = 1 + c_e/c_r = 1, 2, 4, 8, \infty$.

Figure 6:

Consider the following specific example. Let $\varepsilon_{xx} = \varepsilon_{yy} = 0$, and $\varepsilon_{zz} = \varepsilon^0 Re(\exp(i\omega t))$. Also, let $\sigma_{zz} = Re\left(G^* \varepsilon^0 \exp(i\omega t)\right)$, where

$$G^* = (c_x N)\, kT \left(2 - \frac{2}{5}\frac{1}{x} f(x, N)\right) \tag{35}$$

In equation (35),

$$c_x \equiv \text{number of chains per unit volume}$$
$$c_x N \equiv \text{number of steps of primitive path per unit volume} \tag{36}$$

i.e., c_x is the density of cross links, and $c_x N$ is the density of crosslinks plus the density of the entanglements, so $c_x N = c_x + c_e$.

There are a number of limiting cases:

1. $$\frac{c_e}{c_x} = 0 \quad G^* = 2c_x kT \quad (\text{i.e.} N = 1) \tag{37}$$

2. $$\frac{c_e}{c_x} \to \infty \quad G^* = 2\,(c_x + c_e)\, kT \left[1 - \frac{1}{5}\frac{(1-\exp(-x))}{x}\right] \quad (\text{i.e.} N = \infty) \tag{38}$$

3. $$G^*(\omega \to \infty) = 2uT\,(c_x + c_e) \quad (\text{plateau}) \tag{39}$$

4. $$G^*(\omega \to 0) = 2kT\left(c_x + \tfrac{4}{5}c_e\right) \left(\text{for large } \mathrm{N}c_e >> c_x, \text{therefore} \tfrac{8}{5}\,(c_x N)\, kT\right) \tag{40}$$

For the general Rayleighan problem, consider the simple case of unentangled chains: $\mathbf{r}(\mathrm{s}_\mathrm{b}^\mathrm{a}) = \mathbf{r}(\mathrm{s}_\mathrm{a}^\mathrm{b})$

$$\mathcal{R} = -\sum_a \frac{3kT}{2l} \int \left(\frac{\partial r_a}{\partial s_a}\right)^2 \frac{ds}{dt} + \sum_{a,b} \int \lambda_{ab}(t) \left(r_a\left(s_a^b t\right) - r_b\left(s_b^a t\right)\right)\, dt$$
$$+ \sum_a \frac{m}{2} \int \dot{r}_a^2(s_a)\, ds_a dt \;+\; \frac{\nu}{2} \int \tilde{v}_a^2 ds_a dt \;+\; \text{Noise source} \tag{41}$$

where $\tilde{v} = v - \bar{v}$ is the average velocity.

This gives:

$$\rho\ddot{r}_a + \nu\frac{\partial}{\partial t}(r_a - \bar{r}_a) + \frac{3kT}{l}\frac{\partial^2 r_a}{\partial s_a^2} + \sum_b \lambda_{ab}\delta\left(s_a - s_a^b\right) = f_a \tag{42}$$

and we model the sum by $\frac{3kT}{l}q_0^2(r_i - \bar{r}_i)$ to give

$$q_0^2 = \left\langle \sum_b \frac{\delta\left(s_a - s_a^b\right)}{G(0,\omega)} \right\rangle \tag{43}$$

where G is the mean Green function

$$\left[m\omega^2 + i\nu\omega + \frac{3kT}{l}\left(q^2 + q_0^2\right)\right] G = 1 \tag{44}$$

and this yields

$$q_0 = \frac{c_x}{L} \tag{45}$$

The equations above extend the locus of chains into ω variation due to the fluctuation of cross link positions.

One can now generalise the earlier model, but the algebra is difficult.