Theor Chim Acta (1992) 82: 407–417

Theoretica Chimica Acta

Topologically entangled polymers

D. Thirumalai

Institute for Physical Science and Technology and Department of Chemistry, University of Maryland, College Park, MD 20742, USA

Received April 9, 1991/Accepted June 10, 1991

Summary. The statistical mechanics of a ring polymer confined to a plane and entangled with many randomly placed thin rods perpendicular to the plane are considered. The entanglements are characterized by the Gauss linking number. If the statistics of the random distribution of the rods is given by only the second cumulant then it is shown that the resulting entanglement problem can be solved formally exactly. For this special case the exact solution becomes possible because the problem can be reduced to one involving the winding of the polymer around one infinitely thin rod. The exact solution can be obtained for both the annealed and the quenched random distribution of obstacles. The entanglement of the ring polymer around the obstacles leads to a repulsive topological potential which is an effective interaction between the polymer and the rods. The origin of this potential is solely due to the constraint that the winding number be conserved. It is shown that for $R^2/Ll \ll l$ (R is the location of the polymer segment, L is the total length of the polymer, and l is the length of the monomer) the topological potential for the annealed random case goes as $N \ln \ln(Ll/R^2)$ where N is the number of obstacles whereas for the quenched random case the potential is given by $C \ln Ll/R^2$, where C is a numerical constant that depends on N.

Key words: Ring polymer – Entanglement of polymers – Polymer entanglement – Topological potential

1. Introduction

In 1967 Prager in collaboration with Frisch published a remarkable paper [1] on the statistical mechanics of a simple entanglement in polymer systems. It had been previously established that entanglements must be extremely important in the description of gels, rubber, and other crosslinked systems [2]. Nowadays it is suspected that effects of entanglements are relevant in the theory of the dynamics of polymer solutions even in the infinite dilution limit [3]. However no microscopic treatment of entanglement in polymeric systems has been possible because a complete analysis of entanglement requires the incorporation of constraints

imposed by the topological relationship between a pair of polymer molecules into the statistical mechanics calculation [4, 5]. Strictly speaking the classification of these constraints must involve the theory of knots [6], which is a subject that is still being developed. Prager and Frisch recognized the difficulties associated with treating the statistical mechanics of entanglements. In order to provide a simple illustration of the significance of topological entanglements they used a simple analytical invariant, namely the Gauss invariant, to characterize the different topological classes that results when the Gaussian chain loops around the thin rod. In this case the winding number is conserved, and the configurations having different winding numbers belong to distinct topological classes. The statistical mechanics of the resulting problem, which involves the incorporation of the constraint that the winding number be a constant, was solved exactly by Prager and Frisch. These results were independently obtained by Edwards [7] using path integral methods. These two papers were the first, and perhaps the most instructive ones that showed how the results for a simple system (a Gaussian chain) can be profoundly changed when the constraint is taken into account. The most dramatic consequence of incorporating the constraint into the theory is that the system can support an application of stress indefinitely, i.e., it behaves like an elastic system. The nature of the elastic response for this simple system turns out to be extremely complex as was first pointed out by Prager and Frisch. It is for this reason the treatment of topological entanglements is believed to be relevant in dense polymeric systems which invariably exhibit viscoelastic properties. The Prager–Frisch–Edwards (PFE) model has been extended in a variety of interesting ways over the last twenty-four years [5, 8–12].

In this paper the PFE model is generalized to include the possibility of entanglement of a phantom ring polymer confined to a plane (two dimensions) in the presence of several randomly placed rods perpendicular to the plane. This model was considered earlier by Tanaka [13] who provided an approximate solution in the case when the randomness is annealed. Our solution to the problem, which is very different from the one provided by Tanaka, follows more closely the path integral approach introduced by Edwards [7, 14]. In particular we show that if the statistics of the randomly placed obstacles is Gaussian requiring only two moments to specify the statistics then the problem can be mapped onto the entanglement of the ring polymer with a single rod. The latter problem is precisely that solved by PFE, and the results obtained by these authors can be profitably used. Although this mapping allows the problem to be solved exactly the approximate variational estimate of the annealed free energy obtained by Tanaka is quite useful.

The basic physics of the problem is easy to understand. The topological constraint, namely that the winding number be a constant, leads to a considerable reduction in entropy. The reduction in entropy can be expressed as an effective repulsive potential of mean force, and is referred to as the topological potential. The reason this model is useful is because in dense polymer systems the motion of a given polymer is impeded by constraints due to topological entanglement with other polymer molecules. The simplest way of describing such constraints, encountered for example in vulcanized materials [15], is by using the Gauss invariant. In these systems if one is concerned with times less than the typical creep times then the topological constraints due to the rods may be analogous to the restrictions a typical polymer molecule encounters due to the other polymer molecules.

2. Annealed randomness

Consider a long polymer molecule confined to lie in a plane. In this paper the excluded volume interactions between the monomer segments will be ignored and, hence the polymer is a phantom chain. The effects of excluded volume on the statistics of polymers with topological constraints will be treated separately [16]. The configuration of the polymer molecule can be specified as a random walk of step length l, which roughly corresponds to the Kuhn length. In the continuum limit the probability that a polymer molecule at time 0 (the role of time being played by the distance along the arc length of the polymer) is at R_1 and at a later time L it is at R_2 is given by [4]:

$$G(R_2, L; R_1, 0) = \int_{r(0)=R_1}^{r(L)=R_2} D[r(s)] \exp\left(-\frac{1}{l}\int_0^L \left(\frac{dr}{ds}\right)^2 ds\right)$$
$$= \left(\frac{1}{2\pi Ll}\right) \exp\left(-\frac{(R_2 - R_1)^2}{Ll}\right). \tag{1}$$

Now suppose there is a nonselfentangled curve D in this space. For the calculations reported in this paper this curve D is a line that results from the thin rod placed perpendicular to the two dimensional plane. The question of interest is the way in which topologically distinct sets are to be classified. In addition it is of interest to calculate the probability of realization of these classes for a given set of chain parameters. The simplest way to classify topological entanglement is through the specification of the Gauss linking number, i.e., [1, 4, 7]:

$$I = \int_C dr \cdot \frac{1}{4\pi} \int_D \frac{(r-s) \times ds}{(r-s)^3} \tag{2}$$

where C is the curve specifying the polymer configuration. For our problem I simply turns out to be the winding number:

$$m = \int_0^L \left(\frac{dr}{ds}\right) \cdot A(r(s))\, ds \tag{3}$$

where the vector field with zero divergence, $A(r(s))$, is given by:

$$A(r(s)) = \left(-\frac{y}{x^2+y^2}, \frac{x}{x^2+y^2}\right) \tag{4}$$

with $r = (x, y)$, and $m = 0, \pm 1, \pm 2$, etc. The winding number (which is the topological constraint in the problem) can be written as:

$$m = \int_0^L \left(\frac{d\theta}{ds}\right) ds \tag{5}$$

with

$$\frac{d\theta}{ds} = \frac{(x\dot{y} - y\dot{x})}{x^2+y^2} \tag{6}$$

where the dot denotes a time derivative. Notice that the winding number can have positive and negative integer values as well as zero. The above problem has been solved by Prager and Frisch [1] and independently by Edwards [7]. The exact solution to the problem can be used to calculate various properties of the system [8].

We now generalize the problem to the case where there are N rods that are randomly placed. The rods are assumed to be needle like, i.e., the aspect ratio of the rods is essentially infinite. A physical situation where this may be relevant is in the description of a polymer molecule in a gel or rubber. The topological constraint is assumed to arise from the cross links in the medium. Needless to say that the problem we are considering is at best a caricature of the situation that occurs in the more interesting physical systems. The various topologically distinct classes are characterized by a set of winding numbers, m_i, $(i = 1, 2, \ldots, N)$ where:

$$m_i = \int_0^L \left(\frac{d\theta_i}{ds}\right) ds = \int_0^L \frac{\left[(x(s) - P_x^i)\frac{dy}{ds} - (y(s) - P_y^i)\frac{dx}{ds}\right]}{(x - R_x^i)^2 + (y - R_y^i)^2} ds \tag{7}$$

with $P = (P_x^i, P_y^i)$ being the position of the ith rod. The propagator of interest can be written as:

$$G(R_2, L; R_1, 0) = \int_{r(0)=R_1}^{r(L)=R_2} D[r(s)] \exp\left(-\frac{1}{l}\int_0^L \dot{r}^2(s)\right) \prod_{i=1}^{N} \delta\left[\int_0^L \dot{\theta}_i(s)\, ds - m_i\right] \tag{8}$$

where N is the number of obstacles. Notice the constraint is imposed by the delta function in the path integral. The delta function in Eq. (9) is to be interpreted as the Kronecker delta function whose integral representation is given by:

$$\delta(m) = \int_{-\pi}^{\pi} \frac{dx}{2\pi} e^{ixm}. \tag{9}$$

The integral representation of the delta function given in Eq. (9) can be used to write Eq. (8) as:

$$G(R_2, L; R_1, 0) = \int \prod_i \frac{d\lambda_i}{2\pi} e^{i\lambda_i m_i} \int D[r(s)]\, e^{-\frac{1}{l}\int_0^L \dot{r}^2(s)\, ds + \sum_{i=1}^{N} i\lambda_i \int_0^L ds A[r(s) - P_i] \cdot \dot{r}(s)]} \tag{10}$$

where the vector field, $A(r(s) - P_i)$, is about the location of the ith rod. We first consider the case of annealed randomness in which the randomly placed obstacles are in equilibrium with the polymer molecule. By annealed we mean that the rods are allowed to equilibrate among themselves on time scales in which the internal degrees of freedom of the polymer molecule relax. In contrast if the time scales for equilibration of the obstacles are much longer than the polymer relaxation times then one is faced with the case of quenched randomness. The latter problem is treated in the following section. In both cases it is assumed that the configurations of the polymer are at equilibrium. For the case of annealed randomness the physical quantities of interest should be calculated by averaging over the distribution of the randomly placed rods. The distribution function describing the location of the rods is assumed to be proportional to $1/S$ where S is the area of the plane. This assumption about the distribution function implies that there is no correlation between the rods. The averaging over the distribution of the rods can be represented in terms of the usual cumulant expansion [17]:

$$\left\langle \exp \sum_{i=1}^{N} i\lambda_i \int_0^L ds A[r(s) - R_i] \cdot \dot{r}(s) \right\rangle \simeq \exp(-\tfrac{1}{2} C_2 \Lambda_2) \tag{11}$$

where

$$\Lambda_2 = \sum_{i=1}^{N} \lambda_i^2 \tag{12}$$

and

$$C_2 = \int dP \int_0^L ds \int_0^L ds' [\dot{r}(s) \cdot A(\dot{r}(s) - P)][\dot{r}(s') \cdot A(r(s') - P)]. \tag{13}$$

Notice the expansion in Eq. (11) has been truncated at the second cumulant, the first one being zero. Thus the propagator averaged over the random distribution of rods is:

$$\langle G(R_2, L; R_1, 0)\rangle = \int \prod_i \frac{d\lambda_i}{2\pi} e^{im_i\lambda_i} Q_{[\lambda]}(R_2, L; R_1, 0) \tag{14}$$

where $\langle \cdots \rangle$ denotes averaging over the distribution of obstacles and:

$$Q_{[\lambda]} = \int_{r(0)=R_1}^{r(L)=R_2} D[r(s)] \exp\left[\left(-\frac{1}{l}\int_0^L \dot{r}^2(s)\, ds - \Lambda_2 \int dP \int_0^L ds \right.\right.$$
$$\left.\left. \times \int_0^L ds' (\dot{r}(s) \cdot A(r(s) - P))(\dot{r}(s') \cdot A(r(s') - P))\right)\right]. \tag{15}$$

If the transformation $r(s) \to r(s) - P$ is made then the following identity:

$$\int_{-\infty}^{\infty} \frac{dx}{\sqrt{2\pi}} e^{-\frac{x^2}{2} + iax} = e^{-\frac{a^2}{2}} \tag{16}$$

can be used to write Eq. (15) as:

$$Q_{[\lambda]} = \int DZ \int_{r(0)=R_1}^{r(L)=R_2} D[r(s)] \exp\left[-\frac{1}{l}\int_0^L \dot{r}^2(s)\, ds + iz\beta \int_0^L ds \dot{r}(s) \cdot A(r(s))\right], \tag{17}$$

where

$$\beta = \left(\frac{\Lambda_2}{2}\right)^{1/2}, \tag{18}$$

and

$$DZ = \frac{e^{-\frac{z^2}{2}}}{\sqrt{2\pi}} dz. \tag{19}$$

In obtaining Eq. (17) we have made use of the fact that $Q_{[\lambda]}$ should be independent of P due to translational invariance. The path integral in Eq. (17) is precisely that associated with the entanglement around an isolated rod and can be calculated either by using the equivalent Schrödinger equation [7] or by using a discretized path representation of $Q_{[\lambda]}$ [18]. This is exactly soluble and one obtains:

$$Q_{[\lambda]} = \int DZ \sum_{n=-\infty}^{n=+\infty} \exp(in(\theta'' - \theta')) \left(\frac{1}{\pi L l}\right)$$
$$\times \exp\left[-\left(\frac{R_2^2 + R_1^2}{Ll}\right)\right] I_{|n-\beta z|}\left(\frac{2R_2R_1}{Ll}\right) \tag{20}$$

where $I_y(x)$ is the modified Bessel function. In obtaining Eq. (20) the use of translational invariance of Q has been made. Using Eq. (20) the free energy of the entangled polymer system may be obtained using the relation:

$$\mathscr{F}_A/k_B T = -\ln \int \langle G(R, L; R, 0)\rangle \, dR \tag{21}$$

where k_B is the Boltzmann constant and T is the temperature. In Eq. (21) R is the location of the end points which for the case of ring polymer specifies the position of an arbitrary monomer. This completes the formal solution to the problem of calculation of the free energy of an entangled ring polymer in the annealed random case. The propagator and the free energy, F_A, can then be used to calculate the correlation functions, elastic constants, and osmotic pressure.

Although the formal solution to the problem is complete the analytic evaluation of the integrals that occur in the expression for the free energy proves to be formidable. Thus we present an approximate evaluation of certain quantities of interest namely the topological potential and the resulting topological force or equivalently the elastic force.

The topological force can be calculated from the propagator for the ring polymer which is given by:

$$\langle G(R, L; R, 0)\rangle = \int \prod_i \frac{d\lambda_i}{2\pi} e^{i\lambda_i m_i} \int DZ \sum_{n=-\infty}^{n=+\infty} \left(\frac{1}{\pi Ll}\right) \times \exp\left(-\frac{2R^2}{Ll}\right) I_{|n-\beta z|}\left(\frac{2R^2}{Ll}\right). \tag{22}$$

For small values of R such that $x = 2R^2/Ll \ll 1$ the modified Bessel function may be written as [19]:

$$I_{|n-\beta z|}(x) \simeq \left(\frac{x}{2}\right)^{|y|} \Gamma^{-1}(|n-\beta z|+1) \tag{23}$$

where $y = (n - \beta z)$. Since x is small the maximum contribution to Eq. (23) comes from $y \sim 0$, and in this limit $\Gamma^{-1}(y+1)$ may be replaced by unity [20]. By the same reasoning it is also easy to show that the maximum contribution to the summation over the index n comes from $n = 0$. With these approximations the probability of finding the random distribution of the rods, $P_A(R) = \langle G(R, L; R, 0)\rangle$, becomes:

$$P_A(R) \sim \frac{\exp\left[-\left(\frac{2R^2}{Ll}\right) + \frac{Nm^2}{2\left[\ln\left(\frac{Ll}{R^2}\right)\right]^2}\right]}{\left[\ln\left(\frac{Ll}{R^2}\right)\right]^N} \tag{24}$$

where m^2 is the mean square degree of entanglement per rod:

$$m^2 = \frac{1}{N}\sum_{i=1}^{N} m_i^2. \tag{25}$$

From Eq. (24) the probability that the ring polymer has zero value for the mean square degree of entanglement per rod, i.e., $m^2 = \text{zero}$ is given by:

$$P_A^0(R) \sim \frac{e^{-\frac{2R^2}{Ll}}}{\left[\ln\left(\frac{Ll}{R^2}\right)\right]^N} \tag{26}$$

which coincides with the result for entanglement with one obstacle [21] when N is unity [22]. The result given in Eq. (26) is not very surprising. Since there is no correlation between the rods we expect that $P_A^0(R)$ should roughly be given by $P_0^N(R)$ where $P_0(R)$ is the probability of no entanglement when just one rod is present. A topological free energy for the annealed random case can be defined as

$$\frac{F_A(R)}{k_B T} = -\ln P_A(R) \tag{27}$$

and using Eq. (24) we get:

$$\frac{F_A(R)}{k_B T} \sim -\frac{Nm^2}{2\left[\ln\left(\frac{R^2}{Ll}\right)\right]^2} + N \ln\ln\left(\frac{Ll}{R^2}\right) \tag{28}$$

where k_B is the Boltzmann constant, and T is the temperature. The topological force (or disjoining pressure) is given by $-\partial F_A(R)/\partial R$ and using Eq. (28) we obtain:

$$\frac{f_A(R)}{k_B T} \sim \frac{2N}{R \ln\left(\frac{Ll}{R^2}\right)} + \frac{2Nm^2}{R\left[\ln\left(\frac{R^2}{Ll}\right)\right]^2 \ln\left(\frac{Ll}{R^2}\right)} \quad \text{for } \left(\frac{R^2}{Ll}\right) \ll 1. \tag{29}$$

This purely repulsive force can be thought of as a potential of mean force experienced by a segment located at R, and is purely topological in nature. It arises because the distinct topological classes have a certain constraint. In our case the constraint is expressed by requiring that the winding number be fixed. When the averaging over the random distribution of obstacles is done the topological classes are distinguished by the different values of m^2. Notice that this force diverges strongly as R tends to zero. From Eq. (24) it is also clear that the elastic response (which can be studied by imposing an external field and calculating the response of the system to this field) can be extremely complicated as was first shown by Prager and Frisch for the case of winding of a polymer molecule around one obstacle.

3. Quenched randomness

If the obstacles, namely the rods that are placed perpendicular to the plane, are treated as quenched random impurities then one has to average the free energy over the random distribution of obstacles. This is to be contrasted with the case of annealed randomness treated earlier in which the propagator $G(R, L; R, 0)$ (or equivalently the partition function) was averaged over the random distribution of rods. The quenched random average can be calculated using the replica trick

which was introduced by Edwards in the treatment of rubber elasticity [23]. In general the treatment of problems involving quenched randomness is extremely difficult. However we will show that for the problem considered earlier the formal calculation of the quenched random free energy is (at least formally) surprisingly simple.

The reason for considering the case in which the obstacles are treated as quenched random impurities in modelling entanglements is the following. In gels or in systems where the molecules are permanently crosslinked with one another (like elastic networks) the precise topological relationship between polymer segments belonging to different chains act as constraints [15]. In this paper these constraints are modelled by insisting that the winding numbers be constant. Thus for a particular realization of the sample one has to specify the location of the rods, and the associated probability of realizing such a configuration. The control parameter in our case is the position of rods and for a given realization of the obstacles the chain topology is specified by a set of N winding numbers. If the time scale for changes in the position of the rods (this may correspond to creep times of the network) is much longer than the relaxation time for the internal degrees of freedom of the ring polymer then one is lead to the computation of free energy for a given realization of the obstacles. The quenched free energy is obtained by averaging the free energy for a given set of $\{R_i\}$ over the random distribution of obstacles. The separation in time scale given above is often met in gels, rubbers [15], spin glasses [24], and other systems. In our case the quantity of interest is $\langle \ln G(R, L; R, 0)\rangle$ from which the quenched topological potential, $F_Q(R)$, for the ring polymer case can be computed using:

$$\frac{F_Q(R)}{k_B T} = -\langle \ln G(R, L; R, 0)\rangle. \tag{30}$$

By using the replica trick [23, 24] the average of logarithm of the propagator can be written as:

$$\langle \ln G(R_2, L; R_1, 0)\rangle = \lim_{n\to 0}\left[\frac{(\langle G^n(R_2, L; R_1, 0)\rangle - 1)}{n}\right]. \tag{31}$$

By following the procedure outlined in the previous section $\langle G^n(R, L; R, 0)\rangle$ can be written as:

$$\langle G^n(R_2, L; R_1, 0)\rangle = \int \frac{d\{\lambda\}}{2\pi} e^{i\Sigma\lambda_j m_j} \langle Q^n_{\{\lambda\}}\rangle \tag{32}$$

where $d\{\lambda\} = \prod d\lambda_i$ and:

$$\langle Q^n_{\{\lambda\}}\rangle = \int DZ \int \prod_{\alpha=1}^{n} D[r_\alpha(s)] \exp \sum_\alpha \left[-\frac{1}{l}\int_0^L r_\alpha^2(s)\, ds + i\beta z \int_0^L r_\alpha(s)\cdot A(r_\alpha(s))\, ds \right]$$

$$\equiv \int DZ K^n. \tag{33}$$

The path integral in K is precisely the quantity that occurs when the polymer is entangled with one rod, and the result is explicitly given by Eq. (20). The quantity of interest in Eq. (30) can be obtained using Eqs. (31) and (32), and for

the case of ring polymers the explicit result for the quenched topological potential is given by:

$$\frac{F_Q(R)}{k_B T} = -\int \frac{d\{\lambda\}}{2\pi} \exp\left(i \sum_j \lambda_j m_j\right) \int DZ \ln \Omega \tag{34}$$

where

$$\Omega = \sum_{n=-\infty}^{n=\infty} \left(\frac{1}{\pi Ll}\right) e^{-\frac{2R^2}{Ll}} I_{|n-\beta z|}\left(\frac{2R^2}{Ll}\right). \tag{35}$$

This once again formally solves the problem of the calculation of the quenched free energy for our model of entanglement.

The explicit computation of $F_Q(R)$ for a given set of system parameters (L, N, and mean entanglement index per rod) is not possible and thus Eq. (34) has to be evaluated numerically. However some insight may be obtained by computing $F_Q(R)$ for small values of R^2/Ll. By using the approximations given in Eqs. (23) the topological potential $F_Q(R)$ corresponding to the probability that the phantom ring polymer has zero mean square degree of entanglement per rod is given by:

$$\frac{F_Q^0(R)}{k_B T} \sim C \ln\left(\frac{Ll}{2R^2}\right) \quad \text{for} \left(\frac{R^2}{Ll} \ll 1\right) \tag{36}$$

where C is a numerical constant that depends on N. It is interesting to compare this result with the topological potential $F_A(R)$ for the annealed random case which can be obtained by setting $m^2 = 0$ in Eq. (28). The potential $F_Q(R)$ is considerably more repulsive than $F_A(R)$. This result is general, i.e., the free energy for the quenched random case is always higher than the corresponding case of annealed randomness. This follows from the entropy reduction that results because the obstacles are treated as quenched random impurities. One can in principle use Eq. (34) in the expression for the free energy of polymer networks to calculate corrections (Mooney–Rivlin terms) to the classical theory of high elasticity of polymer networks. This may be useful especially in light of the work of Nechaev and Khokhlov [25] who suggested that the entanglement restrictions of a large number of obstacles is necessary to obtain significant corrections to the classical theory of elasticity.

4. Conclusions

In this paper we have generalized the PFE model to assess the effect of both annealed and quenched randomness on the statistical mechanics of simple entanglement. It can be argued that the presence of many randomly placed rods with which the chain can become entangled is a better caricature of the physics in physically interesting systems. We have shown that as long as the statistics of the randomly placed uncorrelated rods is adequately described by a Gaussian process both the annealed random problem as well as the quenched random problem can be formally exactly solved. Our major result is that for small values of the argument R^2/Ll one obtains a repulsive topological potential arising merely from the constraint that the winding number be conserved. The topological potential for the situation that the polymer has zero mean square entanglement per rod is found to be considerably more repulsive for the quenched

random case than for the annealed random problem. Explicitly we have obtained:

$$\frac{F_0(R)}{k_B T} \sim \begin{cases} C \ln\left(\frac{Ll}{R^2}\right) & \text{(quenched)} \\ N \ln\ln\left(\frac{Ll}{R^2}\right) & \text{(annealed)} \end{cases} \tag{37}$$

where C is a N-dependent constant. The above equation for the repulsive elastic force on the ring polymer confined to a plane due to entanglement with the obstacles is our principle result.

In a certain sense the results of the present excercise are somewhat dissappointing. It has been transparent already from the studies of Prager, Frisch, and Edwards that $F(R)$ for entanglements with one obstacle has basically (apart from the factor of N) the structure that we have obtained for the annealed random problem. The second important point Prager and Frisch made was that the simple Gauss invariant constraint can make the phantom ring polymer behave like a system having a very complicated elastic response. Both these lessons are reaffirmed in our present analysis. It is also unlikely that the more realistic modelling of entanglement attempted here will be useful in providing a better understanding of the experimental situation of elasticity in networks. Perhaps the most interesting result of the present work is the demonstration that the case of quenched randomness can be formally exactly solved. It also appears that there is no evidence for replica symmetry breaking in this model which has only short range interactions. Furthermore the explicit calculation of the topological potential shows that in the limit of small values of (R^2/Ll) the potential for the quenched random case is considerably more repulsive than the potential for the annealed case.

Acknowledgements. It is a pleasure to dedicate this article to Prof. Stephen Prager for whom I had the privilege of being a teaching assistant in Statistical Mechanics for nearly three years. Stephen Prager most directly taught me the importance of imagination in solving scientific problems. My own interest in polymers began when I heard some unforgettable lectures by S. Prager on microemulsions and welding of polymers at interfaces, and I am grateful to him for introducing me to this field. I am grateful to Prof. A. R. Khokhlov for a discussion of applicability of the theory developed here to elasticity of dry polymer network. I would like to thank Prof. M. E. Fisher and an anonymous referee for several useful comments on an earlier version of this paper. This work was supported in part by a grant from the National Science Foundation. Additional support from the Camille and Henry Dreyfuss Foundation is greatly acknowledged.

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22. If $m^2 = 0$ then it follows that $m_i = 0$ for all i's. The condition that all m_i's are zero does not imply that the polymer is not entangled with any of the rods. It is possible that even with all the m_i's equal to zero the chain can be highly entangled. This is best illustrated with the following simple example (provided by the referee). Suppose one has only two rods. Consider a polymer configuration obtained by the following construction. Let the chain wind around counterclockwise around the rod labelled 1 twice followed by another counterclockwise rotation around rod 2. If this is followed by two clockwise rotations around rods 1 and 2 and then the ends of the chain are joined one would correctly conclude that both m_1 and m_2 are equal to zero. However the polymer is highly entangled. Notice that in two dimensions as soon as one introduces selfavoidance the above configuration would be disallowed and in this case the condition $m_i = 0$ for all values of i does imply that the polymer is not entangled.
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