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The dynamics of polymer networks

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Abstract. The dynamics of a cross-linked, entangled, network of polymer molecules is studied, using a gaussian chain model. The motion of the molecules is solved in a way which leads to the equations of motion of the resulting elastic medium. Thus a direct evaluation of the elastic constants results, by-passing difficulties arising from the use of statistical mechanics. The calculation also gives the fluctuation spectrum of the rubber, ie Rayleigh and Brillouin scattering, and evaluates the damping of elastic waves in terms of the elastic constants, and molecular viscosities.

1. Introduction

Rubber elasticity has been studied in many papers from the point of view of statistical mechanics. This view considers the free energy of a cross-linked network which has suffered a gross deformation $\lambda_1, \lambda_2, \lambda_3$. By differentiating the free energy, particularly for small deformation, the elastic equations of motion are produced, but of course the elastic constants follow from the differentiation of the free energy in perfectly static conditions. If the material is incompressible, the simplest theories all agree that

$$F = \nu n_c \kappa T \sum_i \lambda_i^2 \quad (\lambda_1 \lambda_2 \lambda_3 = 1) \quad (1.1)$$

where n_c is the number of cross links, and ν is a constant. The value of ν , however, varies with different approaches, and whereas the value unity arises in simple models, the inclusion of more elaborate configurations of links appears to depress ν , and a very general approach which considers the whole network starting from an exact formal expression of the statistical mechanics gives $\frac{1}{2}$ (Edwards 1972). Although there is still a gulf between these discussions and experiment, since links can be wasted, or enhanced by entanglements, it is an important point of principle and deserved further study. At the same time the fluctuations of the system, and those dynamical properties such as damping of elastic waves which do not follow from a knowledge of the free energy, are now of importance because of the new developments in light scattering. In this paper therefore the network is studied as a problem in dynamics, without evoking statistical mechanics as such, and produces the elastic constants in that they appear in the elastic equations of motion. The situation is analogous to that of simpler problems in condensed matter. One can invoke a general formula like

$$e^{-A/\kappa T} = \int e^{-H/\kappa T}$$

and, given H , calculate A , without reference to dynamics. Alternatively one can set up

the Boltzmann equation by a statistical treatment of the equation of motion, and although this usually means more stringent approximations being made, the final answer gives both transport coefficients as well as the thermodynamic variables.

The present calculation is set up very much in the spirit of the author's previous work on the statistical mechanics of networks and again yields $\nu = \frac{1}{2}$. The elastic equations of motion are (see, for example, Landau and Lifshitz 1959)

$$(E^2 - c^2 k^2 - \Delta(E, k) - i\gamma(k, E)) \mathbf{u}_{\mathbf{k}, E} = \mathbf{F}_{\mathbf{k}, E} \quad (1.2)$$

where

$$c^2 = \frac{\kappa T}{m} \omega_0 \quad (c = \text{velocity of sound}), \quad (1.3)$$

$$\Delta = \frac{l}{6} \frac{E^2 k^2}{\omega_0} \quad (1.4)$$

is the frequency displacement,

$$\gamma = \left(\frac{\zeta \omega_0}{6} + \frac{\nu}{\omega_0} \right) \frac{k^2 E l}{m} \quad (1.5)$$

is the damping ($= \mu k^2 E$),

$$\omega_0^2 = \frac{n_c}{L} \omega_0 + C \rho \quad (1.6)$$

and where $\mathbf{F}_{\mathbf{k}, E}$ is the random external force, n_c is the number of cross links, ρ is the density of the polymer, l is the Kuhn effective step length of the polymer,

$$\mu = \left(\frac{\zeta \omega_0}{6} + \frac{\nu}{\omega_0} \right) \frac{l}{m},$$

ν is the molecular viscosity, ie the viscosity experienced by a section of the polymer in the gel, not the macroscopic viscosity derived in μ above, ζ is the viscosity of nonlinear transmission of energy along the polymer (discussed in detail below), $L = l$ times the mean number of monomers between cross links, and ml is the mass of a monomer.

The calculation has assumed

$$\nabla \cdot \mathbf{u} = 0. \quad (1.7)$$

The force $\mathbf{F}_{\mathbf{k}, E}$ will be considered to be fluctuating instantaneously so that, allowing for the fact that $\mathbf{F}_{\mathbf{k}, E}$ must leave $\nabla \cdot \mathbf{u} = 0$

$$\langle F_i(\mathbf{k}, E) F_j^*(\mathbf{k}_1, E_1) \rangle$$

$$= A(k) (\delta_{ij} - k_i k_j / k^2) \delta(\mathbf{k} - \mathbf{k}_1) \delta(E - E_1) \quad (1.8)$$

$$= A \mathcal{D}_{ij} \delta(\mathbf{k} - \mathbf{k}_1) \delta(E - E_1) \quad (1.9)$$

say.

Since the kinetic energy of any classical system is $\frac{3}{2} \kappa T$ per mode, one can now derive the value for A

$$\langle u_i(\mathbf{k}, E) u_j^*(\mathbf{k}_1, E_1) \rangle = \frac{A(k) \mathcal{D}_{ij} \delta(\mathbf{k} - \mathbf{k}_1) \delta(E - E_1)}{(E^2 - c^2 k^2 - \Delta)^2 + \gamma^2} \quad (1.10)$$

$$\frac{1}{2} \rho \int E E_1 \langle u_i(\mathbf{k}, E) u_j^*(\mathbf{k}_1, E_1) \rangle d^3 \mathbf{k}_1 d^3 \mathbf{k} dE dE_1 = \kappa T \mathcal{D}_{ij}. \quad (1.11)$$

Hence

$$\kappa T = A(k) \int \frac{E^2 dE}{(E^2 - c^2 k^2 - \Delta)^2 + \gamma^2} \quad (1.12)$$

and the fluctuation spectrum is

$$\begin{aligned} \langle u_i(\mathbf{k}, E) u_j^*(\mathbf{k}_1, E_1) \rangle \\ = \frac{\kappa T \mathcal{D}_{ij} [(E^2 - c^2 k^2 - \Delta)^2 + \gamma^2]^{-1} \delta(\mathbf{k} - \mathbf{k}_1) \delta(E - E_1)}{\int E_2^2 [(E_2^2 - c^2 k^2 - \Delta)^2 + \gamma^2]^{-1} dE_2}. \end{aligned} \quad (1.13)$$

The spectrum has the usual three peaks, two at $E \simeq \pm ck$ and the central peak near $E = 0$ with width c^2/μ .

These forms are of course standard in structure. The object of the present paper is to relate the constants c, Δ, γ to the density of cross links and the number density of the polymer, and to molecular viscosities, densities and sizes.

2. The equations of motion

The problem can be cast in full generality by writing the lagrangian of the system. It will be assumed possible to consider the α th polymer chain represented by a variable $r_\alpha(s_\alpha, t)$, where s is the arc length, with mass per unit length of m . There will be an intermolecular potential V , and Lagrange multiplier $P_{\alpha\beta}$ for the cross linkage of chain α with chain β at s_α^i, s_β^j respectively, and $Q_{\alpha\beta}$ for the entanglement of chains α, β and finally $w_\alpha(s)$ for the inextensibility of the chain:

$$\begin{aligned} L = \frac{1}{2} m \sum_\alpha \int \dot{r}_\alpha^2(s_\alpha) ds_\alpha + \sum_{\alpha\beta} P_{\alpha\beta} \cdot (\mathbf{r}_\alpha(s_\alpha^i, t) - \mathbf{r}_\beta(s_\beta^j, t)) + \sum_{\alpha\beta} Q_{\alpha\beta} (I_{\alpha\beta} - I_{\alpha\beta}^{(0)}) \\ + \sum_\alpha \int w_\alpha(s_\alpha) r_\alpha'^2 ds_\alpha + \sum_{\alpha > \beta} \iint V(\mathbf{r}_\alpha(s_\alpha) - \mathbf{r}_\beta(s_\beta)) ds_\alpha ds_\beta. \end{aligned} \quad (2.1)$$

Only the first invariant will be considered, and it will be assumed that the presence of the cross links will indeed make it an invariant, ie loose ends are ignored. This lagrangian causes difficulty when the effect of the forces from V are considered. These have two effects: they make the material virtually incompressible, and they give rise to a molecular viscosity in the sense that if any point $r_\alpha(s_\alpha, t)$ moves, it suffers a viscosity by brushing against other molecules. The incompressibility can always be put in later, but to handle the viscosity it is preferable to replace V by a rayleighian term in the velocities v which will put in this viscosity as an empirical term. The equations of motion with a rayleighian M become

$$\frac{\delta \int L dt}{\delta r} + \frac{\delta \int M dt}{\delta v} = 0 \quad (2.2)$$

and M appropriate to the present problem will be

$$\frac{1}{2} v(\mathbf{v}(s, t) - \bar{\mathbf{v}}(s, t))^2 + \mathbf{F} \cdot \mathbf{v} \quad (2.3)$$

where $\bar{\mathbf{v}}$ is the average velocity of all the polymer in the position $\mathbf{r}(s, t)$ and \mathbf{F} is the random force which goes with it from the surroundings. This average will appear as a main

concern of this paper so should be introduced in more detail. Let $r_0(s)$ be $r(s, t)$ taken at some origin in time $t = 0$. Then at any time we can consider

$$r(s, t) = r_0(s) + \bar{r}(s, t) + u(r_0(s), t). \tag{2.4}$$

Here u is the average displacement in the neighbourhood of $r(s, t)$. Strictly speaking one should here involve some neighbourhood function and write

$$u(x, t) = \int K(x - r_{x0}(s)) (r_x(s, t) - r_{x0}(s)) ds, \tag{2.5}$$

where K is chosen so that enough molecules are included in it for u to be considered as a macroscopic displacement whilst the range of K is small compared to any elastic wavelength to be considered. In practice however since we do not consider any molecular thickness in $r(s, t)$, one may treat K as a δ function and define

$$\rho(x)u(x, t) = \int (r_x(s, t) - r_{x0}(s)) \delta(x - r_{x0}(s)) \left(\frac{ds}{l} \right) \tag{2.6}$$

where ρ is the mean (number or length) density :

$$\rho = \int \frac{ds}{l} \delta(x - r_0(s)). \tag{2.7}$$

It will be seen that u is taken labelled by the initial positions, whereas it could be more convenient in large deformation theory to take u relative to present positions, ie

$$\rho u(x, t) = \int (r_x(s, t) - r_{x0}(s)) \delta(x - r_x(s, t)) \left(\frac{ds}{l} \right), \tag{2.8}$$

but since nonlinear effects are not studied here, definition (2.6) is adopted. Thus \bar{v} is \dot{u} , but it will be left as \bar{v} since in the rayleighian form velocities in frictional terms are written as such. Another simplification is in the consideration of inextensibility. It is well known that, as far as the statistical distribution of distant points on a gaussian chain are concerned, the distribution is accurately given by the Wiener form

$$P([r_0(s)]) = .A \cdot \exp\left(-\frac{3}{2l} \int r_0'^2(s) ds\right) \tag{2.9}$$

or, using the Fourier form, taking the chains to be long

$$r_0(\omega) = \frac{1}{2\pi} \int_{-\infty}^{\infty} e^{i\omega s} r_0(s) ds \tag{2.10}$$

$$r_0(s) = \int_{-\infty}^{\infty} e^{-i\omega s} r_0(\omega) d\omega \tag{2.11}$$

$$\int r_0'^2(s) ds = 2\pi \int_{-\infty}^{\infty} \omega^2 |r_0(\omega)|^2 d\omega \tag{2.12}$$

$$P([r_0(\omega)]) = .A \cdot \exp\left(-\frac{3\pi}{l} \int \omega^2 |r_0(\omega)|^2 d\omega\right). \tag{2.13}$$

This distribution implies an entropy

$$S = -\frac{3\pi\kappa}{l} \int \omega^2 |r_0(\omega)|^2 d\omega \quad (2.14)$$

and a free energy

$$A = \frac{3\pi}{l} \kappa T \int \omega^2 |r_0(\omega)|^2 d\omega. \quad (2.15)$$

Thus the term $\int w_x(s)r_x'^2(s) ds$ in the lagrangian can, in this simple picture, be identified with A , with $w = 3\kappa T/2l$, a constant. In fact one can work directly from the lagrangian (2.1) (as is done, for example, by Edwards and Goodyear 1972), and determine $w(s)$ by the condition that $r'^2(s) = 1$. The mean value of w will indeed be $3\kappa T/2l$, but it will have fluctuations, which will give rise to friction and transport terms which are outside the scope of the thermodynamic variables. This analysis will not be repeated here but the results used. A brief account will appear in § 4 since it is a good analogy for the entanglement problem. Just as the forces V give rise to friction terms which can be incorporated in the rayleighian, the fluctuations in constraint multiplier $w(s)$ give rise to a friction term which physically leads to the transfer of energy from one point to another along the chain. This friction can only involve the motion of one part of the chain relative to another, so will have the form $\alpha(\omega)v(\omega)$, where $\alpha(0) = 0$, so that in the first approximation $\alpha = \zeta\omega^2$. This friction must have with it a random force in the usual way, so the lagrangian and rayleighian terms for the chain alone will be

$$\frac{3\pi\kappa T}{l} \int \omega^2 |r(\omega, t)|^2 d\omega + \frac{1}{2}\zeta \int \omega^2 |v(\omega)|^2 d\omega + \int f \cdot v_x d\omega. \quad (2.16)$$

There will be an interaction between the constraint of inextensibility and that of cross linkage, but this is ignored in the present treatment.

The modified rayleighian form is now

$$\begin{aligned} & \sum_x \frac{1}{2} \int m \dot{r}_x^2 ds_x - \sum_x \frac{3\kappa T}{2l} \int r_x'^2 ds + \sum_{\alpha\beta} P_{\alpha\beta} \cdot (r_\alpha(s_\alpha^i, t) - r_\beta(s_\beta^j, t)) + \sum_{\alpha\beta} Q_{\alpha\beta} (I_{\alpha\beta} - I_{\alpha\beta}^{(0)}) \\ & + \frac{1}{2} v \sum_x \int [v_\alpha(s_x, t) - \bar{v}(r_{\alpha 0}(s, t))]^2 ds - \frac{1}{2} \zeta \int |v(\omega)|^2 \omega^2 d\omega \\ & + \sum_x \int f_x \cdot v_x + \sum_x \int F_x \cdot v_x. \end{aligned} \quad (2.17)$$

It is perhaps worth commenting that the principle of using Lagrange multipliers works perfectly well for rayleighian functions provided that the constraint is written either in terms of coordinates, or in terms of velocities, but is not mixed.

The equations of motion are therefore

$$m\ddot{r}_\alpha - \frac{3\kappa T}{l} r_\alpha'' + v(v_\alpha - \bar{v}) - \zeta v_\alpha'' = \sum_\beta P_{\alpha\beta} \delta(s_\alpha^i - s) + \sum_\beta Q_{\alpha\beta} \nabla_\alpha I_{\alpha\beta} + f_\alpha \quad (2.18)$$

or

$$m\ddot{r}_\alpha + v(\dot{r}_\alpha - \bar{v}) + \rho \dot{r}_\alpha'' - \frac{3\kappa T}{l} r_\alpha'' = \sum_\beta P_{\alpha\beta} \delta(s_\alpha^i - s) + \sum_\beta Q_{\alpha\beta} \nabla_\alpha I_{\alpha\beta} + f_\alpha. \quad (2.19)$$

The force f introduced above for the representation of single chain dynamics will now be taken quite generally as the random forces acting at $r(s, t)$ due both to the motion of the rest of the chain, and to the other chains and this incorporates F .

3. Solution of the equations of motion

The equation of motion (2.19) cannot be solved exactly because it represents a virtually infinite coupled system of equations. What will be done is to argue what form, on physical grounds, the final form should take, then see how the exact form produces this form. The picture offered is that of a long chain held, in an approximately constant position relative to its surroundings, by cross links and entanglements. The initial position $\mathbf{r}_0(s)$ will serve as a label for the whole configuration, so one can expect that, if \mathbf{r} is written

$$\mathbf{r}_\alpha = \mathbf{r}_{\alpha 0} + \bar{\mathbf{r}}_\alpha + \mathbf{u} \quad (3.1)$$

that $\bar{\mathbf{r}}_\alpha$ will represent a deviation from the average position taken by the chain which was at $\mathbf{r}_{\alpha 0}$ and has suffered the elastic deformation \mathbf{u} . Thus when a long elastic wave moves through the system, one expects \mathbf{u} , the mean displacement, to change slowly, but be possibly large, whereas $\bar{\mathbf{r}}$ will change quickly, but be of small amplitude. The effect of the cross links and entanglements will be expected therefore to produce an effective term in the equation of motion restricting the value of $\bar{\mathbf{r}}$, eg proportional to $\bar{\mathbf{r}}$. Thus one can expect an effective equation like

$$m\ddot{\mathbf{r}}_\alpha - \epsilon[\mathbf{r}_\alpha'' - \omega_0^2(\mathbf{r}_\alpha - \mathbf{u} - \mathbf{r}_{\alpha 0})] + \nu(\dot{\mathbf{r}}_\alpha - \dot{\mathbf{u}}) - \zeta\dot{\mathbf{r}}_\alpha'' = \mathbf{f}_\alpha \quad (3.2)$$

or in Fourier transform

$$m\ddot{\mathbf{r}}_\alpha + \epsilon[\omega^2\mathbf{r}_\alpha + \omega_0^2(\mathbf{r}_\alpha - \mathbf{u} - \mathbf{r}_{\alpha 0})] + \nu(\dot{\mathbf{r}}_\alpha - \dot{\mathbf{u}}) + \zeta\omega^2\dot{\mathbf{r}}_\alpha = \mathbf{f}_\alpha \quad (3.3)$$

where ϵ has been written for $3\kappa T/l$. The procedure now will be to assume that the effect of the links and entanglements is to produce such an equation, and to look at just one link (later one entanglement), work out its effect which will indeed look like the form chosen, and hence deduce an equation for ω_0 . Thus one needs to solve the problem of two chains, entrained to be close to the $\mathbf{r}_0 + \mathbf{u}$ positions, cross linked to one another. The equations of motion are then

$$D\mathbf{r}_1 = P_{12}\delta(s - s_1^{(2)}) + \phi_1 \quad (3.4)$$

$$D\mathbf{r}_2 = -P_{12}\delta(s - s_2^{(1)}) + \phi_2 \quad (3.5)$$

where

$$D = m\frac{\partial^2}{\partial t^2} + \nu\frac{\partial}{\partial t} - \zeta\frac{\partial}{\partial t}\frac{\partial^2}{\partial s^2} + \epsilon\left(-\frac{\partial^2}{\partial s^2} + \omega_0^2\right) \quad (3.6)$$

or in Fourier transform on s

$$D = m\frac{\partial^2}{\partial t^2} + \nu\frac{\partial}{\partial t} + \zeta\omega^2\frac{\partial}{\partial t} + \epsilon(\omega^2 + \omega_0^2) \quad (3.7)$$

or in Fourier transform on s and Laplace transform on t

$$D = mp^2 + \nu p + \zeta\omega^2 p + \epsilon(\omega^2 + \omega_0^2). \quad (3.8)$$

In this form, it will be possible for ω_0 to be a function of p and ω , and it will indeed involve p . Also ϕ contains the remainder

$$\phi = F + \epsilon\omega_0^2(\mathbf{r}_0 + \mathbf{u}) + \nu p\mathbf{u} + P_{12}(p)\exp(p s_1^{(2)}) + \sum_{ij} P_{ij}(p)\exp(p s_1^{(j)}). \quad (3.9)$$

Some of the symbols are in an abbreviated form, for example u in (3.2)–(3.9) is understood to mean

$$\int e^{i\omega s} \mathbf{u}(r_0(s), t) e^{pt} dt ds. \quad (3.10)$$

To avoid difficulties in counting the contribution of links, it is easiest to consider all the chains as one great chain cross linked to itself. It will always be assumed that there are a large number of links on any molecule, so this is only a matter of neglecting end effects, nevertheless it is easier. Equations (3.4) and (3.5) now become

$$D\mathbf{r} = P_{12}(\delta(s-s_1) - \delta(s-s_2)) + \tilde{\phi} \quad (3.11)$$

where

$$\tilde{\phi} = \phi - P_{12}(\delta(s-s_1) - \delta(s-s_2)), \quad (3.12)$$

which is solved using the Green function G :

$$[mp^2 + vp + \zeta\omega^2 p + \epsilon(\omega^2 + \omega_0^2)]G(\omega, p) = 1 \quad (3.13)$$

$$G(s-s', p) = \frac{1}{2\pi} \int G(\omega, p) e^{i\omega s} d\omega \quad (3.14)$$

$$= \frac{1}{\epsilon + \zeta p} \frac{\exp(-A(p)|s-s'|)}{A(p)} \quad (3.15)$$

where

$$A(p) = \left(\frac{mp^2 + vp + \epsilon\omega_0^2}{\epsilon + \zeta p} \right)^{1/2} \quad (3.16)$$

In terms of G

$$\mathbf{r}(s, p) = P_{12}(p)(G(s-s_1, p) - G(s-s_2, p)) + \mathbf{G}\Phi \quad (3.17)$$

where $\Phi = \tilde{\phi} + (r_0, v_0)$, (r_0, v_0) being the initial condition term usual in Laplace transform inversions. (It is left rather vague, for ω_0^2 is $\omega_0^2(p)$ but it will shortly disappear again, so is not dwelt upon.) Then $\mathbf{r}(s_1, p) = \mathbf{r}(s_2, p)$ gives

$$P = \frac{\int G(s_1-s', p)\Phi(s') - \int G(s_2-s', p)\Phi(s')}{2[G(s_1-s_2, p) - G(0, p)]}. \quad (3.18)$$

In fact the two points s_1 and s_2 will in general be remote from one another so that $G(s_1-s_2, p)$ is negligible, and the denominator is $2G(0, p)$ where

$$G(0, p) = \frac{1}{\epsilon + \zeta p} \frac{1}{A(p)}. \quad (3.19)$$

One now has

$$D\mathbf{r} = \frac{(\delta(s-s_1) - \delta(s-s_2)) \int [G(s_1-s', p) - G(s_2-s', p)]\Phi(s') ds'}{-2G(0, p)}. \quad (3.20)$$

This will be the case for each cross link, so can be regarded as a term in the expansion of

$$\left(mp^2 + vp + \eta\omega^2 p + \epsilon\omega^2 + \sum_i \frac{\delta(s-s_i)}{G(0, p)} \right) \mathbf{r} = \mathbf{F} + (\epsilon\omega_0^2 + vp)\mathbf{u} \quad (3.21)$$

that is,

$$\epsilon\omega_0^2 = \text{average} \sum_i \frac{\delta(s-s_i)}{G(0,p)} \quad (3.22)$$

which, since there are n_c cross links in a length L , and using (3.19)

$$\epsilon\omega_0^2 = \frac{n_c}{L} A(\epsilon + \zeta p). \quad (3.23)$$

At $p = 0$ one has

$$\omega_0^2 = \frac{\eta_c}{L} \omega_0 \quad (3.24)$$

$$\omega_0 = \frac{n_c}{L}, \quad (3.25)$$

a result obtained earlier. However, it is worth noting that (3.23) implies that under dynamic conditions there are substantial changes in the equation of motion. For small p one gets, keeping only the terms in νp and mp^2

$$\omega_0 = \frac{n_c}{L} \left(1 + \frac{\nu p}{2\epsilon\omega_0^2} + \frac{mp^2}{2\epsilon\omega_0^2} + \frac{\zeta p}{2\epsilon} \right), \quad (3.26)$$

so the effective viscosity and mass is substantially changed. However, our primary concern now is to go on to the elastic equations where these violent changes do not appear.

It will be seen that equation (3.21) in itself does not describe a static equilibrium situation unless there are special properties given to \mathbf{F} , ie putting $\mathbf{u} = 0$ and $\mathbf{F} = 0$ does not lead to $\mathbf{r} \equiv 0$. Physically this corresponds to the fact that if a series of chains are cross linked, they will exert a reduced pressure on any container, and ultimately contract in syneresis. In this paper we are only concerned with fluctuations about, and small deviations from, equilibrium. What will happen upon cross linking is that the system will adjust itself so that a net non-vanishing force will arise which cancels the static (negative) pressure resulting from the cross links. We must therefore alter F to $\tilde{\mathbf{F}} + \bar{\mathbf{F}}$ where $\bar{\mathbf{F}}$ is chosen to cancel any force which appears in equilibrium on the left-hand side. This means that whereas adopting (3.21) directly we would get

$$m(\ddot{\mathbf{r}} + \ddot{\mathbf{u}}) + \nu(\dot{\tilde{\mathbf{r}}} - \dot{\mathbf{u}}) + \epsilon(\tilde{\mathbf{r}}'' + \mathbf{u}'' + \mathbf{r}_0'') + \zeta\dot{\tilde{\mathbf{r}}}' + \epsilon\omega_0^2(\tilde{\mathbf{r}} - \mathbf{u}) + \epsilon\omega_0^2 \sum_{ij} (\mathbf{r}_0(s_i) - \mathbf{r}_0(s_j)) = \tilde{\mathbf{F}} + \bar{\mathbf{F}} \quad (3.27)$$

F will take on a value which removes the terms in \mathbf{r}_0'' on the left, so that finally we have

$$m\ddot{\tilde{\mathbf{r}}} + m\ddot{\mathbf{u}} + \nu(\dot{\tilde{\mathbf{r}}} - \dot{\mathbf{u}}) - \epsilon\tilde{\mathbf{r}}'' + \zeta\dot{\tilde{\mathbf{r}}}' + \epsilon\omega_0^2(\tilde{\mathbf{r}} - \mathbf{u}) = \tilde{\mathbf{F}}. \quad (3.28)$$

Adopting (3.28) one can now solve for r

$$\begin{aligned} \mathbf{r} = & \int G(s, s'; t, t') [\epsilon\omega_0^2 \mathbf{u}_k(t') \exp(\mathbf{ik} \cdot \mathbf{r}_0(s')) + \nu \dot{\mathbf{u}}_k \exp(\mathbf{ik} \cdot \mathbf{r}_0(s'))] dt' ds' \\ & + (\mathbf{r}_0, \mathbf{v}_0) + \int GF ds' dt' \end{aligned} \quad (3.29)$$

so that

$$\mathbf{u}_{\mathbf{k}}(t) = \frac{V}{NL} \int \mathbf{f}(s, t) \exp(i\mathbf{k} \cdot \mathbf{r}_0(s)) ds \quad (3.30)$$

satisfies

$$\begin{aligned} \mathbf{u}_{\mathbf{k}}(t) = & \frac{V}{NL} \int \sum_j e^{i\mathbf{k} \cdot \mathbf{r}_0(s)} G(ss', tt') [\epsilon \omega_0^2 \mathbf{u}_j(t') \exp(i\mathbf{j} \cdot \mathbf{r}_0(s')) + v \dot{\mathbf{u}}_j(t') \exp(i\mathbf{j} \cdot \mathbf{r}_0(s'))] ds ds' dt \\ & + \int \exp(i\mathbf{k} \cdot \mathbf{r}_0) (\mathbf{r}_0, \mathbf{v}_0) + \int \exp(i\mathbf{j} \cdot \mathbf{r}_0(s)) \mathbf{F}(s, t) ds. \end{aligned} \quad (3.31)$$

At this point the configurational average over $\mathbf{r}_0(s)$ may be taken

$$\langle \exp(i\mathbf{k} \cdot \mathbf{r}_0(s) + i\mathbf{j} \cdot \mathbf{r}_0(s')) \rangle = \delta_{\mathbf{k}, \mathbf{j}} \exp(-\frac{1}{6}k^2|s-s'|) \quad (3.32)$$

so that

$$\mathbf{u}_{\mathbf{k}}(p) = \int \left\langle \frac{V}{NL} \exp(i\mathbf{k} \cdot \mathbf{r}_0(s) + i\mathbf{j} \cdot \mathbf{r}_0(s')) G(ss', p) (\epsilon \omega_0^2 + vp) \mathbf{u}_j(p) \right\rangle ds ds' + \mathbf{f} \quad (3.33)$$

$$= \frac{1}{NL} \int ds \exp(-\frac{1}{6}k^2|s-s'| - A|s-s'|) \frac{\epsilon \omega_0^2 + vp}{\epsilon + \zeta p} \frac{\mathbf{u}_{\mathbf{k}}}{A} + \mathbf{f}. \quad (3.34)$$

So finally if

$$\mathbf{f}_{\mathbf{k}} = \int \exp(i\mathbf{j} \cdot \mathbf{r}_0(s)) \mathbf{F}(s, t) ds \quad (3.35)$$

and

$$\int (\mathbf{r}_0, \mathbf{v}_0) \exp(i\mathbf{k} \cdot \mathbf{r}_0(s)) ds = (\mathbf{U}_0, \dot{\mathbf{U}}_0) \quad (3.36)$$

$$[(\epsilon + \zeta p)A(A + \frac{1}{6}k^2l) - \epsilon \omega_0^2 - vp] \mathbf{u}_{\mathbf{k}}(p) = \mathbf{f}_{\mathbf{k}}(p). \quad (3.37)$$

It will be appreciated that in studying the elastic fluctuations or elastic waves, one always deals with small values of k and p relative to molecular distances and times, so the roots can be expanded to give

$$(\epsilon + \zeta p) \left(\omega_0^2 + \frac{mp^2 + vp}{\epsilon + \zeta p} + \frac{1}{6}k^2l\omega_0 + \frac{k^2}{\omega_0} \left(\frac{mp^2 + vp}{\epsilon + \zeta p} \right) - \epsilon \omega_0^2 - vp \right) \mathbf{u}_{\mathbf{k}} = \mathbf{f}_{\mathbf{k}} \quad (3.38)$$

$$\left(\epsilon \omega_0^2 + \zeta p \omega_0^2 + mp^2 + vp + \epsilon k^2 l \omega_0 + \zeta k^2 l p \omega_0 + \frac{k^2 m p^2}{\omega_0} - \epsilon \omega_0^2 - vp - \zeta p \omega_0^2 \right) \mathbf{u}_{\mathbf{k}} = \mathbf{f}_{\mathbf{k}} \quad (3.39)$$

$$\left(mp^2 + \frac{1}{6}\epsilon \omega_0 l k^2 + \frac{1}{6}\epsilon \omega_0 l k^2 p \zeta + \frac{v l k^2 p}{12} + \frac{m l k^2 p^2}{12 \omega_0} \right) \mathbf{u}_{\mathbf{k}} = \mathbf{f}_{\mathbf{k}} \quad (3.40)$$

or, introducing densities,

$$\rho = \frac{NLm}{V}, \quad \mu = \frac{\zeta \omega_0 \epsilon l}{6m} + \frac{vl}{12m\omega_0}, \quad \zeta = \frac{l}{12\omega_0} \quad (3.41)$$

$$c_0^2 = \frac{\epsilon \omega_0 l}{6m}, \quad \Delta = \frac{k^2 p^2 l}{12\omega_0}$$

$$(p^2 + c_0^2 k^2 + \mu k^2 p + \Delta) \mathbf{u}_{\mathbf{k}} = \mathbf{f}_{\mathbf{k}} \quad (3.42)$$

that is,

$$\left(\frac{\partial^2}{\partial t^2} - c_0^2 \nabla^2 + \mu \frac{\partial}{\partial t} \nabla^2 - \xi \frac{\partial^2}{\partial t^2} \nabla^2 \right) \mathbf{u}(r, t) = \mathbf{f}(r, t) \quad (3.43)$$

is the elastic equation of motion. This derivation has, however, ignored effects coming from the normal intermolecular forces. Apart from the cross linkages and the inextensibility of the molecules (and the entanglements which will be considered shortly) the state of matter is that of a liquid. Thus there will be additional terms in the equation of motion which will invoke the compressibility as against shear, ie to order u , terms like $\theta \nabla(\nabla \cdot \mathbf{u})$. The full equation of motion is then

$$\left(\frac{\partial^2}{\partial t^2} - c_0^2 \nabla^2 + \mu \frac{\partial}{\partial t} \nabla^2 - \xi \frac{\partial^2}{\partial t^2} \nabla^2 \right) \mathbf{u} - \theta \nabla(\nabla \cdot \mathbf{u}) = \mathbf{f}. \quad (3.44)$$

Thus the shear fluctuations have

$$\left(\frac{\partial^2}{\partial t^2} - c_0^2 \nabla^2 + \mu \frac{\partial}{\partial t} \nabla^2 - \xi \frac{\partial^2}{\partial t^2} \nabla^2 \right) (\nabla \times \mathbf{u}) = \mathbf{f}_s \quad (3.45)$$

and the compressional fluctuations

$$\left(\frac{\partial^2}{\partial t^2} - (c_0^2 + \theta) \nabla^2 + \mu \frac{\partial}{\partial t} \nabla^2 - \xi \frac{\partial^2}{\partial t^2} \nabla^2 \right) (\nabla \cdot \mathbf{u}) = \mathbf{f}_c. \quad (3.46)$$

Our results therefore only throw light on shear waves. The argument has so far considered fluctuations about equilibrium, but clearly for slowly varying forces, an external \mathbf{f}_s will likewise generate curl \mathbf{u} by the same equation.

The theory must now be generalized to include the entanglements of the molecules.

4. Entanglements

Since the simplest gels have no permanent cross links, one must develop the theory of entanglements of the chains. We will not be concerned with creep in the present work, so consider the chains effectively infinite in length. The fact that they cannot pass through one another is somewhat like a cross link in effect, although the kind of highly knotted topology between a pair of chains, which is obviously like a cross link, will be rather infrequent. It is the simple property that chains sweep out a constant angle around one another which provides the principal source of entropy for the system. It is important to realize that the average effect of entanglements is weaker than one might suppose at first sight, because for example in figure 1 whereas chains a, c exert a pressure in one sense on chain e, chains b, d exert a pressure in the opposite sense.

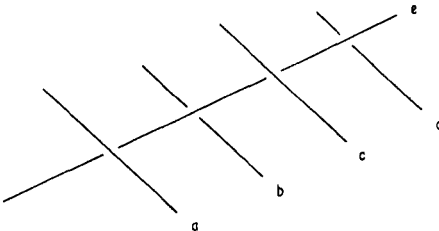


Figure 1.

The net effect is due to fluctuations, and it will be found that it contributes to elastic constants like $\rho^{1/2}$ rather than ρ which might have been guessed by counting contacts. This offers a justification for treating the effects as weak and using the much simpler mathematical techniques which are then permissible. Although some exact results are available for pairs of chains (Edwards 1967, 1968) the mathematics seems too difficult to apply statistically, and is anyway unnecessary.

To see the method, a brief account will be given of the treatment of the inextensibility of the chain, and then the entanglement theory developed by analogy. The probability distribution for a chain $r(s)$ is

$$\mathcal{N} \exp\left(-\frac{3}{2l} \int r'^2(s) ds\right), \quad (4.1)$$

where \mathcal{N} is an uninteresting normalization, from which the free energy will be

$$A = -\frac{3\kappa T}{2l} \int r'^2(s) ds \quad (4.2)$$

and the force exerted $(3\kappa T/l)r''(s)$. Now one should be able to derive this without invoking thermodynamics, directly from the equations of motion. Following Edwards and Goodyear (1972), the rayleighian is then

$$\int ds \left(\frac{1}{2m} \dot{r}^2 + \frac{v}{2} v^2 + \frac{\eta}{2} r'^2 + \Phi \right) \quad (4.3)$$

where η is the Lagrange multiplier, and the equation of motion

$$-m\ddot{r} + v\dot{r} + (\eta r')' = F. \quad (4.4)$$

Now

$$\begin{aligned} r'^2 = 1, \quad \text{so that} \quad r' \cdot r'' = 0 \quad \dot{r}' \cdot r' = 0 \\ r''^2 + r' \cdot r''' = 0 \\ \dot{r}'^2 + \dot{r}' \cdot r'' = 0. \end{aligned} \quad (4.5)$$

Thus

$$-m\ddot{r}' + v\dot{r}' + \eta r''' + 2\eta'' r' + \eta' r'' = F' \quad (4.6)$$

which when multiplied by r' gives, using the relations above,

$$m\dot{r}'^2 + \eta'' - r''^2 \eta = F' \cdot r'. \quad (4.7)$$

This can be solved for η using the two free end boundary conditions, but only the mean value is of interest to us, so that a first approximation is got by directly averaging (4.7), giving

$$\eta \simeq \frac{m \langle \dot{r}'^2 \rangle}{\langle r''^2 \rangle}. \quad (4.8)$$

At this point one can see that both numerator and denominator are badly behaved if evaluated using the continuous probability distribution for $r(s)$, and the Maxwell distribution for $v(s)$, but will be well behaved if one returns to rods of length l . This is to be expected for although the Wiener distribution is written in a local form, its validity is restricted to large distances compared to l , and the rough and ready rule is that it can

be used provided nothing goes wrong; if something goes wrong one reverts to the full local detail. Clearly upon averaging

$$\eta = \text{constant } \kappa T \quad (4.9)$$

and the constant will come out to $3/2l$ when the calculation is done accurately.

Entanglements can be treated similarly. The condition that two chains α, β sweep out a constant angle around one another is expressed by $I_{\alpha\beta} = \text{constant}$, ie

$$I_{\alpha\beta}(\mathbf{r}_\alpha, \mathbf{r}_\beta) = I(\mathbf{r}_{0\alpha}, \mathbf{r}_{0\beta}) \quad (4.10)$$

where

$$I = \iint \frac{(\mathbf{dr}_\alpha \times \mathbf{dr}_\beta) \cdot (\mathbf{r}_\alpha - \mathbf{r}_\beta)}{|\mathbf{r}_\alpha - \mathbf{r}_\beta|^3} \quad (4.11)$$

or

$$\iint (\mathbf{r}'_\alpha \times \mathbf{r}'_\beta) \cdot \nabla \frac{1}{r_{\alpha\beta}} ds_\alpha ds_\beta. \quad (4.12)$$

As with cross links, consider two chains to start with, assuming the totality will appear as an ω_0^2 term as before. Then chain α will have an equation of motion

$$m\ddot{\mathbf{r}}_\alpha + \nu\dot{\mathbf{r}}_\alpha + Q_{\alpha\beta} \frac{\delta I_{\alpha\beta}}{\delta \mathbf{r}_\alpha(s, t)} = \mathbf{F}_\alpha \quad (4.13)$$

and chain β :

$$m\ddot{\mathbf{r}}_\beta + \nu\dot{\mathbf{r}}_\beta + Q_{\alpha\beta} \frac{\delta I_{\alpha\beta}}{\delta \mathbf{r}_\beta(s, t)} = \mathbf{F}_\beta, \quad (4.14)$$

where $Q_{\alpha\beta}$ is the Lagrange multiplier. The analogues of (4.5) are $\dot{I} = 0$, ie

$$\int \dot{\mathbf{r}}_\alpha(s) \cdot \frac{\delta I_{\alpha\beta}}{\delta \mathbf{r}_\alpha(s)} ds + \int \dot{\mathbf{r}}_\beta \cdot \frac{\delta I_{\alpha\beta}}{\delta \mathbf{r}_\beta} ds = 0 \quad (4.15)$$

$\dot{I} = 0$, ie

$$\begin{aligned} \int \dot{\mathbf{r}}_\alpha(s) \cdot \frac{\delta I_{\alpha\beta}}{\delta \mathbf{r}_\alpha} ds + \int \dot{\mathbf{r}}_\beta \cdot \frac{\delta I_{\alpha\beta}}{\delta \mathbf{r}_\beta} + \int \dot{\mathbf{r}}_\alpha(s_1) \dot{\mathbf{r}}_\alpha(s_2) \frac{\delta^2 I}{\delta \mathbf{r}_\alpha \delta \mathbf{r}_\beta} ds_1 ds_2 \\ + 2 \int \dot{\mathbf{r}}_\alpha \dot{\mathbf{r}}_\beta \frac{\delta^2 I}{\delta \mathbf{r}_\alpha \delta \mathbf{r}_\beta} ds_1 ds_2 + \int \dot{\mathbf{r}}_\beta \dot{\mathbf{r}}_\beta \frac{\delta^2 I}{\delta \mathbf{r}_\beta \delta \mathbf{r}_\beta} ds_1 ds_2 = 0. \end{aligned} \quad (4.16)$$

If the equations of motion are multiplied by $\delta I / \delta r$ and integrated, the friction terms vanish from (4.13) and (4.14), when the equations are added and

$$\int \ddot{\mathbf{r}}_\alpha \frac{\delta I}{\delta \mathbf{r}_\alpha} + \int \ddot{\mathbf{r}}_\beta \frac{\delta I}{\delta \mathbf{r}_\beta} + \int Q_{\alpha\beta} \frac{\delta I}{\delta \mathbf{r}_\alpha} \cdot \frac{\delta I}{\delta \mathbf{r}_\alpha} + \int Q_{\alpha\beta} \frac{\delta I}{\delta \mathbf{r}_\beta} \cdot \frac{\delta I}{\delta \mathbf{r}_\beta} = \int \mathbf{F}_\alpha \cdot \frac{\delta I}{\delta \mathbf{r}_\alpha} + \int \mathbf{F}_\beta \cdot \frac{\delta I}{\delta \mathbf{r}_\beta}. \quad (4.17)$$

As before one may replace $r\ddot{r}$ by $\dot{r}\dot{r}$ and take the average, replacing Q by a constant value

$$Q_{\alpha\beta} = \sum_{a,b=\alpha,\beta} \iint \dot{\mathbf{r}}_a \dot{\mathbf{r}}_b \frac{\delta^2 I}{\delta \mathbf{r}_a \delta \mathbf{r}_b} ds_a ds_b \left(\sum_{a,b=\alpha,\beta} \int \frac{\delta I}{\delta \mathbf{r}_a} \cdot \frac{\delta I}{\delta \mathbf{r}_a} ds_a \right)^{-1}. \quad (4.18)$$

Now returning to the equation of motion, one can argue that in a full entangled system $\mathbf{r} = \tilde{\mathbf{r}} + \mathbf{r}_0 + \mathbf{u}(\mathbf{r}_0)$ will have $\tilde{\mathbf{r}}$ rather small, so that one can expand

$$\frac{\delta I}{\delta \mathbf{r}} = \left. \frac{\delta I}{\delta \mathbf{r}} \right|_{\tilde{\mathbf{r}}=0} + \int \tilde{\mathbf{r}}(s_1) \frac{\delta^2 I}{\delta \mathbf{r}(s) \delta \mathbf{r}(s_1)} ds_1. \quad (4.19)$$

The equation of motion now becomes

$$m\ddot{\tilde{\mathbf{r}}}_x + v\dot{\tilde{\mathbf{r}}}_x + \left[\left(\int \int \dot{\mathbf{r}} \frac{\delta^2 I}{\delta \mathbf{r} \delta \mathbf{r}} ds ds_1 \times \int \frac{\delta^2 I}{\delta \mathbf{r} \delta \mathbf{r}} \left(\frac{\delta I}{\delta \mathbf{r}} \cdot \frac{\delta I}{\delta \mathbf{r}} + \int \frac{\delta I}{\delta \mathbf{r}} \cdot \frac{\delta I}{\delta \mathbf{r}} \right)^{-1} \right] \tilde{\mathbf{r}}_x = F_x \quad (4.20)$$

and averages can replace the complicated entanglement integrals and the effects of the many chains can be included, to leave

$$m\ddot{\tilde{\mathbf{r}}}_x + v\dot{\tilde{\mathbf{r}}}_x + \omega_1^2 \tilde{\mathbf{r}}_x = F \quad (4.21)$$

where

$$\omega_1^2 = \left\langle \int \int \dot{\mathbf{r}} \frac{\delta^2 I}{\delta \mathbf{r} \delta \mathbf{r}} ds_1 ds_2 \int \frac{\delta^2 I}{\delta \mathbf{r} \delta \mathbf{r}} ds_3 ds_4 \right\rangle \left\langle \int \frac{\delta I}{\delta \mathbf{r}} \cdot \frac{\delta I}{\delta \mathbf{r}} ds_1 ds_2 + \int \frac{\delta I}{\delta \mathbf{r}} \cdot \frac{\delta I}{\delta \mathbf{r}} ds_1 ds_2 \right\rangle^{-1} \quad (4.22)$$

This expression has the dimension of a velocity squared, and contains terms from each chain averaged over the volume of the system. It must follow then that

$$\omega_1^2 = \rho \kappa T C \quad (4.23)$$

where ρ is the density of chains and C a constant. Now I in the average is taken independent of $\tilde{\mathbf{r}}$, ie we are working at small $\tilde{\mathbf{r}}$; moreover the transformation $\mathbf{r}_0 \rightarrow \mathbf{r}_0 + \mathbf{u}(\mathbf{r}_0)$ is a continuous, indeed differentiable, distortion of the body and as such will not alter I ; I is invariant under continuous deformations of the embedding three-dimensional space. Therefore \mathbf{u} can be simply omitted from the calculation and the averages taken about the initial configurations. As with the inextensibility condition, the integrals are badly behaved, but their value does not involve anything but the individual specification of the chains, ie just l for freely-hinged rods. Hence the assertion that

$$\omega_1^2 = \rho \kappa T C. \quad (4.24)$$

One can note that a direct thermodynamic argument can also be applied. The probability distribution function must contain

$$\prod_{\alpha\beta} \delta_{\mathbf{K}}(I_{\alpha\beta}(\mathbf{r}_\alpha, \mathbf{r}_\beta) - I_{\alpha\beta}(\mathbf{r}_{0\alpha}, \mathbf{r}_{0\beta})) \quad (4.25)$$

where $\delta_{\mathbf{K}}$ is the *Kronecker delta*, not the Dirac delta. This means that one can parametrize $\delta_{\mathbf{K}}$ by

$$\frac{1}{2\pi} \int_{-\pi}^{\pi} e^{i\lambda x} d\lambda = \delta_{\mathbf{K}}(x). \quad (4.26)$$

But I is rather like the hamiltonian in the statistical mechanics of a microcanonical ensemble. The constraint of the $\delta_{\mathbf{K}}$ is a gentle one and if we think of

$$\frac{1}{2\pi} \int_{-\pi}^{\pi} e^{i\lambda x} d\lambda \simeq \frac{1}{2\pi} \int_{-\pi}^{\pi} \left(1 + i\lambda x - \frac{\lambda^2 x^2}{2} + \dots \right) d\lambda \quad (4.27)$$

$$\simeq 1 - \frac{1}{6}\pi^2 x^2 + \dots \quad (4.28)$$

$$\simeq \exp(-\frac{1}{6}\pi^2 x^2). \quad (4.29)$$

The effect of $\Pi\delta_{\mathbf{k}}(I - I_0)$ is like

$$\exp\left(-\frac{1}{3}\pi^2 \sum_{\alpha\beta} (I_{\alpha\beta} - I_{\alpha\beta 0})^2\right) \simeq \exp\left(-\frac{\pi^2}{3} \iint \bar{\mathbf{r}}(s_1)\bar{\mathbf{r}}(s_2) \frac{\delta I}{\delta \mathbf{r}_1} \frac{\delta I}{\delta \mathbf{r}_2} ds_1 ds_2\right) \quad (4.30)$$

$$\simeq \exp\left(-\frac{\pi^2}{3} \iint \bar{\mathbf{r}}^2(s) \left\langle \frac{\delta I}{\delta \mathbf{r}(s)} \cdot \frac{\delta I}{\delta \mathbf{r}(s)} \right\rangle ds\right) \quad (4.31)$$

$$= \exp\left(-\frac{C}{2}\rho \int \bar{\mathbf{r}}^2(s) ds\right). \quad (4.32)$$

Just as before $\dot{\mathbf{r}}^2/\mathbf{r}''^2$ appeared from the dynamics to play the part of $3\kappa T/l$, one finds $\frac{1}{3}\pi^2 \langle (\delta I/\delta \mathbf{r})^2 \rangle$ being represented by the unpleasant integrals of (4.22). By either method however, the difficulties are buried in the constant C and one may now build in the work of this section into the earlier results. The effect is simply to add a term to the definition of ω_0 :

$$\omega_0^2 = \frac{n_c \omega_0}{L} + C\rho \quad (4.33)$$

a result previously derived by purely thermodynamic arguments (Edwards 1972). There are two obvious limits

$$\omega_0 = n_c/L \quad \text{for predominant cross linkages}$$

$$\omega_0 = (C\rho)^{1/2} \quad \text{for predominant entanglements.}$$

5. Conclusion

This paper has derived a statistical dynamics of networks, based on the concept of a region of freedom of movement of the chains of the network. It is possible to derive this region of freedom in terms of the density of cross links and the number density of the chains, which produce effective cross links due to entanglements. With this concept it is possible to derive the velocity of sound, frequency shift and damping, of shear waves. The paper has not given any account of the hydrodynamic interaction of a gel network with its surroundings, employing rather a simple viscosity coefficient, in the Rouse manner. Nor has it studied in detail the high frequency compliance which involves the local correlation functions as well as the long wave elastic fluctuations. It is hoped to return to both of these subjects in later papers.

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