Polymer network in solution—free energy of deformation

R. C. Ball and S. F. Edwards
Cavendish Laboratory, Madingley Road, Cambridge CB3 OHE, UK
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In a polymer network, the introduction of crosslinks affects both the configurational entropy of the chains and the short range repulsions between individual monomers. The 'replica method' calculation outlined gives the elastic properties – both bulk and shear – of a polymer network formed in solution, in terms of a free energy of deformation. Corrections due to excluded volume appear on the behaviour under shear, and a change in the osmotic terms due to crosslinking is also found.

INTRODUCTION

Rubber networks and polymer solutions have often been regarded as separate aspects of polymer science. Experimentally, solid, vulcanized rubber is quite a different proposition from a solution of, say, polystyrene in liquid benzene. However, just swelling the rubber with a solvent or chemically crosslinking a solution of polymer gives the same experimental system – a gel.

From a theoretical point of view, the ingredients of polymer solution theory – chain molecules with repulsion between monomers – have always been vital in understanding a rubber. Without any excluded volume effect, the experimental systems are unstable with respect to a collapse, syneresis, and this is just what classical calculations[1] give. However, the classical rubber studies generally neglect any interaction between crosslinkages and the repulsions which stabilize the system: they are calculated quite separately.

In this paper a calculation will be outlined which seeks to bridge the gap between rubber and solution, giving a network stable with respect to density fluctuations. Repulsions will be treated sufficiently well to give a sensible concentrated solution theory in the limit of no crosslinking, and at high polymer concentration and light crosslinking it is found that the classical theory of rubber elasticity emerges.

It is shown that the free energy per monomer for high density is:

$$f = k_B T \left\{ \frac{\omega}{2}\frac{\rho}{B} - \frac{2 \times (3)^{1/2}}{\pi} \omega^{3/2} \left(\frac{\rho}{B}\right)^{1/2} + \frac{3}{2}\frac{\gamma}{1+\gamma}\left[I + \frac{4}{\pi}\left(\frac{3\omega}{B\rho}\right)^{1/2} + \log\left| 1 + \frac{1}{8\pi^2}\left(\frac{3\omega}{B\rho}\right)^{1/2}(1 + I + J)\right| \right] + \text{Order } \nu^{3/2} \right\}$$

with the following quantities all expressed in units of the step length of the polymer: ρ = density of monomers, at network formation; ν = fraction of crosslinks per monomer; ω = monomer excluded volume; α = excluded volume cut-off length; γ = wasted loop correction

$$= \frac{1}{2}\left(\frac{6}{\pi}\right)^{3/2}\frac{1}{\rho\alpha} - \frac{6 \times (3)^{1/2}}{\pi}\left(\frac{\omega}{\rho}\right)^{1/2}$$

The functions of deformation are:

$$I = 1/3 \sum_i \lambda_i^2 - 1$$

the familiar first invariant;

$$B = \prod_i \lambda_i$$

the bulk deformation;

$$J = B[\epsilon^1{}_{-1} - 1]$$

where $\epsilon^1{}_{-1}$ is the spherical average of $|\underline{\underline{\Lambda}} \cdot n|^{-2}$, taking n over a unit sphere and $\underline{\underline{\Lambda}}$ being the strain tensor.

Model system

The starting point is a polymer solution in the régime of concentration $c > c^*$, where c^* is the critical concentration of polymer solution theory[2] above which the coils are forced to intermingle strongly and the long range chain statistics are Gaussian due to screening[3].

In this régime, monomeric repulsions dominate the osmotic pressure and perfect gas terms due to whole chains are not significant. In the present calculation, chain ends will be completely neglected, the material being represented by one very long molecule; entanglement effects will also be ignored. Viscosity experiments suggest that entanglements are not important until c is orders of magnitude greater than c^* (ref 4).

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The molecule will be represented by a continuous curve $\mathbf{r}(s)$ where the parameter s is (loosely) an arc length running from 0 to L. Its polymeric nature will be modelled by the statistical weight of Wiener measure,

$$\frac{3}{2l}\int_0^L \mathbf{r}'^2 \mathrm{d}s$$

this alone gives Gaussian statistics on all length scales, together with an interaction energy:

$$k_B TwE = \frac{1}{2} wk_B T \int_0^L \mathrm{d}s \int_0^L \mathrm{d}s' \lambda[\mathbf{r}(s) - \mathbf{r}(s')]$$

However where this form of interaction gives divergences – very short loops – the δ function will always be interpreted as the narrow normalized Gaussian:

$$\left(\frac{2\pi a^2}{3}\right)^{-3/2} \exp\left(\frac{-3\mathrm{r}^2}{2a^2}\right)$$

The delta function interaction simply models the first virial coefficient of the monomer–monomer interaction, with:

$$k_B T l^2 w = \int \mathrm{d}^3 r\, [\mathrm{e}^{-u(r)/k_B T} - 1]$$

Here $U(r)$ is the monomer–monomer interaction including the net result of polymer–solvent effects; the virial approximation is valid when the monomer concentration is low. The divergences with the δ function arise because the Wiener chain has the freedom to interact with itself and to respond on all length scales. Real polymers have short range rigidity so that interactions below a certain length scale are just constants and do not affect configurations. Taking the Wiener chain which is Gaussian on all length scales we must explicitly suppress the short range interactions and this is readily achieved by broadening the δ function to a narrow Gaussian. The parameter w varies as $T - \theta$ (θ = the Flory temperature), and gives the strength of the interaction[5].

A number N of permanent crosslinks will be introduced into the system, which will be confined within a fixed volume, initially V. As we are concerned with properties under shear we must also specify the shape of the enclosure: it will be taken initially to be a cube with edges defining Cartesian coordinate axes. The deformation considered will be an extension along these axes, the normal strains being $\lambda_1, \lambda_2, \lambda_3$.

The polymer configurations will be subject to periodic boundary conditions: on passing through the boundary the chain reappears at the opposite face[6]. We will of course be concerned with a thermodynamic limit where N, L and V all tend to infinity, keeping both the density of material, $\rho = l^2 L/V$ and the fraction of crosslinks $\nu = NL/l$ fixed.

The physics

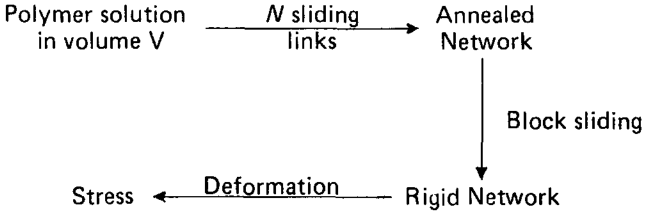
How will this model behave in qualitative terms?

We will not be concerned with the subtleties of the gellation phase transition: this calculation is concerned with securely gelled systems. However, it is worth noting that, because there are no chain ends, all non-zero concentrations of crosslinks will give such a gelled state.

The network then, will definitely be held together and so its tendency to swell – measured by the osmotic pressure π – will be reduced. Indeed it could even develop a negative osmotic pressure, which just means that the network will start to collapse inwards on itself in syneresis until π has increased back to zero: $\pi = 0$ gives the equilibrium size of the swelled network and at higher dilutions phase separation will occur.

Crosslinking will also confer rigidity upon the network. The free energy of the system will increase under shear deformation, and the network will exhibit shear stress. The statistics of the crosslink locations must be treated very carefully, for the only change in the network under shear is that those locations become less thermodynamically favourable.

We take here a specific model for the crosslink statistics, whereby with the network in an initial state the links are totally free to slide along the chain. This is an annealed system and can have no shear stress. Then at some time zero the sliding of all the links is frozen – this is a change only in the dynamics, not altering the entropy – and the network is subsequently deformed. The change in free energy under deformation and hence the osmotic pressure and shear stresses are then calculated.



Experimentally, the link sliding does not literally have to be frozen out: we only need to make the deformations on a faster timescale than the links can slide. Edible table jelly is an example of such a system – if left for long enough under stress it creeps by the links, effectively sliding.

CALCULATION

Formulation

We start from an exact formulation of the problem. Although the expressions are complex, by starting with exact formulations we can be sure to contain all corrections in any expansion. There is not space to explain fully the formalism and the reader is referred to the paper of Deam and Edwards[6]. For ease of reference some details are appended to the present work.

As is shown in Appendix A, the free energy of the deformed system is:

$$\tilde{F} = -k_B T \frac{\int \prod_{i=1}^{N} \mathrm{d}s_i \mathrm{d}s_i'\, Z(s_1, s_1' \ldots s_N s_N') \log \tilde{Z}(s_1, s_1' \ldots s_N, s_N')}{\int \prod_{i=1}^{N} \mathrm{d}s_i \mathrm{d}s_i'\, Z(s_1, s_1' \ldots s_N, s_N')}$$

on averaging over initial crosslink locations. Here $Z(s_1, s_1' \ldots s_N, s_N')$ is the partition function of the polymer solution with links joining the N pairs of points $s_1, s_1' ; s_2, s_2' ; \ldots s_N, s_N'$:

$$Z = \int \delta \mathbf{r}(s) e^{-3/2l \int \mathbf{r}'^2 - w/2 \int\int \mathrm{d}s' \delta(\mathbf{r}(s) - \mathbf{r}(s'))} \prod_{i=1}^{N} \delta(\mathbf{r}(s_i) - \mathbf{r}(s_i'))$$

Z is the same function but with the system in the strained state.

In the Appendix B it is shown that

$$F = \left[\frac{\partial}{\partial n} F_{\mathrm{rep}}(n)\right]_{n=0}$$

where

$$e^{-F_{\mathrm{rep}}/k_BT} = Z_{\mathrm{rep}} = \int \prod_{i=1}^{N} \frac{\mathrm{d}s_i \mathrm{d}s_i'}{2} Z(s,s') [\tilde{Z}(s,s')]^n$$

Z_{rep} is the partition function of a replicated system. in which there are $n + 1$ polymer solutions. For $n = 0, 1, 2 \ldots$ we can write Z_{rep} as:

$$Z_{\mathrm{rep}} = \prod_{i=1}^{N} \int \frac{\mathrm{d}s_i \mathrm{d}s_i'}{2} \prod_{\alpha=0}^{n}$$

$$\left[\int \delta \mathbf{r}\alpha(s) e^{-3/2l \int \mathbf{r}_\alpha'^2 \mathrm{d}s - w/2 \int\int \delta(\mathbf{r}_\alpha) \mathrm{d}s \mathrm{d}s'} \prod_{i=1}^{N} \delta(\mathbf{r}_\alpha(s_i) - \mathbf{r}_\alpha(s_1'))\right]$$

$$= \prod_{\alpha} \int \delta \mathbf{r}_\alpha(s) e^{-3/2l \int \mathbf{r}_\alpha'^2 \mathrm{d}s - w/2 \int\int \delta(\mathbf{r}_\alpha(s) - \mathbf{r}_\alpha(s')) \mathrm{d}s \mathrm{d}s'}$$

$$\left[\int\int \prod_{\alpha} \delta(\mathbf{r}_\alpha(s) - \mathbf{r}_\alpha(s')) \frac{\mathrm{d}s \mathrm{d}s'}{2}\right]^N$$

Replica $\alpha = 0$ is in the undeformed (formation) state and the rest, $\alpha = 1, 2, 3 \ldots$, are all in the strained state. All the replicas have the crosslinks joining the same locations on their chains, but subject to this constraint the replicated links are allowed to slide.

Appendix C shows how we can introduce a chemical potential for crosslinking, giving $Z_{\mathrm{rep}} = \min_{\mu} Z_r(\mu)$ where

$$Z_r(\mu) = \int \delta_{\mathbf{r}} e^{-W - wE + \mu X - N \log \mu}$$

Here we have introduced the following symbolic notations:

$$W = \sum_{\alpha=0}^{n} \frac{3}{2l} \int_0^L \mathbf{r}_\alpha'^2 \mathrm{d}s$$

$$E = \frac{1}{2} \int_0^L \mathrm{d}s \int_0^L \mathrm{d}s' \sum_{\alpha=0}^{n} \delta(\mathbf{r}_\alpha(s) - \mathbf{r}_\alpha(s'))$$

$$X = \frac{1}{2} \int_0^L \mathrm{d}s \int_0^L \mathrm{d}s' \prod_{\alpha=0}^{n} \delta(\mathbf{r}_\alpha(s) - \mathbf{r}_\alpha(s'))$$

Variational approximation

Note that for $n = 0$, when we have only one replica ($\alpha = 0$), E and X are identical. As we wish to expand about this point, it is helpful to rewrite $Z_r(\mu)$ as

$$Z_r(\mu) = \int e^{-W - (w - \mu)E + \mu(X - E) - N \log \mu}$$

Just as in ref 3 we introduce a harmonic potential – denoted Q – to model the localization:

$$Z_r(\mu) = \int e^{-W - (w - \mu)E - Q - N \log \mu + [Q + \mu(X - E)]}$$

$$\geqslant Z_r(\mu q) = \int e^{-W - (w - \mu)E - Q - N \log \mu + \langle Q + \mu(X - E)\rangle}$$

(see Appendix D). Here the average $\langle Q + \mu(X - E)\rangle$ is taken with the distribution

$$e^{-W - (w - \mu)E - Q}$$

We restrict our choice of Q to contain only one variational parameter q:

$$Q = \frac{lq^2}{6} \int_0^L \mathrm{d}s \sum_{\text{Cartesians } i} \frac{1}{(1 + n\lambda_i^2)}$$

$$\sum_{\alpha=1}^{n} \left[(\lambda_i \mathbf{r}_{i0} - \mathbf{r}_{i\alpha})^2 + \sum_{\beta=1}^{n} (\lambda_i \mathbf{r}_{i\alpha} - \lambda_i \mathbf{r}_{i\beta})^2\right]$$

Note that $Q + \mu(X - E)$ vanishes at $n = 0$, so that the variational principle is now exact there. As a result the inequality holds under one differentiation at $n = 0$, as required.

Introduction of density coordinates

We are still left with a formidable problem to evaluate:

$$Z_r(\mu, q) = \int e^{-W - (w - \mu)E - Q - N \log \mu + \langle Q + \mu(W - E)\rangle}$$

First a simplifying approximation will be made in evaluating $\langle X - E\rangle$: we ignore the excluded volume in computing this term.

The problem then remains to calculate

$$z(\mu,q) = \int e^{-W-(w-\mu)E-Q}$$

since $\langle Q\rangle$ can be derived from this function. If we introduce for each replica the density coordinates

$$\rho^{\alpha}(\mathbf{k}) = \int_0^L \mathrm{d}s\, e^{i\mathbf{k}\cdot\mathbf{r}_{\alpha}(s)}$$

then

$$E = \frac{1}{2}\iint \mathrm{d}s\mathrm{d}s' \sum_{\alpha} \delta(\mathbf{r}_{\alpha}(s')) - \mathbf{r}_{\alpha}(s'))$$

$$= \frac{1}{2}\frac{1}{8\pi^3}\int \mathrm{d}^3\mathbf{k}e^{-a^2k^2/6} \sum_{\alpha} \rho^{a}(-\mathbf{k})$$

The Gaussian cut-off $e^{-a^2k^2/6}$ exactly corresponds to replacing the delta function interaction by a narrow Gaussian. Now we can change variables in the integral for $z(\mu,q)$ to obtain:

$$z(\mu,q) = \int e^{-W-Q}\delta\mathbf{r}\int \mathrm{d}\rho^{\alpha}(\mathbf{k})J(\rho^{\alpha}(\mathbf{k}))e^{-(w-\mu)E[\rho^{\alpha}(\mathbf{k})]}$$

where the Jacobian $J(\rho^{\alpha}(\mathbf{k}))$ is the joint distribution of $\rho^{\alpha}(\mathbf{k})$,

$$J[\rho^{\alpha}(\mathbf{k})] = \frac{\int e^{-W-Q}\prod_{\alpha,\mathbf{k}}\delta(\rho^{\alpha}(\mathbf{k}) - \int \mathrm{d}s e^{i\,\mathbf{k}\cdot\mathbf{r}_{\alpha}(s)})\,\delta\mathbf{r}_{\alpha}(s)}{\int e^{-W-Q}\delta\mathbf{r}_{\alpha}(s)}$$

$J(\rho^{\alpha}(\mathbf{k}))$ is here replaced by a joint Gaussian distribution, completely determined by requiring that its zeroth, first and second moments be those of the exact distribution. This is a rather drastic approximation, which will be seen to be equivalent to Edwards' 1966 theory of polymer solutions[7].

This theory, although of validity only in the region of high density, solves that region in a straightforward way and provides the simplest example of the problem of solutions and networks.

Variational free energy

Tedious and lengthy calculation gives:

$$\log[z(\mu,q)] = -\frac{lqL}{2} - \mathscr{F}(w-\mu) - n\mathscr{F}(w-\mu)$$

$$- n\frac{V}{16\pi^2}q\left(\frac{3L}{l\tilde{v}}\right)^{1/2}[\epsilon_1^1 + B(\epsilon_{-1}^1 - 1)] \times$$

$$\left[1 + \text{Order}\left(\frac{ql\tilde{V}}{L(w-\mu)}\right)^{1/2}\right]$$

here $\underline{\underline{\Lambda}}$ is the strain tensor and:

$$\epsilon_{\alpha}^{\beta} = \langle[\mathbf{n}\cdot(\underline{\underline{\Lambda}}^{\mathrm{T}})^{\beta}\cdot(\underline{\underline{\Lambda}})^{\beta}\cdot\mathbf{n})^{\alpha}\rangle = \langle|\underline{\underline{\Lambda}}^{\beta}\cdot\mathbf{n}|^{2\alpha}\rangle$$

(angular average of **n** over a sphere)

so that

$$\epsilon_1^1 = \frac{1}{3}\sum_i \lambda_i^2;\ B = \lambda_1\lambda_2\lambda_3 = \det\underline{\underline{\Lambda}} = \epsilon_{-3}^{-1}$$

$\tilde{V}$ is the deformed volume, $\tilde{V} = V\cdot B$ $k_BT\,\mathscr{F}(w-\mu)$ is the polymer solution free energy as obtained by Edwards:

$$\mathscr{F}(w-\mu) = L\left[\frac{w-\mu}{2}\frac{L}{V} - \frac{2(3)^{1/2}}{\pi}\left(\frac{w-\mu}{l}\right)^{3/2}\right.$$

$$\left.\left(\frac{L}{V}\right)^{1/2} + \frac{1}{4}\left(\frac{6}{\pi}\right)^{3/2}\frac{w-\mu}{al}\right]$$

Neglecting excluded volume gives:

$$\mu\langle X-E\rangle = \mu\left[\frac{L^2}{V\prod_i(1+n\lambda_i^2)^{1/2}}\left(\frac{q}{2\pi}\right)^{3n/2}\right.$$

$$+\frac{L}{2la}\left(\frac{6}{\pi}\right)^{3/2}\left(1 - 3n + \frac{3n}{2}\log\left|\frac{3}{2\pi a^2}\right| +\right.$$

$$\left.\left.\text{Order } n(qa^2)^{1/2}\right)\right] - \frac{\mu}{2}\left[\frac{L^2}{V} + n\frac{L^2}{\tilde{V}} +\right.$$

$$\left.(n+1)\frac{L}{2al}\left(\frac{6}{\pi}\right)^{3/2}(1 + \text{Order } n(qa^2)^{1/2})\right]$$

$$= \frac{n\mu}{4}\left[\frac{L^2}{V}\left(3\log\left|\frac{q}{2\pi}\right| - \sum_i\lambda_i^2\right) - \frac{2L^2}{\tilde{V}}\right.$$

$$+\frac{L}{la}\left(\frac{6}{\pi}\right)^{3/2}\left(\frac{3}{2}\log\left|\frac{3}{2\pi a^2}\right| - 3 +\right.$$

$$\left.\left.\text{Order }(qa^2)^{1/2}\right)\right] + \text{Order } n^2$$

We obtain $\langle Q \rangle$ as

$$-q/2\frac{\delta}{\delta q}\log z = nlLq/4 - \frac{nVq}{32\pi^2}\left(\frac{3L}{l\tilde{V}}\right)^{1/2}[\epsilon_1^1 + B(\epsilon^1{}_1 - 1)]$$

Putting all this together then gives:

$$F_r(\mu,q) = -\log Z_r(\mu,q)$$

$$= L\left[-\frac{2(3)^{1/2}}{\pi}\left(\frac{w-\mu}{l}\right)^{3/2}\left(\frac{L}{V}\right)^{1/2} + \right.$$

$$\left.\frac{1}{4}\left(\frac{6}{\pi}\right)^{3/2}\left(\frac{w-\mu}{al}\right) + \frac{(w-\mu)L}{2V}\right] + N\log\mu$$

$$+ n\left[L\left\{-\frac{2(3)^{1/2}}{\pi}\left(\frac{w-\mu}{l}\right)^{3/2}\left(\frac{L}{\tilde{V}}\right)^{1/2} + \right.\right.$$

$$\left.\frac{1}{4}\left(\frac{6}{\pi}\right)^{3/2}\left(\frac{w-\mu}{al}\right) + \frac{(w-\mu)L}{2\tilde{V}}\right\}$$

$$+ q\left\{\frac{lL}{4} + \frac{V}{32\pi^2}\left(\frac{3L(w-\mu)}{l\tilde{V}}\right)^{1/2}[\epsilon_1^1 + B(\epsilon^1{}_1 - 1)]\right\}$$

$$+ \frac{\mu}{e}\left\{\frac{L^2}{2V}\left(-3\log\left|\frac{q}{2\pi}\right| + \sum_i \lambda_i^2\right) - \right.$$

$$\left.\left.\frac{L}{2la}\left(\frac{6}{\pi}\right)^{3/2}\left(\frac{3}{2}\log\left|\frac{3}{2\pi a^2}\right| - 3\right) + L^2/\tilde{V}\right\}\right] + \text{Order } n^2.$$

We must now determine both μ and q.

It is shown in Appendix E that $F_r(\mu,q)$ is correctly made stationary to first order in n by choosing μ so as to extremize the terms of order n^0. This gives:

$$\frac{1}{\mu_0} = \frac{L^2}{2NV}\left[1 + \frac{V}{Lal}\frac{1}{2}\left(\frac{6}{\pi}\right)^{3/2}\right.$$

$$\left.\frac{6(3)^{1/2}}{\pi}\left(\frac{w-\mu_0}{l}\right)^{1/2}\left(\frac{V}{L}\right)^{1/2}\right]$$

If we take the limit $\mu_0/w \ll 1$, then

$$\mu_0 = \frac{2NV}{L^2(1+\gamma)}$$

where

$$\gamma = \frac{V}{Lal}\frac{1}{2}\left(\frac{6}{\pi}\right)^{3/2} \quad \frac{6(3)^{1/2}}{\pi}\left(\frac{w}{l^3}\right)^{1/2}\left(\frac{V}{L}\right)^{1/2}$$

the wasted loop correction. Note that the excluded volume reduces wasted loops.

To minimize the free energy with respect to q, we first note that $F_r(\mu_0, q)$ = (terms independent of q) + $n(Dq - C\log q)$ where

$$C = \frac{\mu_0}{4}\frac{3L^2}{V}$$

$$D = \frac{lL}{4} + \frac{V}{32\pi^2}\left[\frac{3L(w-\mu_0)}{l\tilde{V}}\right]^{1/2}[\epsilon_1^1 + B(\epsilon^1{}_1 - 1)$$

Making this stationary gives

$$nC(1 - \log[C/D]) = n\frac{3}{4}\mu_0\frac{L^2}{V}$$

$$\left[1 + \log\left|\frac{\frac{lL}{4} + \frac{V}{32\pi^2}\left(\frac{3L(w-\mu_0)}{l\tilde{V}}\right)^{1/2}(\epsilon_1^1 + B(\epsilon^1{}_1 - 1))}{\frac{3}{4}\mu_0 L^2/V}\right|\right]$$

Finally, we can now write down the free energy of deformation.

$$\tilde{F}/k_BT = \frac{\partial}{\partial n}[F_{\text{rep}}/k_BT]_{n=0} \leqslant \frac{\partial}{\partial n}[\underset{\mu q}{\text{Min}}\, F_r(\mu,q)/k_BT]_{n=0}$$

$$= L\left[-\frac{2(3)^{1/2}}{\pi}\left(\frac{w-\mu_0}{l}\right)^{3/2}\left(\frac{L}{\tilde{V}}\right)^{1/2} + \frac{(w-\mu)L}{2\tilde{V}} + \frac{\mu L}{2\tilde{V}}\right]$$

$$+ \frac{\mu_0 L^2}{4V}\left[\sum_i \lambda_1^2 + 3\log\left|1 + \frac{V}{8\pi^2 lL}\left(\frac{3L(w-\mu_0)}{l\tilde{V}}\right)^{1/2}\right.\right.$$

$$\left.\left.\left[\epsilon_1^1 + B(\epsilon^1{}_1 - 1)\right]\right|\right]$$

+ (terms independent of deformation)
Then to first order in the number of crosslinks we have:

$$F/k_BT \leqslant L\left[-\frac{2(3)^{1/2}}{\pi}\left(\frac{w}{l}\right)^{3/2}\left(\frac{L}{\tilde{V}}\right)^{1/2} + \frac{wl}{2\tilde{V}}\right]$$

$$+ \frac{1}{2}\frac{N}{1+\gamma}\left\{\sum_i \lambda_i^2 + \frac{12}{\pi}\left(\frac{3wV}{Ll^3B}\right)^{1/2}\right.$$

$$\left. + 3\log\left|1 + \frac{1}{8\pi^2}\left(\frac{3wV}{Ll^3B}\right)^{1/2}[\epsilon_1^1 + B(\epsilon^1{}_1 - 1)]\right|\right\}$$

For clarity we convert the parameters into dimensionless intensive variables:

monomer volume fraction $\rho = L/l \cdot l^3/V = Ll^2/V$
crosslink number fraction $\nu = Nl/L$
free energy per monomer $\tilde{f} = \tilde{F}l/l$
reduced excluded volume $\omega = w/l$

Then the free energy of deformation per monomer is

$$f = k_B T \Bigg\{ \frac{\omega}{2}\, \rho/B - \frac{2(3)^{1/2}}{\pi}\, \omega^{3/2} (\rho/B)^{1/2}$$

$$+ \frac{3}{2}\, \frac{\gamma}{1+\gamma} \Bigg[I + \frac{4}{\pi} \left(\frac{3\omega}{B\rho}\right)^{1/2} +$$

$$\log \left| 1 + \frac{1}{8\pi^2} \left(\frac{3\omega}{B\rho}\right)^{1/2} \quad 1 + I + J) \right| \Bigg] \Bigg\}$$

where the three functions of deformation are:

$$I = \epsilon_1^1 - 1 = \frac{1}{3} \sum_i \lambda_i^2 - 1;\; B = \lambda_1 \lambda_2 \lambda_3;$$

$$J = B(\epsilon^1_{-1} - 1);$$

and

$$\gamma = \frac{1}{2} \left(\frac{6}{\pi}\right)^{3/2} \frac{1}{\rho\alpha} - \frac{6(3)^{1/2}}{\pi} \left(\frac{\omega}{\rho}\right)^{1/2}$$

with $\alpha = a/l$ = reduced cut-off length.

RESULTS AND DISCUSSION

The free energy terms, in order, may be interpreted as follows.

(i) $\omega\rho/2B$. This is just the interaction energy of one monomer with the mean density of material, ρ/B being the density in the deformed state.

$$\text{(ii)} \quad \frac{-2(3)^{1/2}}{\pi}\, \omega^{3/2} \left(\frac{\rho}{B}\right)^{1/2}$$

This is a correction to the mean density value of repulsion energy, arising because of cooperation along the chains; in repelling each other, two monomers also keep their respective neighbours apart.

$$\text{(iii)} \quad \frac{3}{2}\, \frac{\nu}{1+\gamma}\, I = \frac{\gamma}{2(1+\gamma)} \left(\sum_i \lambda_i^2 - 3 \right)$$

This term gives the familiar phantom network entropy of deformation. The factor $1/(1+\gamma)$ simply corrects for the incidence of 'wasted loops' where the chain loops back on itself before connecting to any other part of the network. Clearly such a link contributes nothing to the phantom network shear modulus.

$$\text{(iv)} \quad \frac{3\nu}{2}\, \frac{1}{1+\gamma}\, \frac{4}{\pi} \left(\frac{3\omega}{B\rho}\right)^{1/2}$$

Due to crosslinks, this gives exactly the opposite effect to term (ii). By forcing two monomers together at a link their neighbours are brought into enhanced contact. Note that both effects are screened and so vary as $B^{-1/2}$ at high density.

$$\text{(v)} \quad \frac{3\nu}{2}\, \frac{1}{1+\gamma} \log \left| 1 + \frac{1}{8\pi^2} \left(\frac{3\omega}{B\rho}\right)^{1/2} (1 + I + J) \right|$$

This gives the increase in repulsive energy under shear due to the material being confined to affine deformation: this impedes the density relaxation.

Limitations

Although it is possible to take the calculation further, the present work has been taken only to the lowest order in the crosslink fraction ν.

The largest terms neglected are of order:

$$k_B T \frac{\nu}{1+\gamma} \left[\frac{\nu}{(1+\gamma)\rho} \right]^{1/2}$$

and do contribute to the deformation dependence of the elastic free energy. The régime where crosslink fraction $\nu = Nl/L$ is less than volume fraction $\rho = Ll^2/V$ is highly restrictive. There μ/w is of order ν/ρ so that to study the system close to collapse, the case $\nu \sim \rho$ must be considered: the authors hope to carry this out in a later paper. Another point left to later investigation is a proper evaluation of $\langle X - E \rangle$ including excluded volume.

An alternative view of the above limitations is that they restrict this treatment to the high density regime. This is consistent with the polymer solution theory which it subsumes[7].

CONCLUSIONS

First and foremost, this theory gives a network which is stable against density fluctuations. This is assured by the polymer solution terms which have emerged from a full network calculation. By forcing chains into close contact, the crosslinking increases the effect of excluded volume to the extent of:

$$\frac{\nu}{2(1+\gamma)}\, \frac{12}{\pi} \left(\frac{3\omega}{\rho B}\right)^{1/2}$$

Note that this term comes about as a correction to the fluctuation part

$$\frac{-2(3)^{1/2}}{\pi}\, \omega^{3/2} \left(\frac{\rho}{B}\right)^{1/2}$$

and not the mean density term $\omega\rho/B$; crosslinking does not affect the mean density.

The elastic behaviour under shear takes exactly the familiar phantom form[1,6] at high densities:

$$\tilde{f} \to \frac{\nu}{2} k_B T \sum_i \lambda_i^2 + \text{bulk terms as } \rho \to \infty$$

The modification to the shear properties at lower densities appears always to be weak. At its most extreme the modification is from I to I + logarithm $(1 + I + J)$, though the shortcomings of the present calculation at low density should be born in mind here.

It is interesting that this is precisely the sort of behaviour – increase in modulus and more complicated elastic functions – which when seen experimentally is attributed to entanglements. Entanglements have been ignored in the present work and may swamp this effect, but the feature of increasing as density is lowered might prove sufficiently distinctive experimentally.

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APPENDIX A

Without crosslinking, the statistical weight of a polymer configuration is

$$\exp\left\{-\frac{3}{2l}\int \mathbf{r}'^2\,\mathrm{d}s - \frac{w}{2}\int\int \mathrm{d}s\mathrm{d}s'\delta\,[\mathbf{r}(s) - \mathbf{r}(s')]\right\}$$

The statistical weight of a system with N crosslinks joining $s_1, s_1' \ldots s_N, s_N'$ is simply the sum of all the weights of the contributing configurations:

$$Z(s_1, s_1' \ldots s_N, s_N') = \int \delta\mathbf{r}(s) \prod_{i=1}^{N} \delta\,[\mathbf{r}(s_i) - \mathbf{r}(s_i')] \times$$

$$\times \exp\left[-\frac{3}{2l}\int \mathbf{r}'^2\,\mathrm{d}s - \frac{w}{2}\int\int \mathrm{d}s\mathrm{d}s'\delta\right]$$

The integral is a sum over all paths within the volume and $\delta\,[\mathbf{r}(s_i) - \mathbf{r}(s_i')]$ picks out only those configurations which touch, i.e. are linked, at s_i and s_i'. Just as with the excluded volume, to avoid divergences associated with ever shorter loops – 'wasted loops' – it is convenient to soften the δ function to

$$\left(\frac{2\pi a^2}{3}\right)^{-3/2} e^{-3\mathbf{r}^2/2a^2}$$

If we take the distribution of links to be determined by equilibrium in the formation state, then the probability of a particular set of links is simply $Z(\ldots s_i, s_i' \ldots)$ normalized:

$$p(s_i s_i' \ldots s_N, s_N') = \frac{Z(\ldots s_i, s_i' \ldots)}{\int \mathrm{d}s_i \mathrm{d}s_i' \ldots \mathrm{d}s_N \mathrm{d}s_N'\; Z(\ldots s_i, s_i' \ldots)}$$

By the Gibbs formula, the free energy of the system with a particular set of links is given by:

$$F_1(\ldots s_i, s_i' \ldots) = -k_B T \log Z(\ldots s_i, s_i' \ldots)$$

This remains true under deformation:

$$\tilde{F}_1(s_i) = -k_B T \log \tilde{Z}(s_i)$$

where the *tilde* indicates the deformed boundary conditions. Averaging $\tilde{F}_1$ over the initial crosslink locations then gives:

$$\frac{\tilde{F}}{kT} = \int \mathrm{d}s_i p(s_i)\,(-\tilde{F}_1(s_i)/k_B T)$$

$$= \frac{\int \mathrm{d}s_i Z(s_i) \log \tilde{Z}(s_i)}{\int \mathrm{d}s_i Z(s_i)}$$

APPENDIX B

We can change the order of the logarithm and the average over link locations, by the 'Replica Trick', using:

$$\log x = \lim_{n\to 0}\left(\frac{x^n - 1}{n}\right) = \left(\frac{\partial}{\partial n}x^n\right)_{n=0}$$

Then

$$\tilde{F} = -k_B T \frac{\int Z\left(\frac{\partial}{\partial n}\tilde{Z}^n\right)_{n=0}}{\int Z}$$

$$= -k_B T\left[\frac{\frac{\partial}{\partial n}\int Z\tilde{Z}^n}{\int Z\tilde{Z}^n}\right]_{n=0}$$

$$= -k_B T \frac{\partial}{\partial n}\left[\log \int Z\tilde{Z}^n\right]_{n=0} = \frac{\partial}{\partial n}[F_{rep}(\mathbf{n})]_{n=0}$$

where

$$F_{\mathrm{rep}}(\mathbf{n}) = -k_B T \log Z_{\mathrm{rep}}(n)$$

$$Z_{\mathrm{rep}}(n) = \int Z\tilde{Z}^n$$

APPENDIX C

To introduce a chemical potential for crosslinking we use the identity:

$$X^N = \frac{1}{2\pi i}\oint_C \frac{\mathrm{d}\mu}{\mu^{N+1}} N!\,e^{\mu X}$$

(where C is a contour enclosing $\mu = 0$ in the complex μ plane)

$$= \frac{1}{2\pi i}\oint_C \mathrm{d}\mu N!\,e^{\mu X - (N+1)\log\mu}$$

In the thermodynamic limit only the steepest descent point of $\exp(\mu X - N\log\mu)$ contributes (for a gelled state) so we are left with:

$$Z_{\mathrm{rep}} = \underset{\mu}{\mathrm{ext}} \int e^{-W \quad wE + \mu X - N \log \mu} \delta\, \mathbf{r}_{\alpha}(s)$$

APPENDIX D

We require the identity $\langle e^{y} \rangle \geqslant e^{\langle y \rangle}$ where $\langle\ \rangle$ denotes some particular average. Now

$$e^{y} = e^{c} e^{y-c} \geqslant e^{c}(1 + y \quad c)$$

so

$$\langle e^{y} \rangle \geqslant e^{c}(1 + \langle y \rangle - c)$$

hence

$$\langle e^{y} > \geqslant e^{\langle y \rangle}$$

choosing $c = \langle y \rangle$, which maximizes the above.

APPENDIX E

We wish to show that the stationary value of

$$F(\mu) = F_0(\mu) + nF_1(\mu) + \mathrm{Order}\,(n^2)$$

is correctly given to order n by taking $\mu = \mu_0$ where

$$\left[\frac{\partial F_0(\mu)}{\partial \mu}\right]_{\mu=\mu_0} = 0$$

Let the true stationary point be $\mu^*, \mu = \mu^* + \mathrm{Order}\ n$: then expanding about $\mu = \mu_0$ gives

$$F(\mu^*) = F_0(\mu_0) + (\mu^* - \mu_0)F_0'(\mu_0) + \mathrm{Order}\,(\mu^* - \mu_0)^2$$

$$+\ nF_1(\mu_0) + \mathrm{Order}\ n(\mu^* - \mu_0)$$

$$= F_0(\mu_0) + nF_1(\mu_0) + \mathrm{Order}\ n^2$$