Elasticity of entangled networks

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Entanglements are modelled by links which make a sliding contact between polymer networks. A formal solution to this problem is given using the replica formalism and the contribution of an entanglement to the free energy of shear is given by:

$$\frac{1}{2}kT\sum_i \frac{\lambda_i^2(1+\eta)}{1+\eta\lambda_i^2} + kT\Sigma\log(1+\eta\lambda_i^2)$$

where λ_i are the Cartesian extension ratios and η is a measure of the freedom of a link to slide compared with the freedom of movement of a chain. The expression quoted gives correct limits in the (trivial) case of η zero, and η infinity, when it is merely a negative contribution to the osmotic pressure of the network.

INTRODUCTION

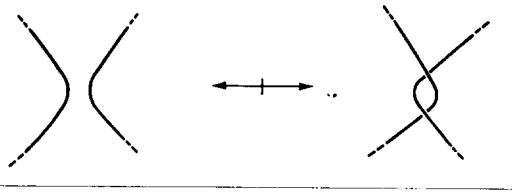
The classical theory of rubber elasticity[1] contains an unrealistic assumption. It assumes that the polymer chains move through each other as 'phantoms' held only by crosslinks, and that the whole system is prevented from collapsing by the assumption of repulsive forces which generate a bulk modulus but are otherwise ignored.

The neglect of repulsive effects in calculating the shear elasticity has been shown by two of the present authors[2] to be reasonable for systems where the repulsions are screened, but this does not take into account the simple constraint that real polymer chains cannot pass through each other. In any polymer system with closed loops of chain, this leads to permanent constraints upon the motion: the state of topological entanglement must be completely preserved.

The complete classification of entanglement constraints is an outstanding problem in pure mathematics and direct physical attacks upon it demand gross approximations. However, the local consequences of entanglement are intuitively obvious, and by adopting a simple model of these we can convert this understanding into predictions of elastic behaviour.

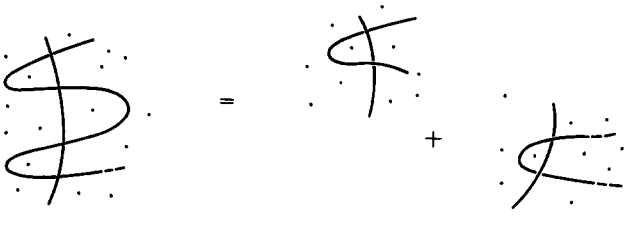
PHYSICAL CONSTRAINTS

Deam and Edwards[3] replaced the full entanglement constraints by the constraint of conserving a partial description of the topology, the winding numbers between chains. These constraints were then added incoherently in an approximation which treats best the simplest configurations of constraint as shown below:



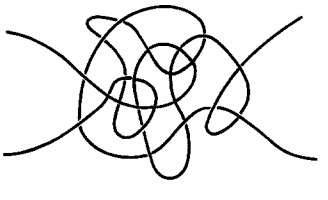
(1)

Essentially their calculation assumes that other chains intervene before multiple approaches arise, so that all the constraining contacts contribute independently as portrayed in (2) below. However, for a solvated gel, the chains are highly flexible compared with the incidence of chain contacts, and under these circumstances the simplest entanglements as in (1) do not dominate.



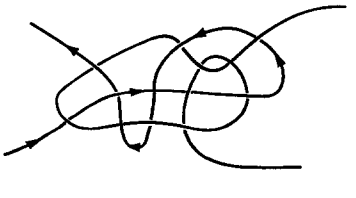
(2)

The effect of the constraints is then highly correlated as in such configurations as:



(3)

Following Edwards[4] and de Gennes[5], Doi and Edwards[6] focussed attention on the feature that whatever the entanglements, linear chains can, given enough time, succeed in sliding along through them. This is illustrated below:



(4)

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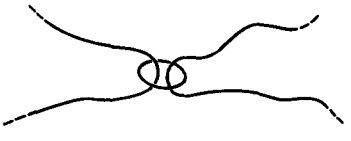
Adopting the high density, simplest entanglements picture of Deam and Edwards[3] leads to the concept of an effective tube of constraint, only within which the chains can move comparatively freely. This model has proved extremely fruitful in its application to viscoelasticity and molecular diffusion[7], but Graessley[8] has shown that the diameter of the tube, which Doi and Edwards leave free to parameterize the strength of entanglement, is of order 2 nm even for a polyethylene melt. Whilst the experimental agreement is then by previous standards remarkable, except for the magnitude of the viscosity, this very large degree of lateral freedom somewhat contradicts the original picture of the tube. Even for a dense rubber, therefore, the constraining effect of interchain contacts must be highly correlated and the effective entanglement must be more like that of diagram (3) than (2). Some sort of tube concept must remain valid, but there is a motivation to explore other points of view.

SLIPLINK MODEL

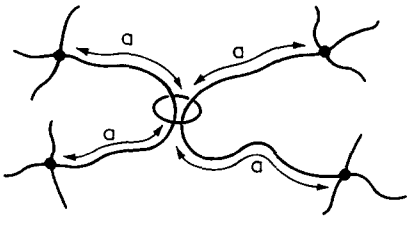
A complementary view to that of the tube model is provided by the slipping link. Here complicated entanglements such as (3) are represented by the constraint of a contact through which each chain is free to slide: pictorially this is equivalent to the diagram below:



(5)

This picture of sliplinks is rather more general than that discussed by Doi and Edwards[6].

Physically the presence of other entanglements of proper crosslinks will in a network restrict the extent to which the links can slide independently along either of their connecting chains. This will be put into the calculations as the freedom to slide only an arc length $\pm a$ in any one direction:



(6)

The total number of sliplinks, N_s, will simply be taken as given, so that we will arrive initially at a two parameter theory. However, from the above comments we will relate a to the numbers of links N_s and N_c. What we do in this paper is to calculate the free energy caused by such a link. To do this one must firstly set up a formalism which permits a rigorous translation of the physical problem into a mathematical problem. This is accomplished by the replica formalism, and the tricky limiting mathematics contained in this method is amply compensated by the precision and completeness it confers on the calculation. However, the final results are in some ways surprising and the large number of authors of this paper is due to careful checking of results which seem at variance with conventional wisdom, a point which will be expanded upon later.

The structure of the paper will be to give the formal analysis of the problem in the next section. Then we shall present the simple limiting cases of $a \to 0$ and $a \to \infty$, followed by an outline of the intermediate case. The complete calculation is relegated to an Appendix. Finally the results will be discussed in a wider framework.

THE REPLICA FORMALISM

The formal difficulty of any study of the statistical mechanics of an amorphous system is that it is the free energy which has finally to be averaged over those degrees of freedom whose frozen values make the material amorphous. To average a free energy is much more difficult than the averaging of the normal partition function, because it is already the logarithm of the partition function of those degrees of freedom which are not frozen. The formalism will be eased somewhat by noting that for the purposes of this paper it is sufficient to consider all the chains as parts of one long chain of length L, the total arc length of all the chains. Thus in our particular case of a cross and slip-linked network let the chain be represented by $\mathbf{r}(s)$. Then suppose the crosslinks join points s_i and s_i' so that link i imposes the constraint:

$$\mathbf{r}(s_i) = \mathbf{r}(s_i'). \tag{7}$$

The free energy is then a function of the incidence matrix $(s_i, s_i') = \underline{\underline{S}}$,

$$F(\underline{\underline{S}}) = -k_B T \log \int \prod_i \delta(\mathbf{r}(s_i) - \mathbf{r}(s_i')) e^{-H/k_B T} P(\mathbf{r})(\delta \mathbf{r}) \tag{8}$$

where H is the Hamiltonian of the system and $\int(\delta \mathbf{r})$ signifies integration over all configurations of the chains. The function $P(\mathbf{r})$ represents the connectivity of the chains and is adequately represented by the Brownian random path formulation, succintly expressed by the Wiener integral:

$$N \exp\left[-\frac{3}{2l} \int_0^L \mathbf{r}'^2(s) ds \right] \tag{9}$$

for each chain. N is the normalization (which need concern us no further). In this paper we do not consider the interaction between chains in detail, since the conventional approach of considering that repulsive short range forces with attractive van der Waals forces will lead to an acceptable bulk modulus, which need not be studied in detail, is an adequate viewpoint here. However, for completeness one can write it in pseudopotential form:

$$H = w \int_0^L \int_0^L \delta(\mathbf{r}(s) - \mathbf{r}(s')) ds \, ds'. \tag{10}$$

Finally we must ask how F is to be averaged. If it is assumed that the crosslinks are placed at random along the chain, the initial probability will be precisely the usual statistical mechanical formula in which the crosslinks are allowed to be anywhere along the chains. Thus:

$$\bar{F} = \int P(\underline{\underline{S}}) F(\underline{\underline{S}}) \prod_i ds_i ds_i' \tag{11}$$

and

$$\mathscr{P}(\underline{\underline{S}}) = \int P(\mathbf{r}) e^{-H/k_B T} \prod_i \delta(\mathbf{r}(s_i) - \mathbf{r}(s_i'))(\delta\mathbf{r}) \tag{12}$$

In order to handle the logarithm we note that:

$$\log X = \text{coefficient of } n \text{ in } X^n. \tag{13}$$

It helps to understand this representation if we consider:

$$\left[\int P(\mathbf{r}) e^{-H/k_B T} \prod_i \delta(\mathbf{r}(s_i) - \mathbf{r}(s_i'))\delta\mathbf{r})\right]^n \tag{14}$$

as

$$\int \cdots \int \prod_{\alpha=1}^{n} P(\mathbf{r}^\alpha) e^{-\sum_\alpha H^\alpha/k_B T} \prod_{\alpha=1}^{n} \prod_i \delta\left(\mathbf{r}^\alpha(s_i) - \mathbf{r}^\alpha(s_i')\right)\left(\prod_\alpha \delta\mathbf{r}^\alpha\right) \tag{15}$$

further, we can identify the physical free energy as the coefficient of n in the free energy $\mathscr{F}(n)$ of $n+1$ systems:

$$e^{-\mathscr{F}(n)/k_B T} =$$

$$\int \cdots \int \prod_{\alpha=0}^{n} P(\mathbf{r}^\alpha) e^{-\sum_\alpha H^\alpha/k_B T} \prod_{\alpha=0}^{n} \prod_i \delta\left(\mathbf{r}^\alpha(s_i) - \mathbf{r}^\alpha(s_i')\right) \prod_i ds_i ds_i' \left(\prod_i \delta\mathbf{r}^\alpha\right). \tag{16}$$

If the system is now strained with extensions λ_i, the integral is taken over $n+1$ 'replicas', the first being in the unstrained system, and the other n replicas being taken over the strained volume. Since the N_c crosslinks are conveniently described by a chemical potential μ:

$$\left[\iint \prod_\alpha \delta\left((\mathbf{r}^\alpha(s) - \mathbf{r}^\alpha(s'))ds ds'\right]^{N_c} =$$

$$\varphi \frac{N_c!}{2\pi_i} \exp\left[-N_c \log\mu + \mu \iint \prod_\alpha \delta\left((\mathbf{r}^\alpha(s) - \mathbf{r}^\alpha(s'))ds ds'\right] d\mu \tag{17}$$

we reach the final formula:

$$\tilde{F} = \text{coefficient of } n \text{ in } \mathscr{F}(n) \tag{18}$$

where

$$e^{-\mathscr{F}(n)/k_B T} = \varphi \frac{d\mu}{2\pi i} \int_{\text{unstrained}} (\delta\mathbf{r}^0) \prod_{\alpha=1}^{n} \int_{\substack{\text{strained by} \\ \lambda_1, \lambda_2, \lambda_3}} (\delta\mathbf{r}^\alpha) \exp\left[-\sum_\alpha \int_0^L \frac{3}{2l} \mathbf{r}'^{\alpha 2} ds\right.$$

$$\left. - w \sum_\alpha \int_0^L \int_0^L \delta(\mathbf{r}^\alpha(s) - \mathbf{r}^\alpha(s'))ds ds' + \mu \int_0^L \int_0^L \prod_\alpha \delta(\mathbf{r}^\alpha(s) - \mathbf{r}^\alpha(s'))ds ds'\right] \tag{19}$$

Note that the crosslinks, which are fixed, appear as a *product* in the replica indices in the exponent, whereas the chain–chain interactions, which are not fixed, appear as a *sum* in the replica indices in the exponent. This is how the replica formalism handles in a quite explicit and precise way the essential difference between these facets of the chain–chain relationship.

Now we are in a position to handle the sliplinks. The formula for the crosslinks

$$\prod_i \delta(\mathbf{r}(s_i) - \mathbf{r}(s_i')) \tag{20}$$

is replaced by:

$$\prod_i \delta(\mathbf{r}(s_i + \tau_i) - \mathbf{r}(s_i' + \tau_i')). \tag{21}$$

This sliding τ_i is not a frozen variable but a full degree of freedom. Hence whereas in the replica formalism a true crosslink appears as:

$$\int_0^L \int_0^L \prod_{\alpha=0}^{n} \delta(\mathbf{r}^\alpha(s) - \mathbf{r}^\alpha(s'))ds ds'. \tag{22}$$

we now have separate τ integrals for each replica giving:

$$\int_0^L \int_0^L \prod_{\alpha=0}^{n} \int_a^a d\tau_\alpha \int_a^a d\tau_\alpha' \, \delta(\mathbf{r}^\alpha(s + \tau_\alpha) - \mathbf{r}^\alpha(s' + \tau_\alpha'))ds ds' \tag{23}$$

Thus a complete formal statement of the problem is obtained by adding equation (23) to the exponent in (19) with a chemical potential μ_s and number N_s to give the final, comparatively compact formula:

$$e^{-\mathscr{F}(n)/k_B T} = \varphi N_c! \frac{d\mu_c}{2\pi i} e^{-N_c \log\mu_c} \varphi N_s! \frac{d\mu_s}{2\pi i} e^{-N_s \log\mu_s}$$

$$\times \int \prod_\alpha (\delta\mathbf{r}^\alpha) \exp(-W - wE + \mu_c X_c + \mu_s X_s) \tag{24}$$

where

$$W = \frac{3}{2l} \int_0^L \sum_\alpha \mathbf{r}^{\alpha/2} ds;$$

$$E = \sum_\alpha \int_0^L \int_0^L \delta(\mathbf{r}^\alpha(s) - \mathbf{r}^\alpha(s'))ds ds';$$

$$X_c = \int_0^L \int_0^L ds ds^1 \prod_\alpha \delta(\mathbf{r}^\alpha(s) - \mathbf{r}^\alpha(s'));$$

$$X_s = \int_0^L \int_0^L ds ds' \prod_\alpha \int_a^a \int_a^a d\tau_\alpha d\tau_\alpha' \delta(\mathbf{r}^\alpha(s + \tau_\alpha) - \mathbf{r}^\alpha(s' + \tau_\alpha^1))$$

We will not consider the interaction of the chains in further detail (though see Ball and Edwards[2]).

CALCULATION

The effect of crosslinkage is to confine chains to a well-defined region, and their mean positions must be transfor-

med approximately affinely under strain; indeed for a Gaussian network the mean positions will be exactly affinely deformed. However, the chain has considerable freedom about this mean position and this suggests the method of transforming to collective coordinates so that each $\mathbf{r}^\alpha$ is close to the affine value $\bar{\mathbf{r}}^\alpha$. The most symmetric way to do this is by using the roots of unity in the transformation employed by Deam and Edwards:

$$X_{\alpha i} = T^{\alpha\beta}_{(i)} \mathbf{r}^\beta_i \tag{26}$$

but it is more convenient to keep all the coordinates real by using, for example, the transformation given in Appendix B. This is an orthonormal transformation and therefore:

$$\sum_\alpha \mathbf{r}'^{\alpha 2} = \sum_\alpha X'^2_\alpha \tag{27}$$

and

$$\prod_\alpha (\mathbf{r}^\alpha(s) - \mathbf{r}^\alpha(s')) = \prod_\alpha \delta(\mathrm{X}_\alpha(s) - \mathrm{X}_\alpha(s')). \tag{28}$$

To evaluate equation (24) we can employ a trial function:

$$Q = \frac{1}{6l} \int_0^L \mathrm{d}s \sum_{\alpha=1}^{n} \prod_i q_i^2 X^2_{\alpha i} \tag{29}$$

to mirror the crosslink δ function, and employ the variational principle that:

$$\int \mathrm{e}^{A+B} \geqslant \int \mathrm{e}^{A+\langle B\rangle} \quad \text{where} \quad \langle B\rangle = \frac{\int \mathrm{e}^A B}{\int \mathrm{e}^A}. \tag{30}$$

Then for the functional integral in equation (17) (with $w=0$) we obtain

$$\int \mathrm{e}^{-w-Q+Q+\mu_c X_c+\mu_s X_s} \geqslant \int \mathrm{e}^{-w-Q+\langle Q+\mu_c X_c+\mu_s X_s\rangle}. \tag{31}$$

Note that the exponent of the r.h.s. depends on the chemical potentials μ_c and μ_e purely linearly. It follows that we may unravel directly the use of the chemical potential to obtain:

$$\mathrm{e}^{-\mathscr{F}(n)/k_BT} \geqslant \int \mathrm{e}^{-w-Q+\langle Q\rangle} \langle X_x\rangle^{N_c} \langle X_s\rangle^{N_s}. \tag{32}$$

(It should be noted that as long as we are working in the $3n+3$ dimensions, $\mathscr{F}$ is a conventional free energy and the above calculation is a conventional variational calculation of a free energy. However, when the calculation is complete, *then* we take the limit $n\to 0$, and $\tilde{F}$ being the free energy of a system in which not all degrees of freedom are accessible, need not have the conventional properties of a free energy.)

Let us first consider the case of crosslinks only. The evaluation of the various expressions is quite straightforward and is discussed in detail by Deam and Edwards and recapitulated briefly by Ball and Edwards. (Note that these do not take q_i to depend on i, but the extension is trivial.) The value of $\int \mathrm{e}^{-W-Q}$ is:

$$\mathrm{e}^{-n\sum_i lq_iL/6} \tag{33}$$

and

$$\langle X_c\rangle = \prod_i \left(\frac{q_i}{2\pi}\right)^{n/2} \frac{L^2}{V^0}$$
$$\langle Q\rangle = \frac{1}{12}\sum_i n l q_i L \tag{34}$$

where

$$\frac{1}{V_0} = \langle \delta(\mathrm{X}_0(s) - \mathrm{X}_0(s'))\rangle. \tag{35}$$

The quantity V_0 is the volume available to $\mathrm{X}_0(s)$, which ranges over the cuboid generated by the three edges:

$$V^{1/3}(1,\ 0,\ 0,\ [\lambda_1,\ 0,\ 0]n \text{ times}) \text{ and similarly for } y \text{ and } z \tag{36}$$

these are each of length $V^{1/3}\ (1+n\lambda_i^2)^{1/2}$, respectively. Thus

$$\frac{1}{V_0} = \frac{1}{V}\prod_i (1+n\lambda_i^2)^{-1/2} \tag{37}$$

It is in this rather oblique way that the replica method reproduces the classical results, for variation now gives:

$$q_i = \frac{6Nl}{L} \tag{38}$$

(confirming the earlier neglect of dependence upon i). Hence:

$$\tilde{F} = \tfrac{1}{2} N_c k_B T \sum_i \lambda_1{}^2 + (\text{terms independent of deformation}). \tag{39}$$

Now we turn to the sliplink problem. The only new term with which we are confronted is the configurational average of a replicated sliplink appearing as $\langle X_s\rangle$ in equation (32).

TWO SPECIAL CASES

With the advent of slip the linkage function X_s is not isotropic in the replica indices, in other words when we write it in terms of the usual transformed coordinates $\mathrm{X}_\alpha(s)$ it does not transform into anything simple. As this will force further approximations upon the calculation, it is a helpful check to consider the two limiting cases of $a=0$ and $a\to\infty$. The first merely gives back the case of an ordinary crosslink, whereupon we obtain, neglecting wasted loops:

$$\langle X\rangle = \frac{\mathscr{L}^2}{V_0} \prod_i \left(\frac{q_i}{2\pi}\right)^{1/2n} \tag{40}$$

and

$$\frac{\tilde{F}}{k_BT} = \tfrac{1}{2}\sum_i \lambda_i^2 \quad \text{per link.} \tag{41}$$

In the case of $a \to \infty$ we can ignore configurations where any two slip coordinates $s+\tau_\alpha$ are close along the arc. The $n+1$ δ-functions in X_s can then be averaged independently and we obtain:

$$\langle X_s \rangle = \frac{\mathscr{L}^2}{V V^n} \tag{42}$$

and a free energy per link given by:

$$\frac{\tilde{F}}{k_B T} = \log|\prod_i \lambda_i|. \tag{43}$$

This latter is simply a correction to the osmotic pressure, and expresses the fact that a completely sliding contact does nothing save reduce the number of perfect gas degrees of freedom by one, joining together two molecules. These limiting values are to be demanded of the computation for general a.

ELASTICITY CALCULATION

For intermediate ranges of slip it is still trivial but now rather tedious to perform the configurational average of a slipping link constraint. In appendix A this is shown to give:

$$\langle X_s \rangle = \frac{L^2}{V_0} \prod_i \left(\frac{q_i}{2\pi}\right)^{1/2n} \left\{ \prod_i \det{}^{-1/2}(1 + G_i + G_i') \right\} \tag{44}$$

where the curly brackets $\{\}$ denote the outstanding average over slip coordinates:

$$\prod_{\alpha=0}^{n} \int_{-a}^{a} \int_{-a}^{a} \frac{d\tau_\alpha d\tau_{\alpha'}}{4a^2} \tag{45}$$

and the determinant is taken over the replica indices $\beta = 1 \ldots n$ only. The matrix G_i has components:

$$G_i^{\beta\beta'} = q_i \sum_{\alpha\alpha'} T_i^{\beta\alpha} T_i^{0\alpha} T_i^{\beta'\alpha'} T_i^{0\alpha'} \left\{ \frac{l}{3} \theta(\tau_\alpha \tau_{\alpha'}) \min(|\tau_\alpha|, |\tau_{\alpha'}|) - \frac{1}{2q_i} e^{-\frac{lq_i}{3}|\tau_\alpha - \tau_{\alpha'}|} \right\}. \tag{46}$$

The transformation matrix $T_i^{\alpha\beta}$ is precisely the same as that introduced through equation (26).

A simple and tractable approximation which gives the exact results for the two limits of large and small slip a, is to average the matrix G_i itself where it occurs in equation (14) using:

$$\{\prod_i \det{}^{-1/2}(1 + G_i + G_i')\} \geqslant \prod_i \det{}^{-1/2}(1 + \{G_i\} + \{G_i\}) = \prod_i \det{}^{-1/2}(1 + 2\{G_i\}). \tag{47}$$

This inequality is derived in appendix A together with possible improvements. On averaging, G_i is the $n \times n$ matrix:

$$\frac{\eta(x_i)}{2} \begin{pmatrix} \lambda_i^2 + n\lambda_i^2(1-\lambda_i^2) & 0 & 0 & 0 & \ldots \\ 0 & \lambda_i^2 & 0 & 0 & \ldots \\ 0 & 0 & \lambda_i^2 & 0 & \ldots \\ \cdot & \cdot & & \cdot & \end{pmatrix} \tag{48}$$

where the x_i are dimensionless parameters of the slip:

$$x_i = a l q_i / 3 \tag{49}$$

and the function $\eta(x)$ is given by:

$$\eta(x) = x^{-2}(x - x^2 + \frac{2}{3}x^3 - e^{-x}\sinh x). \tag{50}$$

This function is monotonic in $x \geqslant 0$ and has asymptotes as follows:

$$\eta(x) = \frac{1}{3}x^2 + \text{order } x^3 \text{ as } x \to 0 \tag{51}$$

$$\eta(x) = \frac{2}{3}x + \text{order } 1 \quad \text{as } x \to \infty. \tag{52}$$

The approximation (47) can then be evaluated and substituted back into equation (44) to give the result:

$$\langle X_s \rangle = \frac{L^2}{V_0} \exp \tfrac{1}{2} n \sum_i \left\{ \log \frac{q_i}{2\pi} + \log|1 + \eta(x_i)\lambda_i^2| + \frac{\eta(x_i)\lambda_i^2(1-\lambda_i^2)}{1 + \eta(x_i)\lambda_i^2} \right\}. \tag{53}$$

Now we must return to construct formula (32) to obtain the replicated free energy, incorporating N_c crosslinks as well as N_s sliplinks. The component parts are given by equations (33), (40) and (53) taking the terms of order n from each gives the free energy of deformation as:

$$\frac{\tilde{F}}{k_B T} = \tfrac{1}{2}(N_s + N_c) \sum_i \left(\lambda_i^2 + \log \frac{q_i}{2\pi} + \frac{l L q_i}{12} + \frac{N_s}{N_s + N_c} \left(\log|1 + \eta(x_i)\lambda_i^2| + \frac{\eta(x_i)\lambda_i^2(1-\lambda_i^2)}{1 + \eta(x_i)\lambda_i^2} \right) \right) \tag{54}$$

where all the q_i-dependent terms have been retained.

Determination of parameters q_i

The variational parameters q_i only occur in $\mathscr{F}(n)$ to relevant order in as much as they appear in $\tilde{F}$ given above. They can therefore be determined by minimizing the free energy of deformation (equation 54). Writing all the q_i in terms of the x_i, and setting to zero the first derivative of $\tilde{F}$ with respect to the latter then gives:

$$x_i = \frac{2a(N_s + N_c)}{L} \left(1 - \frac{N_s}{N_s + N_c} \lambda_i^2 \eta'(x_i) x_i \frac{2 - \lambda_i^2 + \lambda_i^2 \eta(x_i)}{[1 + \lambda_i^2 \eta(x_i)]^2} \right) \tag{55}$$

where

$$\eta'(x) = \frac{d}{dx}\eta(x). \tag{56}$$

The correction to the value in the absence of slip:

$$\frac{x_i}{a}=\frac{1(N_s+N_c)}{L} \tag{57}$$

is always small, being of order x^2 at small x and N_s/N_s+N_c at large x, so it is always reasonable to take it to first order only. To evaluate the free energy to first order in a perturbation requires only a zero order evaluation of the quantities q_i. This is because the free energy is made stationary with respect to such variational parameters and so at first order is insensitive to their variation. This amounts to neglecting slip in the evaluation of the q_i, whereupon in terms of the x_i they take the value given by equation (57).

RESULTS

The deformation dependent part of the free energy (equation 54) now reduces to:

$$\frac{\tilde{F}}{k_BT}=\tfrac{1}{2}N_c\sum_i\lambda_i^2+\tfrac{1}{2}N_s\sum_i\left[\frac{(1+\eta)\lambda_i^2}{1+\eta\lambda_i^2}+\log|1+\eta\lambda_i^2|\right] \tag{58}$$

where the argument of η is given by equation (57). Note that the required limits of $a\to\infty$ and $a\to0$ are obtained since they give $\eta\to\infty$ and $\eta\to0$, respectively, which in turn yield the perfect sliding and hard-link free energies (43) and (41).

The parameter a can be neatly eliminated if we return to the rationale for its introduction. If each sliplink can on average slide as far as the centres of its topologically neighbouring links, then we have:

$$4a(N_s+N_c)=2L \tag{59}$$

giving $x_i=1$ for all i and $\eta=\eta(1)=\frac{1}{6}+\frac{1}{2e}=0.2343\ldots$

DISCUSSION

The intuitive picture of the behaviour of a sliplink under shear is that it will respond to the shear by moving until it locks onto another entanglement or crosslink, whereupon it behaves as a genuine crosslink, possibly of higher functionality. This means that a sliplink hardens with deformation. Ours softens. That result is reasonable when considered as a function of the freedom to slip a, for as we have seen the two limits of large and small a are correctly covered. What the result implies is that as the deformation λ increases, the sliding distance in space is also increased and the link weakens. The difficulty appears to be in thinking of a network as if it were made of rubber piping, thus behaving in a fashion which hardened on deformation. However the true network is dominated by Brownian motion. Our free energy has the standard form of attributing the shear energy solely to entropy. In such cases it is the amount of phase space that matters and mechanistic pictures, which are really internal energy pictures, are misleading. This is not to say that if higher order corrections were studied in which the multiple correlations of links appeared, then some such effect as the intuitive picture might not appear. The experimental situation, however, is well served by the expressions deduced as discussed below.

In the study of the tensile force under elongation:

$$\frac{\partial}{\partial\lambda}\tilde{F}(\lambda,\lambda^{-\frac{1}{2}},\lambda^{-\frac{1}{2}})=f \tag{60}$$

it is customary to plot the quantity:

$$(k_BT)^{-1}(\lambda-\lambda^{-2})^{-1}f. \tag{61}$$

This we find to be given by $d_0-d_1\varepsilon$ for small deformations $\lambda=1+\varepsilon$, where

$$d_0=N_c+N_s\frac{1+6\eta+3\eta^2}{(1+\eta)^2}=N_c+1.69\,N_s \tag{62}$$

and

$$d_1=N_s4\eta\frac{1+6\eta+2\eta^2}{(1+\eta)^3}=1.25N_s. \tag{63}$$

The numerical values given in equations (62) and (63) are those based on equation (59): they are not sacrosanct. For large deformations expression (61) takes the value N_c+N_s/λ^2. 'Large' in this form may not be a reasonable limit to consider since, given an arc length between links of $a\sim ml$, where m is a small number for a well-linked system, a taut polymer configuration is obtained for $\lambda\sim m^{1/2}$ and the analysis presented above is inadequate. However, the formula for small deformations is well borne out by experiment, exhibiting the decrease in modulus which is often expressed by fitting to the Mooney–Rivlin[9] expression.

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APPENDIX A

The average of a slipping link

As explained in the text, we require to average the slipping link constraint against the harmonic Green function, and subsequently also to integrate over slip coordinates. Using curly brackets $\{\}$ to denote the average (45) and angular brackets $\langle\rangle$ to denote averaging over monomer positions the problem is to evaluate:

$$\langle\{X_s\}\rangle=\left\langle\left\{\int_0^L\int_0^L \mathrm{d}s\mathrm{d}s'\prod_{\alpha=0}^{n}\delta[\mathbf{r}^\alpha(s+\tau_\alpha)-\mathbf{r}^\alpha(s'+\tau'_\alpha)]\right\}\right\rangle \tag{A.1}$$

Parameterizing the δ-functions and ignoring wasted loops (i.e. $s\sim s'$) the average becomes:

$$L^2\left(\prod_{\alpha=0}^{n}\frac{d^3\lambda^\alpha}{(2\pi)^3}\right)\langle\{\exp[i\textstyle\sum_\alpha\lambda^\alpha.\mathbf{r}^\alpha(s+\tau_\alpha)\}\rangle\langle\{e^{-i\sum_\alpha\lambda^\alpha.\mathbf{r}^\alpha(s'+\tau_\alpha)}]\}\rangle \tag{A.2}$$

where L is the total arc length of material and half of each of the slip averages is now redundant: the same notation will still be used, however. Now we make the usual transformation of the position coordinates from $\mathbf{r}^\alpha$ to X_α where

$$X_{\alpha i}=\sum_\beta T_i^{\alpha\beta} r_i^\beta \quad ; \qquad \mathbf{r}_i^\alpha=\sum_\beta T_i^{\beta\alpha} X^{\beta i}. \tag{A.3}$$

The only conditions other than orthogonality

$$\left(\sum_\alpha T_i^{\alpha\beta} T_i^{\alpha\gamma}=\delta_{\beta\gamma}\right)$$

imposed on T by the preceding calculations are:

$$T_i^{00}=(1+n\lambda_i^2)^{-\frac{1}{2}} \quad ; \qquad T_i^{0\alpha}=\lambda_i T_i^{00}\alpha>0. \tag{A.4}$$

Each of the averages in (A.2) now becomes:

$$\left\langle\left\{\exp\left[i\sum_{\alpha\beta i}\lambda_i^\alpha T_i^{\beta\alpha} X_{\beta i}(s+\tau_\alpha)\right]\right\}\right\rangle=\left\{\prod_{\beta=0}^{n}\left\langle\exp\left[i\sum_{\alpha i}\lambda_i^\alpha T_i^{\beta\alpha} X_{\beta i}(s+\tau_\alpha)\right]\right\rangle\right\}$$

where the averaging operations have been commuted and the fact that the propagator is separable over β has been exploited. Next we proceed to evaluate each of the configurational average factors in (A.5). From $\beta=0$ we have

$$\left\langle\exp\left[i\sum_{\alpha i}\lambda_i^\alpha T_i^{0\alpha} X_{0i}(s+\tau_\alpha)\right]\right\rangle=$$

$$\frac{1}{V_0}\prod_i\delta\left(\sum_\alpha\lambda_i^\alpha T_i^{0\alpha}\right)\exp\left[-\tfrac{1}{2}\sum_{ii'\alpha\alpha'}\lambda_i^\alpha T_i^{0\alpha}\lambda_{i'}^{\alpha'} T_{i'}^{0\alpha'}\langle\hat{X}_{0i}(\tau_\alpha)\hat{X}_{0i'}(\tau_{\alpha'})\rangle\right] \tag{A.6}$$

where $$\hat{X}_0(\tau_\alpha)=X_0(s+\tau_\alpha)-X_0(s). \tag{A.7}$$

The δ-function has come from the freedom of $X_0(s)$ to be anywhere in the volume V_0, and we have used the fact that the distribution of the rest of the coordinates is joint Gaussian. The correlation function appearing is given by:

$$\begin{aligned}\langle\hat{X}_{0i}(\tau_\alpha)\hat{X}_{0i'}(\tau_{\alpha'})\rangle&=\delta_{ii'}A^{\alpha\alpha'}\\&=\delta_{ii'}\frac{l}{3}\theta(\tau_\alpha\tau_{\alpha'})\min(|\tau_\alpha|,|\tau_{\alpha'}|)\end{aligned} \tag{A.8}$$

where $\theta(x)=0$, $x<0$; $\theta(x)=1$, $x\geqslant 0$.

For each $\beta>0$ we obtain:

$$\left\langle\exp\left[i\sum_{\alpha i}\lambda_i^\alpha T_i^{\beta\alpha} X_{\beta i}(\tau_\alpha)\right]\right\rangle=$$

$$\exp\left[-\tfrac{1}{2}\sum_{ii'\alpha\alpha'}\lambda_i^\alpha T_i^{\beta\alpha}\lambda_{i'}^{\alpha'} T_{i'}^{\beta\alpha'}\langle X_{\beta i}(\tau_\alpha)X_{\beta i'}(\tau_{\alpha'})\rangle\right] \tag{A.9}$$

where

$$\begin{aligned}\langle X_{\beta i}(\tau_\alpha)X_{\beta i'}(\tau_{\alpha'})\rangle&=\delta_{ii'}B_i^{\alpha\alpha}\\&=\delta_{ii'}\frac{1}{2q_i}e^{-\frac{lq_i}{3}|\tau_\alpha-\tau_{\alpha'}|}.\end{aligned} \tag{A.10}$$

The $\beta>0$ factors of (A.5) can then be combined to give:

$$\exp\left[-\tfrac{1}{2}\sum_{\alpha\alpha' i}\sum_{\beta>0}\lambda_i^\alpha\lambda_i^{\alpha'} T_i^{\beta\alpha} T_i^{\beta\alpha'} B_i^{\alpha\alpha'}\right] \tag{A.11}$$

and we can use the identity

$$\sum_{\beta>0} T_i^{\beta\alpha} T_i^{\beta\alpha'}=\delta_{\alpha\alpha'}-T_i^{0\alpha} T_i^{0\alpha'} \tag{A.12}$$

together with $B_i^{\alpha\alpha}=\frac{1}{2}q_i$ to reduce this to

$$\exp\left[-\tfrac{1}{4}\sum_{\alpha i}\frac{1}{q_i}\lambda_i^\alpha\lambda_i^\alpha+\tfrac{1}{2}\sum_{\alpha\alpha' i}\lambda_i^\alpha\lambda_i^{\alpha'} T_i^{0\alpha} T_i^{0\alpha'} B_i^{\alpha\alpha'}\right] \tag{A.13}$$

Now we can combine results (A.6), (A.8) and (A.13) to obtain (A.5) as:

$$\left\{\frac{1}{V_0}\prod_i\delta\left(\sum_\alpha\lambda_i^\alpha T_i^{0\alpha}\right)\exp-\right.$$

$$\left.\tfrac{1}{4}\sum_{\alpha i}\frac{1}{q_i}\lambda_i^\alpha\lambda_i^\alpha-\tfrac{1}{2}\sum_{\alpha\alpha' i}\lambda_i^\alpha\lambda_i^{\alpha'} T_i^{0\alpha} T_i^{0\alpha'}(A^{\alpha\alpha'}-B_i^{\alpha\alpha'})\right\}. \tag{A.14}$$

It is natural to transform the λ^α by T also, to give new variables of integration

$$\mu_{i\beta}=\sum_\alpha T_i^{\beta\alpha}\lambda_i^\alpha \tag{A.15}$$

in terms of which (A.14) becomes

$$\frac{1}{V_0}\delta(\mu_0)\left\{\exp\left[-\tfrac{1}{4}\sum_{i\beta}\frac{1}{q_i}\mu_{i\beta}\mu_{i\beta}-\tfrac{1}{2}\sum_{\beta\beta' i}\frac{1}{q_i}\mu_{i\beta}G_i^{\beta\beta'}\mu_{i\beta'}\right]\right\} \tag{A.16}$$

where $G_i^{\beta\beta'}$ is the messy product:

$$G_i^{\beta\beta'}=q_i\sum_{\alpha\alpha'} T_i^{\beta\alpha} T_i^{0\alpha} T_i^{\beta'\alpha'} T_i^{0\alpha'}(A^{\alpha\alpha'}-B_i^{\alpha\alpha'}) \tag{A.17}$$

and expression (A.2) can then be reconstructed as

$$L^2\prod_\beta\left(\frac{d^3\mu^\beta}{(2\pi)^3}\right)\left(\frac{\delta(\mu^0)}{V_0}\right)^2\exp\left[-\tfrac{1}{2}\sum_{i\beta}\frac{1}{q_i}\mu_{i\beta}\mu_{i\beta}\left\{e^{-\frac{1}{2}}\sum_{\beta\beta' i}\frac{1}{q_i}\mu_{i\beta}G_i^{\beta\beta'}\mu_{i\beta'}\right\}^2\right]. \tag{A.18}$$

The Jacobian between the integrands $\mu_{i\beta}$ and λ_i^α is unity since T is orthogonal. The squared δ-function is really a Kronecker δ in origin and hence its square is simply:

$$\left(\frac{\delta(\mu^0)}{V_0}\right)^2=\frac{\delta(\mu^0)}{V_0}. \tag{A.19}$$

Let us distinguish the different slip coordinates in the two occurrences of the matrix G in expression (A.18) by a tilda over one of them to obtain:

$$\frac{L^2}{V_0}\prod_\beta\int\frac{d^3\mu^\beta}{(2\pi)^3}\delta(\mu^0)\left\{\exp\left[-\tfrac{1}{2}\sum_{i\beta}\frac{1}{q_i}\mu_{i\beta}\mu_{i\beta}+\sum_{\beta\beta' i}\frac{1}{q_i}\mu_{i\beta}(G_i^{\beta\beta'}+\tilde{G}_i^{\beta\beta'})\mu_{i\beta'}\right]\right\}$$

$$=\frac{L^2}{V_0}\prod_i\left(\frac{q_i}{2\pi}\right)^{\frac{1}{2}n}\{\det{}^{-\frac{1}{2}}(1+G+\tilde{G})\}. \tag{A.20}$$

The factor $\delta(\mu_0)$ removes μ_0 from the coordinates integrated, so that the determinant is over the indices $i=1, 2, 3$ and $\beta=1, 2 \ldots n$. The curly brackets in (A.20) refer to the average over two sets of slip coordinates, as was originally the case. Since the matrices G and $\tilde{G}$ are diagonal in the Cartesian indices we can factorize the determinant:

$$\det(1+G+\tilde{G})=\prod_i \det(1+G_i+\tilde{G}_i) \qquad \text{(A.21)}$$

but the subsequent average over slip will in general couple these factors together.

To approximate the average over slip let us first establish a variational principle for $\{\det^{-\frac{1}{2}} M\}$ where M is any matrix with real positive eigenvalues. By the usual variational principle for exponentials we have:

$$\{\det^{-1/2} M\} = \{e^{-1/2 \text{ trace log } M}\} = \{e^{-R}\}\langle e^{R-1/2 \text{ trace log } M}\rangle \geqslant \{e^{-R}\} e^{\langle R-\frac{1}{2} \text{ trace log } M\rangle} \qquad \text{(A.22)}$$

where $\langle\ \rangle$ denotes average over slip with distribution modified by a weight e^{-R}. Also, given that the eigenvalues of M are positive,

$$\langle \text{trace log } M\rangle \leqslant \text{trace log } \langle M\rangle \qquad \text{(A.23)}$$

so we finally obtain:

$$\{\det^{-\frac{1}{2}} M\} \geqslant \{e^{-R}\} e^{\langle R\rangle} \det^{-\frac{1}{2}}\langle M\rangle. \qquad \text{(A.24)}$$

Applying this to the determinant required in (A.20) gives:

$$\{\det^{-\frac{1}{2}}(1+G+\tilde{G})\} \geqslant \det^{-\frac{1}{2}}(1+2\{G\}) \qquad \text{(A.25)}$$

where the simplest choice of $R=0$ has been adopted and we have used the fact that $\{\tilde{G}\}=\{G\}$.

Note that since G and $\tilde{G}$ are of dimension $3n \times 3n$ the above analysis becomes exact for $n=0$ where these matrices do not exist: thus the inequality established above can in its contribution to the free energy be differentiated at $n=0$. Also vital is that the above inequality runs in the same direction as that already used in formula (32), so that the two inequalities can be composed.

To evaluate the average of G over slip, we refer to its definition (A.17) in terms of A and B. These are in turn given by equations (A.8) and (A.10), from which it is trivial but exceedingly tedious to calculate.

$$q_i(A^{\alpha\alpha'} - B_i^{\alpha\alpha'}) = \tfrac{1}{2}\eta(x_i)\delta_{\alpha\alpha'} + \tfrac{1}{2}\kappa(x_i) \qquad \text{(A.26)}$$

where:

$$x_i = \frac{laq_i}{3} \qquad \text{(A.27)}$$

and

$$\eta(x) = x^{-2}(x - x^2 + \frac{2}{3}x^3 - \tfrac{1}{2}(1-e^{-2x})). \qquad \text{(A.28)}$$

The form of $\kappa(x)$ will not be required. From the above we find:

$$\{G_i^{\beta\beta'}\} = \sum_{\alpha\alpha} T_i^{\beta\alpha} T_i^{0\alpha} T_i^{\beta'\alpha'} T_i^{0\alpha'} (\tfrac{1}{2}\eta\delta_{\alpha\alpha'} + \tfrac{1}{2}\kappa) \qquad \text{(A.29)}$$
$$= \tfrac{1}{2}\eta(x_i) \sum_{\alpha} T_i^{\beta\alpha} T_i^{\beta'\alpha} (T_i^{0\alpha})^2$$

noting that for $G_i^{\beta\beta'}$ we are only interested in the indices β, $\beta'>0$, for which the contribution from κ vanishes identically. This can be further simplified by exploiting the values of $T_i^{0\alpha}$ given by (A.4), specifically that $T_i^{0\alpha} = T_i^{01}$ for $\alpha>0$, giving:

$$\{G_i^{\beta\beta'}\} = \tfrac{1}{2}\eta\left(\sum_{\alpha} T_i^{\beta\alpha} T_i^{\beta'\alpha} (T_i^{01})^2 + T_i^{\beta 0} T_i^{\beta' 0}[(T_i^{00})^2 - (T_i^{01})^2]\right) \qquad \text{(A.30)}$$
$$= \tfrac{1}{2}\eta(\delta_{\beta\beta'}(T_i^{01})^2 + T_i^{\beta 0} T_i^{\beta' 0}[(T_i^{00})^2 - (T_i^{01})^2]).$$

The elements $T_i^{\beta 0}$, $\beta>0$, may be chosen—provided T remains orthogonal—so that only T_i^{10} is non-zero. Deam and Edwards give an example of such a transformation in their Appendix B, although there is no need for T to have complex elements as in their example; an example of a suitable real matrix T is given in Appendix B of the present work. However, all we need to know about these matrix elements can be directly inferred from the normalization condition on the $T_i^{\beta 0}$, which requires for the above special choice:

$$(T_i^{10})^2 + (T_i^{00})^2 = 1 \qquad \text{(A.31)}$$

Using the above, $\{G_i\}$ becomes the matrix:

$$\frac{\eta(x_i)}{2}\begin{bmatrix} (T_i^{01})^2 + [(T_i^{00})^2 - (T_i^{01})^2](1-(T_i^{00})^2) & 0 & 0 & 0 & \ldots \\ 0 & (T_i^{01})^2 & 0 & 0 & \ldots \\ 0 & 0 & (T_i^{01})^2 & 0 & \ldots \\ \cdot & \cdot & \cdot & & \cdot \\ \cdot & \cdot & & \cdot & \cdot \\ \cdot & & & & \end{bmatrix} \qquad \text{(A.32)}$$

Noting that $(T_i^{00})^2 = (1+n\lambda_i^2)^{-1}$ and $(T_i^{01})^2 = \lambda_i^2(1+n\lambda_i^2)^{-1}$, this simplifies to give equation (18) to the relevant order in n.

APPENDIX B

Coordinate transformation

An example is required of an orthogonal transformation matrix T_i with the following properties:

$T_i^{\alpha\beta}$ is real

$\sum_\alpha T_i^{\alpha\beta} T_i^{\alpha\beta'} = \delta_{\beta\beta'}$

$T_i^{00} = (1+n\lambda_i^2)^{-1/2}$

$T_i^{0\beta} = \lambda_i(1+n\lambda_i^2)^{-1/2} = \lambda_i T_i^{00}\ ,\ \beta > 0$

$|T_i^{10}| = n^{1/2}\lambda_i(1+n\lambda_i^2)^{-1/2} = n^{1/2}\lambda_i T_i^{00}$

$T_i^{\beta 0} = 0\ ,\ \beta > 1.$

All of these are obeyed by the following example:

$$T_i^{\alpha\beta} = \begin{bmatrix} \nu & \nu\lambda & \nu\lambda & \nu\lambda & \nu\lambda & \nu\lambda & \dots \\ \frac{\nu\lambda}{z} & z\nu & z\nu & z\nu & z\nu & z\nu & \dots \\ 0 & -z & 1+b & b & b & b & \dots \\ 0 & -z & b & 1+b & b & b & \dots \\ 0 & -z & b & b & 1+b & b & \dots \\ 0 & -z & b & b & b & 1+b & . \\ . & . & . & . & . & . & . \end{bmatrix}$$

where $\nu = (1+n\lambda_i^2)^{-1/2}$; $z = n^{-1/2}$; $b = z^2/(1+z)$; $\lambda = \lambda_i$.