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The contribution to rubber elasticity of topological entanglements

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A microscopic explanation of the departures from the statistical kinetic theory of rubber elasticity is given using a topological description of entanglements. This is accomplished in terms of linking numbers which can be topologically defined between pairs of entangled polymer molecules. A statistical mechanical treatment of the linking numbers is presented and an expression derived for the elastic modulus of an entangled coil. Our results show the expected deformation softening in both uniaxial extension and compression. We identify the dependence of this behaviour on the density, the entangling ability of the molecule and on the details of fabrication of the network. We also show that, with the framework of the concepts developed in the paper, the deformation softening behaviour implies that the system is under-entangled with respect to an intrinsic degree of entanglement characteristic of the system. This intrinsic degree of entanglement is defined in the paper and for states of entanglement exceeding this quantity a deformation hardening is predicted.

(Keywords: rubber elasticity; entanglements; linking numbers; uniaxial deformation; modulus; Mooney–Rivilin equation)

1. INTRODUCTION

Numerous experimental studies on rubber networks have demonstrated significant departures from the statistical-kinetic theory of rubber elasticity. The experimental stress–strain data invariably show a deformation softening effect in elongation. The major source of these deviations from the statistical theory is thought to be due to the high degree of inter-chain entanglement which naturally occurs in the concentrated amorphous state. Recent reviews on the current experimental and theoretical status of rubber elasticity have been given by Mark[1] and Staverman[2].

An immediate explanation for some change in the modulus can be given, in terms of the classical theories of rubber elasticity. In the early work of Kuhn, the network junction points were assumed to be firmly embedded in the surrounding medium and to move affinely with the strain. The later work of Guth and James leaves the chains and junction points entirely free to move through each other (phantom network). For a tetra functional network the modulus predicted by the affine model can be twice as large as that predicted from the phantom model. This had led Flory[3], Ronca and Allegra[4] to argue that despite the copious entanglements present in a network of polymer molecules, the effect on configurational changes is unimportant and that the full force of entanglements is felt in restricting the fluctuations of the network junction points. The theory is phenomenological to the extent that the influence of the entanglements on the range of the junction fluctuations depends on the deformation. The other approaches to modelling entanglements takes the complementary view, emphasising the confining effect that they have on the configuration of the chains by means a 'tube' constructed round a 'primitive path'. These ideas are due to de Gennes[5], Edwards and co-workers[6] and have been developed by Marrucci[7], Edwards *et al.*[8] have also developed a slip link model to account for the deformation softening effects.

In the review[1], Mark has presented clear evidence obtained from well characterized polydimethylsiloxane networks for a deformation induced transition from the affine to the phantom network limit. This is in accord with the Flory theory of entanglements having little effect on the configurational properties and only being effective at junction points. However, in sharp contrast to this conclusion is the work of Dossin and Graessley[9] on polybutadiene networks in bulk and solution and Pearson and Graessley[10] on ethylene–propylene copolymer networks. They show that a topological contribution, as measured from the plateau modulus and assumed to be trapped when the network was formed, dominates in these systems. The values of modulus that they obtain are 2.5 to 6.5 times larger than kT/V, which is the maximum contribution possible from the chemical network. Similar results have also been found on a variety of polymers by Gottlieb *et al.*[11], Kramer[12] and by Ferry and coworkers[13]. In particular, Ferry has shown that, by crosslinking entangled networks of polybutadiene in strained states near T_g, a two network systems is formed with different reference states from which the moduli due to entanglements and crosslinks can be found. Their results demonstrate that the entangled network is neo-Hookian and that the entangled network is described by the Mooney–Rivlin equation.

In this paper we hope to partially reconcile these varying experimental results by calculating the entropic properties of a polymer molecule entangled in a random network. The degree of entanglement will be described by the number of times one random coil molecule can wind round, or entangle, with another random coil. We denote this winding or linking number by '*m*' and insist that it remains unchanged during any subsequent configurational changes i.e. is a topological invariant. Then the deviations of the elastic properties of the coil from the Neo–Hookian behaviour are found to be governed by the

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coefficient

$$kTp^2\alpha(1-m^2/\langle m^2\rangle) \qquad (1)$$

where ρ is the macroscopic density of the network, $\langle m^2\rangle$ an equilibrium winding number, which will be defined, and α a characteristic of the local entangling ability of the molecule ($\langle m^2\rangle$ and α are related). We will show that networks deliberately formed so that $m^2<\langle m^2\rangle$ will exhibit a deformation softening. The condition $m^2<\langle m^2\rangle$ may be regarded as under-entanglement and correspondingly for over-entanglement $m^2>\langle m^2\rangle$ we predict a strain hardening effect. Since crosslinking interferes with the entangling process by trapping coils and thereby permanently fixing in their topological properties, we may also anticipate that in many rubber networks formed under normal conditions $m^2\neq\langle m^2\rangle$. However, for those systems that can achieve this intrinsic linking number $\langle m^2\rangle$, then the Flory contention that entanglements do not effect the elastic properties derived from the configurational properties will be justified. In this paper we do not comment on the effects of entanglements on the fluctuation of crosslink points.

2. A WINDING NUMBER DESCRIPTION OF ENTANGLEMENTS

The classical theory of rubber elasticity starts by calculating the number of degrees of freedom $\Omega_0(\underline{R}, s)$ available to a strand of the molecule which is held a distance $\underline{R}$ apart between two junction points separated by an arc length s along the chain. The result is well known and written as

$$\Omega_0(\underline{R},s)=Z^N(3/2\pi ls)^{3/2}\exp-3R^2/2ls \qquad (2.1)$$

where Z is the number of ways each link of statistical length l can be added to the chain ($Nl=s$). The only modification to this theory that we wish to consider in this paper is that due to the reduction in the number of degrees of freedom by the topological entanglement of this strand with the rest of the network. Our model is shown schematically in *Figure 1*, where the strand we are talking about is drawn in a heavy line C_α, while the rest of the network is represented as a continuous random walk coil C_β (thin line) filling a macroscopic box at a finite density ρ_β. We will take the degree of topological entanglement of these two curves to be given by the number of times C_α is linked to C_β and denote this entangling or linking number by '*m*'. The linking number is given as the value of the following integral, proposed by Gauss and first used by Edwards[14] in the context of polymer physics

$$I_{\alpha\beta}(C_\alpha,C_\beta)=\frac{1}{4\pi}\oint_{C_\alpha}\mathrm{d}s_\alpha\oint_{C_\beta}\mathrm{d}s_\beta\,\dot{\underline{r}}(s_\alpha)\times\dot{\underline{r}}(s_\beta).\frac{\{\underline{r}(s_\alpha)-\underline{r}(s_\beta)\}}{|\underline{r}(s_\alpha)-\underline{r}(s_\beta)|^3} \qquad (2.2)$$

The notation is illustrated in *Figure 1*, with $\dot{\underline{r}}=\mathrm{d}\underline{r}/\mathrm{d}s$ as the tangent vector to the curve.

We will treat the winding numbers of the C_α coil with the network (averaged over all configurations) as gaussian random variables. Then the probability that the C_α configuration is entangled '*m*' times with the network is given by the Gaussian distribution

$$p(C_\alpha;m)=\{2\pi M^2(C_\alpha)\}^{-1/2}\exp-\frac{m^2}{2M^2(C_\alpha)} \qquad (2.3)$$

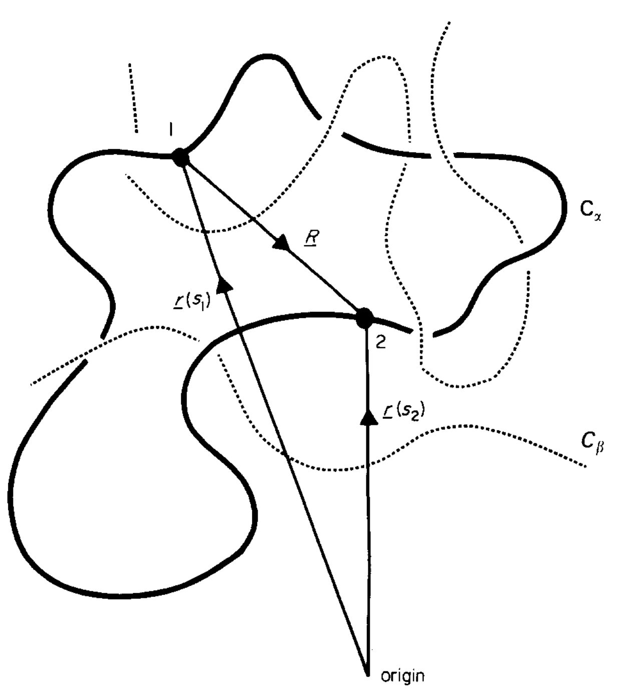

Figure 1 The theory presented in the paper calculates the elastic energy of the strand shown in a heavy line and labelled C_α. The rest of the elastic network is represented by the dotted line C_β and provides the topological constrain on the C_α configuration (———): C_α (elastic strand); (·····): C_β (network)

where $M^2(C_\alpha)$ represents the fluctuation of winding numbers of the C_α coil and is given by

$$M^2(C_\alpha)=\langle I^2_{\alpha\beta}(C_\alpha,C_\beta)\rangle_{\{c\beta\}} \qquad (2.4)$$

An explicit expression for $M^2(C_\alpha)$ is given in Appendix (1).

The influence of the weighting factor in equation (2.3) on the random coil statistics of the C_α configuration represents a very difficult problem which has been considered in previous work[15] as well as a more systematic derivation of equation (2.3). It is not our intention here to pursue the theoretical aspects of this problem instead we will work at a level of approximation that leads to the effect of entanglements on the free energy as being additive. We will replace the configuration dependent quantity $M^2(C_\alpha)$ by an averaged value $\langle m^2\rangle_{R,s}$, where the averaging is done over all the configurations $\{C_\alpha\}$ subject to the constaints that $\underline{r}(s_1)-\underline{r}(s_2)=\underline{R}$, i.e.

$$\langle m^2\rangle_{\underline{R},s}=\langle M^2(C_\alpha)\rangle_{\{c_\alpha\};r_1-r_2=R} \qquad (2.5)$$

so that the distribution equation (2.3) of winding numbers becomes

$$p(C_\alpha;m)\equiv p(\underline{R},s;m)=\frac{1}{\{2\pi\langle m^2\rangle_{R,s}\}^{1/2}}\,exp-\frac{m^2}{2\langle m^2\rangle_{\underline{R},s}} \qquad (2.6)$$

An expression for $\langle m^2\rangle_{R,s}$ is given in Appendix (2). Finally we take as the number of degrees of configurational freedom of a coil held at distance $\underline{R}$ apart between two junction points and entangled '*m*' times with the network the following product of factors

$$\begin{aligned}\Omega(R,s;m)&=Z^N G_0(\underline{R},s)p(\underline{R},s;m)\\&=\Omega_0(\underline{R},s)p(\underline{R},s;m)\end{aligned} \qquad (2.7)$$

Before investigating the consequences of this form for the free energy we need an additional refinement of the model illustrated in *Figure 1*. In particular we wish to take into account the fact that the test coil C_α will be subject to many independent entanglement constraints. In reality we should specify, in terms of winding numbers, the topological relationship between our test coil and every other loop in the system. Of course in order to make the problem tractable and in particular to maintain the topological nature of the constraint we are forced to deal with the rest of the system in the simplified way that we have described. However by filling the macroscopic box with a single long loop of polymer material we allow a large amount of winding number cancellation due to the single loop threading backwards and forwards through the area spanned by the test loop. To avoid this we consider that the test loop is subject to N_c independent entanglement constraints, specified by the linking numbers m_β, $\beta = 1 \cdots N_c$. N_c is then a parameter of our model which we are really not in a position to calculate. This would require a more detailed treatment of the system, including cross links and network structure, than we can give in this paper, a simple estimate of N_c that ultimately accords with experiment may be obtained by the following argument: the volume occupied by the test coil C_α will be $\approx (Nl^2)^{3/2}$ and if we consider that this is also threaded by N_c other independent polymer strands, then we can estimate that within this volume the density ρ of monomer units is

$$\rho \sim N_c N/(Nl^2)^{3/2} \tag{2.8}$$

and so we estimate

$$N_c \sim \rho l^3 \sqrt{N} \tag{2.9}$$

The importance of this estimate will be seen later in equation (3.3) when we show that deviations due to entanglements from the classical theory are proportional to the combination of terms

$$\rho N_c / \sqrt{N}$$

With our estimate for N_c, the deviations are independent of molecular weight and proportional to ρ^2.

To accommodate this aspect of the problem without going into details of network structure etc. we envisage filing or macroscopic box with N_c loops each at a constant density ρ_β with $N_c \rho_\beta = \rho$. Since the entanglement constraints are independent we use a product of factors similar to equation (2.7), so that the number of degrees of freedom is given by

$$\Omega(\underline{R}, s; \{m_\beta\}) = \Omega_0(\underline{R}, s) \prod_{\beta=1}^{N_c} p(\underline{R}, s; m_\beta) \tag{2.10}$$

and the free energy

$$F(\underline{R}, s; \{m_\beta\}) = F_0(\underline{R}, s) + \frac{kT}{2} \sum_{\beta=1}^{N_c} \left\{ \ln\left(\langle m^2 \rangle_{\underline{R},s} + \frac{m^2{}_\beta}{\langle m^2 \rangle_{\underline{R},s}} \right) \right\} \tag{2.11}$$

where F_0 is the free energy in the absence of any topological constraints.

With these approximations the entanglement contribution to the free energy (and hence the elastic properties) is additive and entirely controlled by the functional form of $\langle m^2 \rangle_{\underline{R},s}$. To recap this represents the average of the (winding number)^2 of two coils, one of which is held a distance $\underline{R}$ apart between chain points s_1 and s_2 and the other fills a box at a uniform density. In Appendix (2) we have derived the following expression for $\langle m^2 \rangle_{\underline{R},s}$

$$\langle m^2 \rangle_{\underline{R},s} = \langle m^2 \rangle \left\{ 1 + \sqrt{\frac{l^*}{l}} \frac{1}{\sqrt{N}} \sqrt{\frac{R^2}{Nl^2}} \cdot I(R) \right\} \tag{2.12}$$

where $\langle m^2 \rangle$ represents the average (winding number)^2 between the two coils in the absence of any constraint

$$\langle m^2 \rangle = \langle I^2_{\alpha\beta}(c_\alpha, c_\beta) \rangle_{\{c_\beta\},\{c_\alpha\}} \tag{2.13}$$

whereas

$$\langle m^2 \rangle_{\underline{R},s} = \langle I^2_{\alpha\beta}(c_\alpha, c_\beta) \rangle_{\{c_\beta\}:\{c_\alpha\},\underline{r}_1 - \underline{r}_2 = \underline{R}} \tag{2.14}$$

The quantity l^* is a new short distance length scale ($\sim l$) we are forced to introduce in order to describe the local structure of the polymer with regard to its ability to entangle. In particular the average winding number is related to l^* by (Appendix 2, equation (8)).

$$\langle m^2 \rangle = \frac{\rho_\beta l^3}{36\pi} N \sqrt{\frac{l}{l^*}} \tag{2.15}$$

If we define a new parameter m_0 by

$$m_0^2 = \frac{\rho_\beta l^3}{36\pi} \sqrt{\frac{l}{l^*}} \tag{2.16}$$

then $\langle m^2 \rangle = N m_0^2$.

This assigns to m_0 and entanglements a similar role to that played by l and the size of the molecule, through the relation

$$\langle R^2 \rangle = Nl^2$$

In both cases all local detail is encapsulated in a minimal parameter such as l or l^*. Finally the function $I(R)$ appearing in equation (2.12) is also defined in Appendix (2) by an integral expression for which an analytic form does not seem to be available. However for large R it turns out to be only logarithmically dependent on R. Thus the linear R dependence is the dominant feature in equation (2.12). In the next section we investigate the consequences this form for $\langle m^2 \rangle_{\underline{R},s}$ has on the elastic properties of the coil.

3. ELASTIC PROPERTIES

The free energy of the entangled coil C_α is given by equation (2.11). The derivation of the elastic properties now follows in the usual way. We ignore the difficulties associated with the role of the network and deformation and consider $\underline{R}$ to be related to the vector $\underline{R}_0$ between junction points by

$$\underline{R} = \underline{\underline{\lambda}} \cdot \underline{R}_0 \tag{3.1}$$

where $\underline{\underline{\lambda}}$ is the deformation tensor. For the case of simple extension or compression at constant volume we set

$$R^2=\frac{(\lambda^2+2\lambda^{-1})}{3}R_0^2 \tag{3.2}$$

then the tensile force per unit undeformed area is given by

$$\sigma=\frac{\xi}{V}\frac{\mathrm{d}F}{\mathrm{d}\lambda}(\underline{R},\, s;\, \{m_\beta\}) \tag{3.3}$$

where ξ/V is the number of active strands per unit volume. Using equation (2.11) for the free energy we can write

$$\sigma-\sigma_0=\frac{\xi}{V}\cdot\frac{kT}{2}\frac{N_c}{\langle m^2\rangle_{\underline{R},s}}\left\{1-\frac{1}{N_c}\sum_{\beta=1}^{N_c}\frac{m_\beta^2}{\langle m^2\rangle_{\underline{R},s}}\right\}\frac{\mathrm{d}F}{\mathrm{d}\lambda}\langle m^2\rangle_{\underline{R},s} \tag{3.4}$$

where σ_0 is the Hookean result

$$\sigma_0=kT\cdot\frac{\xi}{V}\cdot\frac{R_0^2}{Nl^2}\cdot(\lambda-\lambda^{-2}) \tag{3.5}$$

An expression for $\langle m^2\rangle_{\underline{R},s}$ has already been presented in equation (2.12), where we pointed out that the dominant dependence of $\langle m^2\rangle_{\underline{R},s}$ on R was linear. For the purpose of discussing the qualitative influence of this term on the elastic properties we will treat the functional form as being exactly linear and write

$$\langle m^2\rangle_{\underline{R},s}=\langle m^2\rangle\left\{1+I\sqrt{\frac{l^*}{l}}\cdot\frac{1}{\sqrt{N}}\cdot\frac{R}{\sqrt{Nl^2}}\right\} \tag{3.6}$$

where the function $I(R)=I$ is treated as a constant. The final results will be presented using a full numerical evaluation of equation (2.12) but do not show any significant difference.

Using equation (3.2) for R we can write

$$\langle m^2\rangle_{\underline{\underline{\lambda}}\cdot\underline{R}_0,s}=\langle m^2\rangle\left\{1+\frac{I}{\sqrt{N}}\cdot\sqrt{\frac{l^*}{l}}\cdot\sqrt{\frac{R_0^2}{Nl^2}\frac{(\lambda^2+2\lambda^{-1})}{3}}\right. \tag{3.7}$$

For deformations $\lambda\ll\sqrt{N}$, the second term in the bracketed expression of $\langle m^2\rangle_{\underline{R},s}$ is small ($\sim N^{-1/2}$) compared to the first term (~ 1). When this term is not differentiated with respect to λ we will approximate it as

$$\langle m^2\rangle_{\underline{R},s}\simeq\langle m^2\rangle \tag{3.8}$$

and write

$$\frac{1}{\langle m^2\rangle_{\underline{R},s}}\frac{\mathrm{d}F}{\mathrm{d}\lambda}\langle m^2\rangle_{\underline{\underline{\lambda}}\cdot\underline{R}_0,s}=\frac{I}{\sqrt{N}}\cdot\sqrt{\frac{l^*}{l}}\cdot\sqrt{\frac{2R_0^2}{3Nl^2}}\frac{\lambda-\lambda^{-2}}{\sqrt{\lambda^2+2\lambda^{-1}}} \tag{3.9}$$

It is usual to write the reduced stress σ^* or modulus as

$$\sigma^*=\sigma/(\lambda-\lambda^{-2}) \tag{3.10}$$

so that using equations (3.9) and (3.10) in equation (3.4) we get

$$\sigma^*-\sigma_0^*=\frac{\xi}{V}\cdot\frac{N_c}{\sqrt{N}}kT\sqrt{\frac{R_0^2}{Nl^2}}\times\left\{1-\frac{1}{N_c}\sum_{\beta=1}^{N_c}\frac{m_\beta^2}{\langle m^2\rangle}\right\}\frac{I}{\sqrt{\lambda^2+2\lambda^{-1}}} \tag{3.11}$$

This might be regarded as the major qualitative result of this paper. The deviations due to entanglements from the classical theory of rubber elasticity are entirely contained in the term $(\lambda^2+2\lambda^{-1})^{-1/2}$. This has the form of a broad maximum at $\lambda=1$ and falls off slowly in compression as $(\lambda^{-1})^{-1/2}$ and is linear in λ^{-1} in extension for $\lambda\gg 1$. These features are confirmed by an exact evaluation of equation (2.12) based on the full form for $I(R)$ given by equation (16) in Appendix (2). The result is shown in *Figure 2* and agrees qualitatively with the experimental results of Gottlieb *et al.*[11].

The linear dependence on λ^{-1} in extension is reminiscent of the phenomenological equation proposed by Mooney and Rivlin to account for the departures of rubber elasticity from the statistical theory. They wrote

$$\sigma^*=\frac{\sigma}{\lambda-\lambda^{-2}}=2C_1+2C_2/\lambda \tag{3.12}$$

While our result is significantly different from this over the whole range of deformations, we can in the limit $\lambda\gg 1$ approximately identify the Mooney–Rivlin constant C_2 as

$$C_2=\frac{\xi}{V}\cdot\frac{N_c}{\sqrt{N}}kT\cdot\left\{1-\frac{1}{N_c}\sum_{\beta=1}^{N_c}\frac{m_\beta^2}{\langle m^2\rangle}\right\}I \tag{3.13}$$

This expression for C_2 has three features worth commenting on:

(i) it depends quadratically on the density since the number of active strands per unit volume ξ/V is clearly proportional to the density and for the number of chains

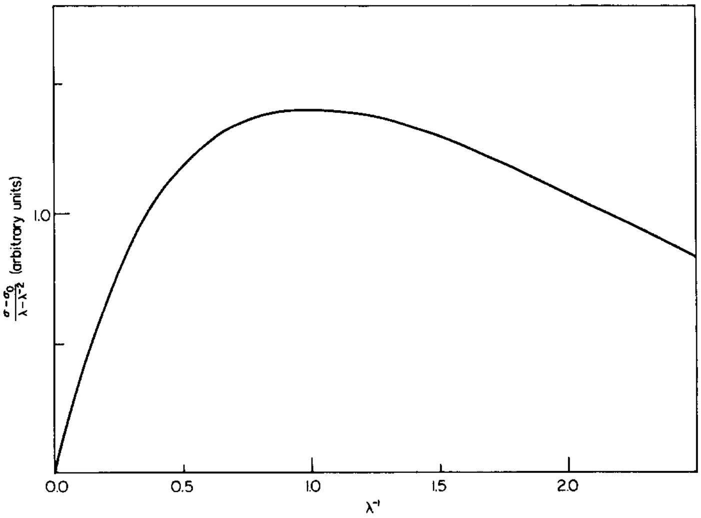

Figure 2 The reduced stress or modulus calculated numerically from equations (2.12, 3.4) plotted as a function of the (deformation)$^{-1}$ in a uniaxial test. Approximate Mooney–Rivlin behaviour is shown in extension ($\lambda^{-1}<1$)

N_c pervading the volume of a single chain has already been plausibly estimated in equation (2.9) to be given approximately by

$$\frac{N_c}{\sqrt{N}} \sim \rho l^3$$

(ii) C_2 depends on the local atomic ability of the molecule to entangle through the parameter l^* which was related in section 3 to the average (linking number)^2 of a coil of N segment by

$$\langle m^2 \rangle = \rho_\beta l^3 N \sqrt{\frac{l}{l^*}}$$

(iii) The factor of

$$\left\{1 - \frac{1}{N_c} \sum_\beta m_\beta^2 / \langle m^2 \rangle\right\}$$

in the expression for C_2 depends explicitly on the actual distribution of linking number $\{m_\beta\}$ present in the system. This will depend on the conditions and method of preparation of the network and may well explain the sensitivity of the C_2 term to these features. In particular if during the fabrication of the network the degree of entanglement can be maintained at or close to the characteristic value $\langle m^2 \rangle$, defined in section (3) equation (3.7), then the Mooney–Rivlin term should be largely absent.

This result would also seem to confirm an opinion of Flory, which has also been expressed by Prager and Frisch[16] that it is probably better to assume that the attractive and repulsive effects of entanglements just cancel and to ignore their influence on the elastic properties altogether. In all of this work we have not dealt with the influence of entanglements on the fluctuations of network junction points, however, under circumstances when the configurational effects are minimal, i.e. $m^2 = \langle m^2 \rangle$, the entanglement restricted junction theory of Flory may well be justified. For networks specifically prepared in controlled circumstances we can expect that the ensemble averaged m^2 of linking numbers $\{m_\beta\}$ will not be equal to the value $\langle m^2 \rangle$. This latter quantity represents the intrinsic degree of entanglement between two unrestricted random walk molecules. In these systems for which $m^2 \neq \langle m^2 \rangle$, then we can expect a topological contribution to the C_2 term. Furthermore, as only positive values of C_2 seem to have been reported in the literature, our result would imply that in the majority of cases of network preparation $m^2 < \langle m^2 \rangle$. In other words an under-entangling, rather than over-entangling ($\langle m^2 \rangle \langle m^2 \rangle$), is generally achieved within the context of the formalism and expressions we have developed in this paper.

CONCLUSION

We have described the topological aspect of polymer chain entanglement by means of a Gaussian distribution of linking numbers. The important quantity $\langle m^2 \rangle_{R,s}$ representing the average (linking member)^2 of two random coils was calculated using a topological result due to Gauss. This term leads to deviations from the classical theory of rubber elasticity and suggests why such deviations as measured by the Mooney–Rivlin coefficient C_2 are sensitive to the method of preparation of the network. For experimental situations reported in the literature which invariably show a positive C_2 term, we showed that this implies that these systems are under entangled with respect to an intrinsic degree of entanglement $\langle m^2 \rangle$ characteristic of the particular system. It would clearly be interesting to produce an over entangled situation which should then show a negative or strain hardening C_2 term. For systems where the degree of entanglement fabricated into the material by the cross linking process corresponds to the intrinsic entanglement number $\langle m^2 \rangle$, then the topological contribution to the Mooney–Rivlin term will vanish. However, we have not considered in this paper the effect of entanglements on the fluctuation of the junction points. Under these circumstances the theory of Flory may well apply to give a contribution in addition to the topological result.

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APPENDIX A

The average of I^2

The winding number $I_{\alpha\beta}$ between the chains C_α and C_β from equation (3.1) can be written in the form of a line integral

$$I_{\alpha\beta} = \oint_{C_\alpha} \mathrm{d}\underline{r}_\alpha \cdot \underline{A}_\beta(\underline{r}_\alpha) \tag{A.1}$$

where the vector field $\underline{A}_\beta(\underline{R})$ is given from equation (3.1) as

$$\underline{A}_\beta(R) = (4\pi)^{-1} \oint_{C_\beta} \mathrm{d}\underline{r}_\beta \times \frac{(\underline{r}_\beta - \underline{R})}{|\underline{r}_\beta - \underline{R}|^3} \tag{A.2}$$

The averaging over the configurations of C_α and C_β of $I_{\alpha\beta}^2$ is given by

$$\langle I_{\alpha\beta}^2 \rangle_{C_\alpha, C_\beta} = \oint_{C_\alpha} \oint_{C_\beta} \sum_{ij} \langle \mathrm{d}\underline{r}_{\alpha i} \mathrm{d}\underline{r}'_{\alpha j} \langle \underline{A}_{\beta i}(\underline{r}_\alpha) \underline{A}_{\beta j}(\underline{r}'_\alpha) \rangle_{c_\beta} \rangle_{c_\beta} \tag{A.3}$$

where i and j label the Cartesian coordinates of the vectors $\mathrm{d}\underline{r}$ and $\underline{A}_\beta(\underline{R})$. In section (2) of the paper we have identified

$$M^2(C_\alpha) = \langle I_{\alpha\beta}^2 \rangle_{\{C_\beta\}}$$

The average of the fluctuations $\langle \underline{A}(\underline{R}) \underline{A}(\underline{R}') \rangle$ of the vector field $\underline{A}$ are most easily dealt with by exploiting an analogy with electromagnetism. We can observe that if C_β represented a line of magnetic flux, then $\underline{A}_\beta(\underline{R})$ would be the vector potential due to this flux line. The flux line is given by Curl $\underline{A}$ which from equation (A.2) is given by

$$\mathrm{Curl}\, \underline{A}_\beta(\underline{R}) = \oint_{C_\beta} \mathrm{d}\underline{r}_\beta \delta(\underline{r}_\beta - \underline{R}) = \underline{U}(\underline{R}) \tag{A.4}$$

$\underline{U}(R)$ is the density of β-chain bond vectors at the space point $\underline{R}$ and is the analogue of the magnetic flux $\underline{B}(R)$.

Using the random walk model for a polymer chain we can readily evaluate the fluctuations in the Curl $\underline{A}(\underline{R})$ field, the result is

$$\langle\{\underline{\nabla}\times\underline{A}(\underline{R})\}_i\{\underline{\nabla}\times\underline{A}(\underline{R})\}_j\rangle_{c_\beta}=\rho_\beta l^2\delta(\underline{R}-\underline{R}')\delta_{ij} \quad (A.5)$$

and in terms of the Fourier transform $\tilde{\underline{A}}(q)$ of $\underline{A}(R)$, equation (A.5) reads

$$\langle\{\underline{q}\times\tilde{\underline{A}}(\underline{q})\}_i\{\underline{q}'\times\tilde{\underline{A}}(\underline{q}')\}_j\rangle_{c_\beta}=\rho_\beta l^2(2\pi)^3\delta(\underline{q}+\underline{q}')\delta_{ij} \quad (A.6)$$

For closed loops we also have the condition that $\underline{A}(\underline{R})=0$ and consequently the desired average of the fluctuations of $\underline{A}$ can be found from equation (A.6) as

$$\langle\tilde{A}_1(\underline{q})\tilde{A}_j(\underline{q}')\rangle_{C_\beta}=\rho_\beta l^2(2\pi)^3\delta(\underline{q}+\underline{q}')\frac{1}{3q^2}[\delta_{ij}-\hat{q}_i\hat{q}_j] \quad (A.7)$$

where $\hat{\underline{q}}$ is the unit vector $\underline{q}/|\underline{q}|$. Using this result $\langle I^2_{\alpha\beta}\rangle_{C_\alpha,C_\beta}$ can be written as

$$\frac{\rho l^2}{3}\oint_{C_\alpha}\oint_{C_\alpha}\sum_{ij}\langle \mathrm{d}\underline{r}_{I\alpha}\mathrm{d}\underline{r}'_{j\alpha}$$

$$\times\int\frac{\mathrm{d}^3q}{(2\pi)^3}\exp i\underline{q}\cdot(\underline{r}_\alpha-\underline{r}'_\alpha)\frac{[\delta_{ij}-\hat{q}_l\hat{q}_j]}{q^2}\rangle_{c_\alpha} \quad (A.8)$$

The q integral can be done and gives the Oseen tensor

$$\begin{aligned}t_{ij}(r)&=(2\pi)^{-3}\int\mathrm{d}^3q\exp i\underline{q}\underline{r}[\delta_{ij}-\hat{q}_l\hat{q}_j]/q^2\\&=(8\pi r)^{-1}[\delta_{ij}+\hat{r}_i\hat{r}_j]\end{aligned} \quad (A.9)$$

Therefore we obtain the result in this paper as

$$\begin{aligned}\langle I^2_{\alpha\beta}\rangle_{c_{\alpha},c_\beta}&=\oint_{C_\alpha}\oint_{C_\alpha}\langle\mathrm{d}\underline{r}\cdot\underline{T}(\underline{r}-\underline{r}')\cdot\mathrm{d}\underline{r}'\rangle_{C_\alpha}\\&=\frac{\rho_\beta l^2}{24\pi}\oint_{C_\alpha}\mathrm{d}s\oint_{C_\alpha}\mathrm{d}s'\left\{\frac{\dot{r}(s)\cdot\dot{r}(s')}{|r-r'|}\right.\\&\qquad\left.+\frac{\dot{r}\cdot(r-r')r'\cdot(r-r')}{|r-r'|^3}\right\}\end{aligned} \quad (A.10)$$

APPENDIX B

The evaluation of $\langle \mathrm{m}^2\rangle_{\mathrm{R,s}}$

From equation (2.5) and equation (A.10) of Appendix A, we have that

$$\begin{aligned}\langle m^2\rangle_{\underline{R},s}&=\langle m^2(C_\alpha)\rangle_{C_\alpha;r_1-r_2=R}\\&=\oint_{C_\alpha}\mathrm{d}s\,\mathrm{d}s'\langle\dot{\underline{r}}\cdot\underline{T}(\underline{r}-\underline{r}')\cdot\mathrm{d}\underline{r}'\rangle_{G_0(\underline{R},N)}\end{aligned} \quad (B.1)$$

where $G_0(\underline{R},N)$ signifies that the averaging is to be carried out over a Gaussian distribution of chain vectors with 2 points on the chain a distance L apart held at the fixed $\underline{R}$ apart. The combination $\underline{r}\cdot\underline{T}\cdot\underline{r}'$ with the tensor $\underline{T}$ given by (3.4) can be written as (see equation (8) of Appendix A)

$$\frac{\rho l^2}{3}\int\frac{\mathrm{d}^2q}{(2\pi)^3}\frac{(\underline{q}\times\dot{\underline{r}})\cdot(\underline{q}\times\dot{\underline{r}}')}{q^4}\exp_i\underline{q}\cdot(\underline{r}-\underline{r}') \quad (B.2)$$

It is sufficient to split the average in (B.1) into an average over the term $(\underline{q}\times\dot{\underline{r}})\cdot(\underline{q}\times\dot{\underline{r}}')$ containing only the bond vectors $\dot{\underline{r}},\dot{\underline{r}}'$ and a separate average over the term $\exp i\underline{q}\cdot(\underline{r}-\underline{r}')$ involving only the coordinate vectors $\underline{r}$, $\underline{r}'$. We use the following results:

$$\frac{\langle(\underline{q}\times\dot{\underline{r}})\cdot(\underline{q}\times\dot{\underline{r}}')\rangle_{G_0(\underline{R},N)}}{q^2}$$

$$=\tfrac{2}{3}l\{\delta(s-s')-L^{-1}\}+\frac{R^2}{L^2}(1-\cos^2\theta) \quad (B.3)$$

where θ is the angle between q and R, and

$$\begin{aligned}\langle\exp i\underline{q}\cdot(\underline{r}-\underline{r}')\rangle_{G_0}&=\exp\left[-q^2\frac{|s-s'|l}{6}\right.\\&\quad\left.\times\left\{1-\frac{|s-s'|}{L}\right\}+iqR\cos\theta\frac{|s-s'|}{L}\right]\end{aligned} \quad (B.4)$$

The $\delta(s-s')$ in equation (B.3) gives rise to a cut-off dependent term. We can see this more directly by evaluating the unrestricted linking number $\langle m^2\rangle$, given by

$$\begin{aligned}\langle m^2\rangle&=\langle M^2(C_\alpha)\rangle_{\{C_\alpha\}}\\&=\frac{2}{3}\frac{\rho_\beta l^2}{24\pi}\oint_{C_\alpha}\mathrm{d}s\,\mathrm{d}s'\langle\frac{\dot{r}\cdot\dot{r}'}{|r-r'|}\rangle_{\{C_\alpha\}}\end{aligned} \quad (B.5)$$

For the random coil model, the correlation of bond vectors shows no local monomer structure and is given by

$$\langle\dot{\underline{r}}(s)\cdot\dot{\underline{r}}(s')\rangle=l\delta(s-s') \quad (B.6)$$

The denominator in equation (B.5) is singular at $s=s'$ due to the factor $|r-r'|^{-1}$. The formula equation (B.5) for $\langle m^2\rangle$ we are using is analogous to the self inductance of an electrical circuit. In fact in this approach the average (winding number)^2 of the C_α coil with the uniform background is a measure of the self inductance of the C_α coil. In the electrical case a small distance cut-off occurs in the form of the thickness of the wire. However, in our case we introduce a cut off l^* by modifying

$$|\underline{r}-\underline{r}'|\rightarrow\sqrt{(r-r')^2+ll^*} \quad (B.7)$$

Then

$$\langle m^2\rangle=\frac{1}{36}\frac{\rho_\beta l^3}{\pi}\frac{L}{\sqrt{ll^*}}=Nm_0^2 \quad (B.8)$$

with

$$m_0^2=\frac{1}{36\pi}\rho_\beta l^3\sqrt{\frac{l}{l^*}} \quad (B.9)$$

With this cut off procedure and using (3) and (4) we can write equation (B.1) as

$$\begin{aligned}\langle m^2\rangle_{\underline{R},s}-Nm_0^2&=\frac{\rho l^2}{3}\frac{R^2}{L^2}\int\mathrm{d}s\,\mathrm{d}s'\int\mathrm{d}q\frac{\mathrm{d}\cos\theta}{(2\pi)^2}\\&\quad\left\{(1-\cos^2\theta)-\frac{2Ll}{3R^2}\right\}\\&\quad\times\exp\left[-q^2\frac{tl}{6}(1-t/L)+iqR\frac{t}{L}\cos\theta\right]\end{aligned} \quad (B.10)$$

where $t=|s-s'|$.

The angular integrations over θ are standard and yield the Bessel functions $J_{3/2}, J_{1/2}$.

$$\langle m^2\rangle_{\underline{R},s} - Nm_0^2 = \frac{2}{3}\frac{\rho l^2}{(2\pi)^{3/2}}\frac{R}{L}$$

$$\left[\int_0^L \frac{\mathrm{d}s\mathrm{d}s'}{|s-s'|}\int_0^\infty \mathrm{d}z \exp - z^2\frac{Ll}{6R^2}\frac{1-t/L}{t/L}\right.$$
$$\left.\left\{z^{-3/2}J_{3/2}(z) - \frac{Ll}{3R^2}z^{-\frac{1}{2}}J_{\frac{1}{2}}(z)\right\}\right] \tag{B.11}$$

where

$$z = \frac{R|s-s'|q}{L}$$

The integral over q (or z) is accomplished in terms of the degenerate hypergeometric function $M(a, b, z)$ e.g.

$$\int_0^\infty \mathrm{d}z\, z^{-3/2}J_{3/2}(z)\exp - Z^2/4\alpha = \frac{1}{3\sqrt{2\alpha}}M(\tfrac{1}{2}, 5/2, -\alpha) \tag{B.12}$$

where

$$\alpha = \frac{3R^2}{2Ll}\frac{|s-s'|}{L-|s-s'|}$$

The right-hand side of equation (B.11) becomes

$$\frac{\sqrt{2}}{9}\frac{\rho l^2}{(2\pi)^{3/2}}\frac{R}{L}\int\frac{1}{\sqrt{\alpha}}\left\{M(\tfrac{1}{2}, 5/2, -\alpha)\right.$$
$$\left. - \frac{Ll}{R^2}M(\tfrac{1}{2}, 3/2, -\alpha)\right\}\frac{\mathrm{d}s\,\mathrm{d}s'}{|s-s'|} \tag{B.13}$$

The ds ds' integrals can be transformed to a single integral over the variable α and the final result written as

$$\langle m^2\rangle_{\underline{R},s} - Nm_0^2 = \frac{4}{9}\sqrt{2}\frac{\rho l^3}{(2\pi)^{3/2}}\sqrt{N}\sqrt{\frac{R^2}{Nl^2}}$$
$$\times\int_0^\infty \frac{\mathrm{d}\alpha}{\sqrt{\alpha}}\frac{1}{1+\alpha 2Ll/3R^2}$$
$$\times\left\{M(\tfrac{1}{2}, 5/2, -\alpha) - \frac{Ll}{R^2}M(\tfrac{1}{2}, 3/2, -\alpha)\right\} \tag{B.14}$$

Finally, we can write equation (B.14)

$$\langle m^2\rangle_{R,s} = \langle m^2\rangle\left\{1 + \sqrt{\frac{l^*}{l}}\sqrt{\frac{R^2}{Nl^2}}\frac{1}{\sqrt{N}}I(R)\right\} \tag{B.15}$$

where

$$I(R) = \frac{6}{\sqrt{\pi}}\int_0^\infty \frac{\mathrm{d}\alpha}{\sqrt{\alpha}}\frac{1}{1+\alpha\frac{2Ll}{3R^2}}$$
$$\times\left\{M(\tfrac{1}{2}, 5/2, -\alpha) - \frac{Ll}{R^2}M(\tfrac{1}{2}, 3/2, -\alpha)\right\} \tag{B.16}$$

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