Long time dynamics of rubber networks

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RUBBER ELASTICITY

From the equilibrium theory to the analysis of dynamics

Since the early days of polymer science crosslinked polymer networks have enjoyed a special interest because of the remarkable success of the equilibrium theory of rubber elasticity[1,2]. No such easy reference point exists for the investigation of the mechanical properties of uncrosslinked systems: any such investigation has to be dynamical from the beginning. The complexity of multiple entanglement constraints often suggests mean field treatments, in which each chain is constrained to 'reptate' within a temporary 'tube'[2a], whose slow renewal accounts for the high viscosity usually observed in uncrosslinked systems. Entanglements are present also in crosslinked rubbers[3] and the tube concept can certainly be extended to these systems. However, recent improvements in the equilibrium theory of rubber elasticity[4–7], show that junction–chain entanglements play a dominant role in accounting for the experimentally observed departures from the ideal law of rubber elasticity. Such entanglements impose deformation dependent constraints on the motion of the junctions. These constraints are more effective on unswollen systems at very small deformations, whereas swollen and highly stretched networks obey the ideal phantom network elastic equation[8]. Junction–chain entanglements naturally account for the experimentally observed features of the reduced stress–strain curve, which shows a maximum in the vicinity of the undeformed state. The complete analysis of the dynamics of a rubber network poses problems which, in general, are no less difficult than those connected with a dynamical analysis of uncrosslinked systems. Nevertheless, the remarkable success of the equilibrium theory formulated in terms of chain–junction entanglements[6,5], suggests some specific considerations. Because of their ability to form entanglements, junctions in a crosslinked network must have very high effective friction coefficients, which implies that the relaxation times associated with the diffusive motion of the junctions might be substantially longer, on the average, than those associated with intrachain motions. An early recognition of this special feature is due to Mooney[9], who, in his high frequency treatment of the dynamics of a crosslinked network, considers both ends of the general chain to be fixed in space. If the observation time is longer, we are able to resolve the collective motions of the junctions, but in these conditions the intrachain degrees of freedom are very likely to show an equilibrium behaviour. To this extent, in this time range junctions behave as 'heavy Langevin particles' interacting with one another through Gaussian potentials. Over convenient observation times (typically, $\gtrsim 10^{-4}$ s for highly swollen networks and $\gtrsim 10^{-1}$s for unswollen systems) the dynamics of a rubber network can therefore be described in terms of a many body Langevin equation coupling together the motion of large sets of junctions. We shall only consider highly swollen systems, in which no deformation dependence of the constraints on the mobility of the junctions is to be expected.

SWOLLEN NETWORKS

The network equation of motion, referred to the general junction i, is given by:

$$\Sigma_j[\mathbf{R}_j(t) - \mathbf{R}_i(t)] - \tau[\dot{\mathbf{R}}_i(t) - \gamma(t)\mathbf{R}_i(t)] + \frac{1}{c}\mathbf{F}_i(t) = 0 \qquad (1)$$

where Σ_j is summed over all junctions connected with i by a chain, c is the force constant of the general chain and $\zeta = \tau c$ is the effective junction friction coefficient. $\mathbf{F}_i(t)$, which is the random force acting on the junction, satisfies the 'white noise' correlation:

$$\langle \mathbf{F}_i(t)\mathbf{F}_j(t')\rangle = 2k_BT\zeta\delta(t-t')\delta_{ij}\mathbf{1} \qquad (2)$$

At equilibrium, that is when we put the velocity gradient $\gamma(t) \equiv 0$ in equation (1), equations (1) and (2) give the well-known results of the phantom network theory.

The stress at a given instant of time is:

$$\mathbf{P}(t) = \frac{c}{2}\sum_{i,j}\langle[\mathbf{R}_j(t) - \mathbf{R}_i(t)]\,[\mathbf{R}_j^T(t) - \mathbf{R}_i^T(t)]\rangle + p\mathbf{1} \qquad (3)$$

Writing the general position component $\mathbf{R}_i(t)$ as the sum of an affinely displaced term plus a fluctuating part, we naturally decompose the stress into an equlibrium value and a transient term. The transient term is due to the existence of diffusional modes which are anisotropic because of an applied flow field. These modes extend to a considerable number of junctions at a time; however, we assume that their range is not large enough to contain closed circuits. Under these circumstances, the network (for the sole purpose of computing fluctuating properties and related quantities such as the transient stress or the dynamic structure factor) behaves like a tree. Within this approximation, the equation of motion (1) can be solved exactly, thus providing a general expression for the transient stress[9a]:

$$\mathbf{P}_{\text{trans}} = \frac{2k_BTN}{\tau}\int_{-\infty}^{t} K(t-t')\Lambda(t,t')\Lambda^T(t,t')\mathrm{d}t' + P\mathbf{1} \qquad (4)$$

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where N is the number of junctions per unit volume and $\Lambda(t,t')$ is the evolution operator defined by the equations:

$$\frac{d\Lambda(t,t')}{dt} = \gamma(t)\Lambda(t,t'); \Lambda(t',t') = 1$$

The Kernel function $K(t)$ can be expressed as[9a]:

$$K(t) = 2(f-1)^{1/2} e^{-4ft/\tau} \times$$

$$\int_0^t e^{2ft'/\tau} I_1 \left[\frac{4(f-1)^{1/2}}{\tau} t'\right] \frac{dt'}{t'} + 2e^{-4ft/\tau} \tag{5}$$

where f is the functionality and I_1 is the modified Bessel function. In particular, we can apply equation (5) to a uniaxial stretching experiment. If the ends of the sample are pulled apart at a constant velocity, the resulting stress–strain curve shows a dynamic Mooney effect, in as much as a transition is predicted from the stiffer Flory behaviour approached at small deformations to the softer phantom network elasticity at high elongations. Both the equilibrium Mooney effect for unswollen systems and its non-equilibrium counterpart originate, within our present picture, from the tendency of the fluctuations to follow the deformation affinely. This tendency has a transient nature in the case of the dynamics of a swollen network.

The dynamic structure factor of a swollen network was originally calculated by Tanaka and Benedek[10] on the basis of a continuum model. The use of a continuum model is justified whenever the distance between crosslinks is much less than the fluctuation wavelength. In practice[11], the scattering wavelength range admits the average crosslink distance as a lower bound. In the case of neutron scattering, one can operate in such a way that junctions are the sole effective scatterers.

We define the junction autocorrelation function by the equation:

$$S(\mathbf{K},t) = \left\langle \sum_{ij} \exp\left\{ i\mathbf{K}\cdot[\mathbf{R}_i(0) - \mathbf{R}_j(t)]\right\}\right\rangle$$

$$- \sum_{ij} \langle \exp i\mathbf{K}\cdot\mathbf{R}_i(0)\rangle\langle \exp - i\mathbf{K}\cdot\mathbf{R}_j(0)\rangle \tag{6}$$

The second term in equation (6) corresponds to the infinite time scattering contribution, which does not vanish for a solid. In the absence of an external flow, the equation of motion (1) takes the form:

$$\sum_j [\mathbf{R}_j(t) - \mathbf{R}_i(t)] - \tau\dot{\mathbf{R}}_i + \frac{1}{c}\mathbf{F}_i(t) = \mathbf{0} \tag{7}$$

This is a simplified case of the equation considered by Schurr[12]. In a crosslinked network every junction fluctuates around an average position which is fixed in space. We denote the fluctuation vector by $\mathbf{U}(i,t)$, by $U(i,t)$ the general fluctuation component, and by $\langle U^2\rangle$ the mean square fluctuation component of a given junction. Furthermore, let $\langle d^2\rangle$ be the mean square distance, averaged over all chains, between the average positions of two successive junctions.

Making use of equation (7), one easily obtained the autocorrelation function of a tetrafunctional network[9a]:

$$\frac{S(\mathbf{K},t)}{N} = e^{-K^2\langle U^2\rangle}\left\{e^{K^2B(0,t)} - 1 + \frac{4}{3}\sum_{n=1}^{\infty} 3^n e^{-nK^2\langle d^2\rangle/6}\left[e^{K^2B(n,t)} - 1\right]\right\} \tag{8}$$

where

$$B(n,t) = \langle U(0,0)\, U(n,t)\rangle \tag{9}$$

is the time correlation function relative to junction separated by n chains. From the equation of motion (7) one obtains, for a tetrafunctional network[9a]:

$$B(n,t) = \frac{\langle U^2\rangle}{\pi} 3^{-n/2} \times \left[\int_0^{\pi} \frac{e^{-(4-2\times 3^{1/2}\cos q)t/\tau}\,[4\cos nq - 3\cos(n+2)q - \cos(n-2)q]\, dq}{(4-3\cos^2 q)(2-3^{1/2}\cos q)}\right. \tag{10}$$

It is of some interest to investigate the long time behaviour of $S(\mathbf{K},t)$. If:

$$K^2\langle d^2\rangle > 3 \ln 3 \tag{11}$$

we obtain at long times:

$$S(\mathbf{K},t) \propto t^{-3/2}\exp[-(4-2\times 3^{1/2})t/\tau] \tag{12}$$

Equation (12) is non-exponential. Furthermore, it depends on $\mathbf{K}$ only through a normalizing factor. Alternatively if:

$$K^2\langle d^2\rangle < 3\ln 3 \tag{13}$$

we obtain, for $t/\tau \gg 1$

$$S(\mathbf{K},t) \propto \exp[-\beta(K^2\langle d^2\rangle)t/\tau] \tag{14}$$

where

$$\beta(K^2\langle d^2\rangle) = (e^{K^2\langle d^2\rangle/6} - 1)(3e^{-K^2\langle d^2\rangle/6} - 1) \tag{15}$$

If $K^2\langle d^2\rangle \ll 1$, i.e. in the extreme long wavelength limit:

$$\beta(K^2\langle d^2\rangle) \sim \frac{K^2\langle d^2\rangle}{3} \tag{16}$$

a result which is formally similar to that obtained by Tanaka and Benedek[10] by means of their continuum treatment.
The inequality:

$$\beta(K^2\langle d^2\rangle) \leqslant \frac{K^2\langle d^2\rangle}{3} \tag{17}$$

is always satisfied.

Considering now the range $K^2\langle d^2\rangle < 1$, we can define for the autocorrelation function an initial time and a final time by the equations:

$$\frac{1}{\tau_{in}} = -\frac{\dot{S}(\mathbf{K},0)}{S(\mathbf{K},0)} \tag{18}$$

$$\frac{1}{\tau_{fin}} = \frac{1}{\tau}\beta(K^2\langle d^2\rangle) \tag{19}$$

The quantity τ/τ_{in} is essentially a linewidth index. Another quantity of interest is τ_{fin}/τ_{in}, which may be called an index of deviation from exponential behaviour. At small values of $K^2\langle d^2\rangle$, we obtain:

$$\tau_{fin}/\tau_{in} = 1 + K^2\left(\langle U^2\rangle + \frac{\langle d^2\rangle}{24}\right) + \ldots \tag{20}$$

Equation (20) proves that the autocorrelation function is exponential only in the limit of very small values of the scattering vector. Analogously we obtain:

$$\tau/\tau_{in} = \frac{K^2\langle d^2\rangle}{3}\left[1 + K^2\left(\langle U^2\rangle - \frac{\langle d^2\rangle}{24}\right)\right] + \ldots \tag{21}$$

The correction of order K^4 to the linewidth index τ/τ_{in} is either positive or negative depending on the value of $\langle d^2\rangle/\langle U^2\rangle$. The value of this ratio increases with swelling. For a tetrafunctional network the correction of order K^4 vanishes if the swelling ratio (V/V_0) satisfies the equation:

$$(V/V_0)_{neutral} = 6^{3/2} \sim 14.7$$

Generally, $(V/V_0)_{neutral}$ is an absolute function of functionality.

CONCLUSIONS

In the foregoing treatment no specific mention has been made of the concentration dependence of the relevant parameters C and ζ (force constant and friction coefficient). These data as well as those concerning the deformation dependence of the constraints on the mobility of the junctions for weakly swollen[8] or unswollen rubbers[5,6], require a more rigorous analysis of the chain - junction entanglement concept. This analysis is essential to a dynamic treatment of dense networks, despite the technical simplicity of the procedures by which the deformation dependent constraints could be introduced in a dynamic formulation. Generally, a rigorous statistical mechanical foundation for the very specific role of junctions, as it clearly emerges from recent improvements of the equilibrium theory of rubber elasticity, seems to be an important prerequisite for further progress in a dynamic analysis.

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