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1995 J. Phys. A: Math. Gen. 28 6655

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Statistical mechanics of macromolecular networks without replicas

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Received 1 May 1995, in final form 11 August 1995

Abstract. We report on a novel approach to the Deam–Edwards model for interacting polymeric networks without using replicas. Our approach utilizes the fact that a network modelled from a single non-interacting Gaussian chain of macroscopic size can be solved exactly, even for randomly distributed crosslinking junctions. We derive an *exact* expression for the partition function of such a generalized Gaussian structure in the presence of random external fields and for its scattering function S_0 . We show that S_0 of a randomly crosslinked Gaussian network (RCGN) is a self-averaging quantity and depends only on crosslink concentration M/N , where M and N are the total numbers of crosslinks and monomers. From our derivation we find that the radius of gyration R_g of a RCGN is of the universal form $R_g^2 = (0.26 \pm 0.01)a^2 N/M$, with a being the Kuhn length. To treat the excluded volume effect in a systematic, perturbative manner, we expand the Deam–Edwards partition function in terms of density fluctuations analogous to the theory of linear polymers. For a highly crosslinked interacting network we derive an expression for the free energy of the system in terms of S_0 which has the same role in our model as the Debye function for linear polymers. Our ideas are easily generalized to crosslinked polymer blends which are treated within a modified version of Leibler's mean-field theory for block copolymers.

1. Introduction

Randomly crosslinked macromolecules present a challenging field from a physical as well as from a mathematical point of view with many practical applications in polymer sciences. For this it is very unfortunate that the statistical mechanics of polymer networks is still poorly understood. Although there has been a great deal of theoretical interest in this topic over the last few years [1–8], we feel that a satisfying answer of how to deal with polymer networks from a microscopic point of view is still missing. One of the reasons is that most of the recent work on the subject [4, 5] is based on replica field theory originally introduced into polymer science by Edwards *et al* [1–3] in which, however, much of the underlying physics remains hidden in the complicated mathematics of the replica formalism [9].

It is the purpose of this paper to present an alternative approach to the statistical mechanics of randomly crosslinked macromolecules that goes beyond the earlier phantom type models (for details see, for example, [10]), but at the same time avoids the well known difficulties associated with the replica trick [9]. Our theory is based on the minimal network model by Deam and Edwards [1–7]; however, it avoids replica field theory completely. The strategy in this paper is outlined below. As a generalization of the Wiener measure in the

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theory of linear polymers [11] we introduce the concept of a randomly crosslinked Gaussian network (RCGN) in section 2. As we will show in section 3, the non-interacting problem can be solved exactly, even for random crosslinking junctions. In section 3 we develop our general formalism and derive an exact formula for the partition function of a generalized Gaussian structure in the presence of random external fields. This equation (20) is the central mathematical result of the paper, for it is also a generating function from which further results are obtained. In section 4 we consider some applications. In particular, we calculate the static structure function S_0 for RCGNs without excluded volume interaction. The important finding here is that S_0 is a self-averaging quantity, i.e. it does not depend on the topological details of the model. The consequence is that for RCGNs S_0 is a quasi-universal function that has a similar role for polymer networks as the Debye function for linear polymers. The interacting case is treated in section 5. To take into account excluded volume interaction, we transform our original network Hamiltonian to collective density variables. Here we work in close analogy with the excluded volume problem for dense polymer melts [11]. For highly crosslinked systems it is sufficient to consider only lowest order density fluctuations, although higher order terms are readily calculated within our formalism. In this case it is easy to show that the free energy F can be expressed in terms of the scattering function S_0 of the non-interacting system and the excluded volume parameter. It is crucial to realize that F depends on the frozen degrees of freedom (random crosslinking junctions) only via S_0 , and no further quenched averaging remains to be done. To treat crosslinked polymer blends we apply a modified version of Leibler's theory for microphase separation in block copolymers [12] and show how to obtain similar criteria for phase instability in multi-component networks. Generalizations and outlook are given in section 6. However, more detailed calculations of the latter applications will be presented in a forthcoming publication.

2. Formulation of the model

We consider flexible interacting macromolecules on the level of the Edwards Hamiltonian [1]. For a single polymer chain in d spatial dimensions the Edwards Hamiltonian consists of two parts $H = H_W + H_I$, where

$$\beta H_W = \frac{d}{2a^2} \sum_{i=1}^N (\mathbf{R}_i - \mathbf{R}_{i-1})^2 \quad (1)$$

is the Wiener measure that models the connectedness of the chain as a Gaussian. Self-avoidance between monomers is described by a pseudopotential of the form

$$\beta H_I = v \sum_{0 \leq i < j}^N \delta(\mathbf{R}_i - \mathbf{R}_j) \quad (2)$$

where $\delta(\mathbf{R})$ is the Dirac delta function. In equations (1) and (2) we have adopted the following notation: $v > 0$ is the second virial coefficient [11] that characterizes the repulsive excluded volume interaction between monomers, N is the degree of polymerization, a the Kuhn length, and \mathbf{R}_i ($i = 0, \dots, N$) are monomer coordinates; $\beta = (k_B T)^{-1}$ as usual. For convenience we restrict the following discussion to networks that are modelled from one single but huge polymer chain of macroscopic dimension (figure 1). It was shown that this simplification gives the correct physics for highly crosslinked polymer networks above the percolation threshold [1]. A generalization of our method to multi-polymer networks will be discussed later on in section 6.

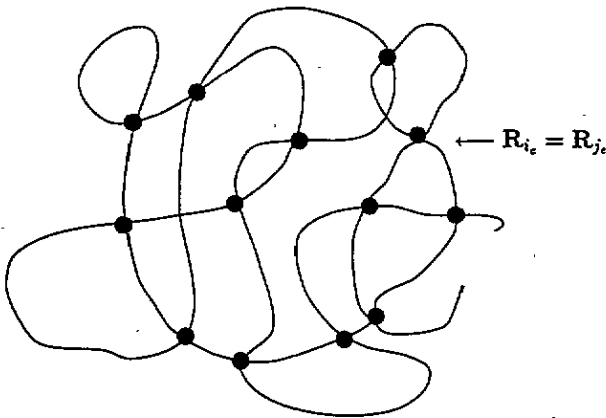


Figure 1. A single-chain network. Only the beads at the crosslink sites are shown. For high crosslink concentrations far above the percolation threshold a single-chain network is practically indistinguishable from a network that is modelled from many polymer chains.

To describe M permanently crosslinked monomers, we specify each junction by a pair of randomly chosen 'crosslink coordinates' i_e, j_e ($0 \leq i_e, j_e \leq N, e = 1, \dots, M$), such that monomer R_{i_e} is connected to monomer R_{j_e} (figure 1). The whole set of junction points $C = \{i_e, j_e\}_{e=1}^M$ represents the random connectivity of the network. Within the framework of the Deam-Edwards model [1] the partition function of a Gaussian phantom network with excluded volume is given by

$$Z(C) = \int_V \prod_{i=0}^N dR_i e^{-\beta(H_W + H_1)} \prod_{e=1}^M \delta(R_{i_e} - R_{j_e}) \quad (3)$$

where the total phase space is now restricted by the additional crosslinking constraints. Equation (3) describes a phantom network in a sense that the polymer chain is free to pass through itself irrespective of entanglements. Chain motion is only restricted by the presence of permanent crosslinks and the excluded volume interaction.

In the replica formalism the next step is to perform a quenched average over the logarithm of $Z(C)$ with a suitable distribution for the 'frozen' crosslink coordinates $\{i_e, j_e\}_{e=1}^M$. Using the replica trick [9] this leads to a non-trivial modification of the interaction term H_1 in which all replicas become coupled [1-5]. Applying standard techniques for setting up field theories in polymer physics, we were able to map equation (3) into a dn -dimensional $O(m)$ field theory in the limit $n, m \rightarrow 0$ [7]. Unfortunately, in the replica formalism further progress relies highly upon crude approximations or variational assumptions [1-7].

Contrary to the replica method we do not carry out the quenched average at this stage of the calculation. Instead we model the delta function in (3) by a Gaussian distribution with width ε in the limit $\varepsilon \rightarrow 0$. Therefore we are keeping all random crosslink coordinates explicitly in the partition function. Formally this means that if the Wiener measure βH_W is replaced by the more general expression for a RCGN

$$\beta H_G = \frac{d}{2a^2} \sum_{i=1}^N (R_i - R_{i-1})^2 + \frac{d}{2\varepsilon^2} \sum_{e=1}^M (R_{i_e} - R_{j_e})^2 \quad (4)$$

we can eliminate the delta constraint in (3). With equations (2) and (4) we are now in a position to introduce our RCGN Hamiltonian as follows:

$$H = H_G + H_1. \quad (5)$$

To enforce the crosslinking constraints we finally have to perform the limit $\varepsilon \rightarrow 0$. It is mathematically convenient to normalize the Gaussian measure defined by (4) with respect to the non-interacting system which will serve us as a reference state. In this case the partition function in (3) can be cast into the more convenient form

$$Z(C) = \langle e^{-\beta H_I} \rangle_0 = \exp(-\beta(F - F_0)) \quad (6)$$

where the average $\langle \dots \rangle_0$ stands for

$$\lim_{\varepsilon \rightarrow 0} \left(\int \prod_{i=0}^N dR_i e^{-\beta H_G} \dots \right) \left(\int \prod_{i=0}^N dR_i e^{-\beta H_G} \right)^{-1}. \quad (7)$$

For $v = 0$ the free energy F of the interacting network reduces to that of a non-interacting RCGN denoted by F_0 . The partition function (6) is completely equivalent to the one used by Edwards *et al* [1–3]. It is also identical to the one used in more recent works by Goldbart and coworkers [4, 5], except for the fact that in this paper we are dealing with a single-chain network exclusively. This is primarily a matter of convenience which has been discussed in greater detail in [1–3]. The Hamiltonian (5) is, of course, easily generalized to multi-chain or multi-component networks.

To make further analytic progress, it will become useful to decouple the interaction term H_I by rewriting (2) in terms of collective density variables $\Phi_k = \sum_{i=0}^N \exp(ikR_i)$ and applying the Hubbard–Stratonovich transformation to (6). Since this is standard procedure [4, 11], we quote here only the final result

$$Z(C) \propto \int \prod_{k>0} d\Phi_k \exp\left(-\frac{v}{V} \sum_{k>0} \Phi_k \Phi_{-k}\right) \left\langle \exp\left(i\frac{v}{V} \sum_{i=0}^N \sum_{k \neq 0} \Phi_{-k} \exp(ikR_i)\right) \right\rangle_0. \quad (8)$$

By $k > 0$ we mean the positive half of k space, i.e. $k_x > 0$, and V is the volume. The partition function (8) in combination with the measure defined by (7) is equivalent to the minimal network model of Deam and Edwards [1] and will be our starting point for further investigations.

3. General formalism

Before dealing with the more complicated excluded volume situation directly, it is easier to develop the mathematical formalism for non-interacting RCGNs at first. To evaluate equation (8) in a systematic fashion, it is standard to expand the first exponential in the entropic, second part of (8) in terms of density fluctuations Φ_{-k} or the excluded volume parameter. In any case the main mathematical task is to calculate averages which are of the general form $\langle \exp(ib^t R) \rangle_0$, where we have introduced $(d \times (N + 1))$ -dimensional ‘supervectors’ $R = (R_0, R_1, \dots, R_N)^t$ and $b = (b_0, b_1, \dots, b_N)^t$. For the moment we assume that b is completely arbitrary, but does not depend on R explicitly. By $b; R_j$ we will always mean a d -dimensional inner vector product, and t denotes the transposed vector. Since $\langle \dots \rangle_0$ involves a Gaussian integration with the measure defined by (7), it is essential to find the inverse matrix of the quadratic form, equation (4), first. For this it is most convenient to switch to matrix notation.

Using matrix notation in which R is the above defined ‘supervector’, the quadratic form in (4) can be written as follows:

$$\beta H_G = \frac{d}{2\varepsilon^2} R^t \left(zW + \sum_{\varepsilon=1}^M \mathcal{K}(i_\varepsilon, j_\varepsilon) \right) R \quad (9)$$

where $z = (\varepsilon/a)^2$, and symmetric $(N + 1) \times (N + 1)$ matrices \mathcal{W} and \mathcal{K} . Here

$$\mathcal{W} = \begin{pmatrix} 1 & -1 & 0 & \dots & 0 \\ -1 & 2 & -1 & \dots & 0 \\ \vdots & \ddots & \ddots & \ddots & \vdots \\ 0 & \dots & -1 & 2 & -1 \\ 0 & \dots & 0 & -1 & 1 \end{pmatrix} \tag{10}$$

denotes the connectivity matrix associated with H_W , and

$$\mathcal{K}(i_e, j_e) = \begin{pmatrix} 0 & 0 & 0 & 0 & 0 \\ 0 & 1 & \vdots & -1 & 0 \\ 0 & \dots & 0 & \dots & 0 \\ 0 & -1 & \vdots & 1 & 0 \\ 0 & 0 & 0 & 0 & 0 \end{pmatrix} \begin{matrix} \vdots \\ \leftarrow i_e \text{th position} \\ \vdots \\ \leftarrow j_e \text{th position} \\ \vdots \end{matrix} \tag{11}$$

represents a single crosslinking junction at random position (i_e, j_e) . Equation (9) is easily verified by inspection.

For the following it is essential to note that the quadratic form, equation (9), is only *semi*positive definite, hence no matrix inverse exists. The non-negativity of H_G follows immediately from (4), since it is a sum of squares. However, there is one zero eigenvalue associated with eigenvector $\mathbf{R} = (1, \dots, 1)^t$. This is easily seen from noting that the column sum of the matrix in (9) is always zero irrespective of the value of z . Before we proceed, we need to transform (9) to a positive-definite quadratic form by removing the mode which belongs to eigenvalue zero. This mode corresponds to a displacement of the centre of mass, and since we are dealing with a simply-connected structure, there can be only *one* such mode. The desired transformation is easily accomplished by switching to internal coordinates $r_i = R_i - R_{i-1}$, or in matrix notation $\mathbf{R} = \mathcal{D}\tilde{\mathbf{r}}$, where

$$\tilde{\mathbf{r}} = \begin{pmatrix} R_0 \\ r_1 \\ \vdots \\ r_N \end{pmatrix} \quad \text{and} \quad \mathcal{D} = \begin{pmatrix} 1 & 0 & \dots & 0 \\ 1 & 1 & \dots & 0 \\ \vdots & \vdots & \ddots & \vdots \\ 1 & 1 & \dots & 1 \end{pmatrix} \tag{12}$$

For the multi-chain network we refer to our discussion in section 6. With the above manipulations the measure corresponding to (9) takes on the simple form

$$Z_0(\mathbf{C}) = \int \prod_{i=0}^N dR_i e^{-\beta H_G} = V \int \prod_{i=1}^N dr_i \exp\left(-\frac{d}{2\varepsilon^2} \mathbf{r}^t \mathcal{M} \mathbf{r}\right) \tag{13}$$

where $\mathbf{r} = (r_1, \dots, r_N)^t$, and we performed an integration over R_0 . In the limit $\varepsilon \rightarrow 0$ equation (13) yields the partition function of a RCGN without excluded volume. The N dimensional matrix \mathcal{M} in (13) is given by

$$\mathcal{M}(z) = z\mathcal{I} + \mathcal{P}\mathcal{P}^t \tag{14}$$

where \mathcal{I} denotes an N -dimensional unit matrix. The outer matrix product $\mathcal{P}\mathcal{P}^t$ is formed with the $N \times M$ ‘crosslink matrix’ $\mathcal{P} = (\mathbf{p}_1, \dots, \mathbf{p}_M)$, where each column vector is defined by

$$\mathbf{p}_e = (0, \dots, 0, \underbrace{1, 1, \dots, 1}_{i_e + 1 \text{ to } j_e}, 0, \dots, 0)^t \quad e = 1, \dots, M. \tag{15}$$

The 1's in (15) run from the $(i_e + 1)$ th to the j_e th position; the rest of the components are 0. For convenience we will assume that j_e is always larger than i_e . Equation (14) is derived in appendix A.

The crosslink matrix \mathcal{P} is defined in such a way that it contains complete information about the crosslink positions in a unique way. By construction it is exactly this extra term in \mathcal{M} that distinguishes the network problem from a linear polymer. For the following derivation it is crucial to have the crosslinking constraint in (14) in form of an *outer* matrix product of \mathcal{P} . Note that \mathcal{M} is positive definite, and thus its inverse exists.

Using equations (13) and (14) the measure in (7) can be redefined in terms of \mathcal{M}

$$\langle \dots \rangle_0 = \lim_{\varepsilon \rightarrow 0} \frac{1}{Z_0(\mathbf{C})} \int \mathbf{R}_0 \int \prod_{i=1}^N dr_i \exp\left(-\frac{d}{2\varepsilon^2} \mathbf{r}^t \mathcal{M} \mathbf{r}\right) \dots \quad (16)$$

In the remainder of this section we will show that this average exists for $\varepsilon \rightarrow 0$ and derive an exact expression.

With equation (16) we are in a position to calculate expectation values of the form $\langle \exp(i\mathbf{b}^t \mathbf{R}) \rangle_0$. Since \mathbf{r} depends only linearly on \mathbf{R} , it is sufficient to consider expressions of the form

$$\langle \exp(i\mathbf{c}^t \mathbf{r}) \rangle_0 = \lim_{\varepsilon \rightarrow 0} e^x p\left(-\frac{\varepsilon^2}{2d} \mathbf{c}^t \mathcal{M}^{-1}(z) \mathbf{c}\right) \quad (17)$$

where \mathbf{c} is again some arbitrary vector which does not depend explicitly on \mathbf{R} . We can always go back to the original monomer coordinates since $\tilde{\mathbf{r}} = \mathcal{D}^{-1} \mathbf{R}$. The key problem here is to find the inverse of $\mathcal{M}(z)$ in the limit $z = (\varepsilon/a)^2 \rightarrow 0$ which depends on all the crosslink coordinates $\{i_e, j_e\}_{e=1}^M$. This is accomplished by invoking an identity due to Frobenius, Schur and Woodbury [13, 14]. An alternative but shorter proof of the theorem is given in appendix B. The important finding is that

$$\mathcal{M}^{-1}(z) = \frac{1}{z} (\mathcal{I} - \mathcal{P}(\mathcal{P}^t \mathcal{P})^{-1} \mathcal{P}^t). \quad (18)$$

Making use of the fact that $\mathcal{P}^+ = (\mathcal{P}^t \mathcal{P})^{-1} \mathcal{P}^t$ is a pseudoinverse of \mathcal{P} , i.e. $\mathcal{P}^+ \mathcal{P} = \mathcal{I}$, it is trivial to show that $\mathcal{P} \mathcal{P}^+$ is a projector for \mathcal{P} . It is also possible to prove the following alternative representations [15]

$$\mathcal{P} \mathcal{P}^+ = \mathcal{X} \mathcal{X}^t = \sum_{e=1}^M \mathbf{x}_e \mathbf{x}_e^t. \quad (19)$$

Here $\mathcal{X} = (\mathbf{x}_1, \dots, \mathbf{x}_M)$ is any orthonormal vector basis \mathbf{x}_e , $e = 1, \dots, M$ for the M -dimensional vector space spanned by the \mathbf{p}_e 's in (15). Combining equations (17)–(19) our central result of this section can now be summarized by the following formulae:

$$\begin{aligned} \langle \exp(i\mathbf{c}^t \mathbf{r}) \rangle_0 &= \exp\left(-\frac{a^2}{2d} \mathbf{c}^t (\mathcal{I} - \mathcal{X} \mathcal{X}^t) \mathbf{c}\right) \\ &= \exp\left(-\frac{a^2}{2d} \left(\mathbf{c}^2 - \sum_{e=1}^M (\mathbf{c}^t \mathbf{x}_e)^2\right)\right). \end{aligned} \quad (20)$$

It is remarkable that equation (20) is of a very simple and special form although the crosslink coordinates $\mathbf{C} = \{i_e, j_e\}_{e=1}^M$ are completely random. $\mathcal{I} - \mathcal{X} \mathcal{X}^t$ is orthogonal to \mathcal{P} and idempotent which can be seen by inspection. As a consequence the only eigenvalues of $\mathcal{I} - \mathcal{X} \mathcal{X}^t$ are 0 and 1 with degeneracies M and $N - M$, and the quadratic form in (20) is semipositive definite. This ensures that the exponent in (20) is never positive. The non-triviality of the network problem enters the calculation in the form of \mathcal{X} which can

be found either by orthonormalizing the p_e 's in (15) or directly from (18). The former is usually accomplished by Gram-Schmidt orthonormalization [13] or numerically by the singular value decomposition [16]. Note that equation (18) only requires inversion of an $M \times M$ matrix, whereas \mathcal{M}^{-1} is N -dimensional with $N \gg M$ for a real network.

It is worthwhile mentioning that equation (20) is also the partition function of a Gaussian structure (random or not depending on the choice of crosslinks $\{i_e, j_e\}_{e=1}^M$) in the presence of random external fields b_1, \dots, b_N . This is easily seen by making the transformation in (20) $c = \mathcal{D}^t b$ back to the original monomer coordinates R_i . In the following section we consider more applications of equation (20) with emphasis on RCGNs.

4. Non-interacting random networks

The reference quantity in the theory of linear polymers and polymer melts [11, 12] is the static structure function of a single non-interacting polymer chain. For a RCGN it is given by

$$S_0(\mathbf{k}, \mathbf{C}) = \left\langle \sum_{i,j=0}^N \exp(i\mathbf{k}(\mathbf{R}_i - \mathbf{R}_j)) \right\rangle_0 \quad (21)$$

The structure function can be measured directly in polymer solutions under Θ -conditions via neutron scattering. Physically it is the Fourier transform of the pair correlation function.

From equation (20) it is easy to derive an exact expression for $S_0(\mathbf{k}, \mathbf{C})$ by setting

$$\mathbf{c} = \mathbf{k} (0, \dots, 0, \underbrace{1, 1, \dots, 1}_{i+1 \text{ to } j}, 0, \dots, 0)^t \quad (22)$$

From equations (20)–(22) we find

$$S_0(\mathbf{k}, \mathbf{C}) = \sum_{i,j=0}^N \exp\left(-\frac{k^2 a^2}{2d} (|i-j| - (\mathbf{y}_i - \mathbf{y}_j)^2)\right) \quad (23)$$

The M -dimensional vectors \mathbf{y}_i ($i = 0, \dots, N$) are given in terms of the orthonormal basis \mathcal{X} in (19)

$$(\mathbf{y}_1, \dots, \mathbf{y}_N) = (\mathcal{D}\mathcal{X})^t \quad (24)$$

where \mathcal{D} is the lower triangular matrix defined in (12), and $\mathbf{y}_0 = \mathbf{0}$. Each \mathbf{y}_i is a vector whose components depend on the whole set of crosslink coordinates \mathbf{C} via \mathcal{X} . Equation (23) is of a similar structure to the result in [17] for a RCGN under external stress obtained by completely different means. Derivations of structure factors that are based on the affine deformation hypothesis [10] can be found in [17, 18] but will not be dealt with in this work.

Although our primary interest here are RCGNs, we can apply equation (23) to problems with non-random connectivities as well. As a simple example which can be solved analytically and to illustrate our formalism, we consider a flexible ring polymer as a trivial example of a non-random network with only one crosslink. For a closed loop the crosslink connects monomer \mathbf{R}_0 with \mathbf{R}_N , and the crosslink matrix \mathcal{P} is of the simple form $\mathcal{P} = p_1 = (1, 1, \dots, 1)^t$. Thus $\mathcal{X} = x_1 = 1/\sqrt{N}(1, 1, \dots, 1)^t$ and with the definition in (24), $\mathbf{y}_i = i/\sqrt{N}$ for $i = 0, \dots, N$. From equation (23) we get the exact result

$$S_0(\mathbf{k}, \text{Ring}) = \sum_{i,j=0}^N \exp\left(-\frac{k^2 a^2 |i-j|}{2d} \left(1 - \frac{|i-j|}{N}\right)\right) \quad (25)$$

There are more cases in which \mathcal{X} can be obtained analytically. Among these are star or branched polymers and networks or manifolds with regular, non-random connectivity. More details of these applications will be given elsewhere. Since equation (23) is exact, it also reduces for $M = 0$ to the well known Debye function for linear polymers [11].

We now specify our discussion to networks with quenched random connectivity. For an arbitrary set of crosslinks we are not able to derive analytic expressions for y_i in (23). Moreover, within the framework of replica theory macroscopic physical observables like S_0 are to be averaged over the 'frozen' variables, here all possible sets of crosslink coordinates C . To make further progress it is therefore absolutely crucial to understand that in the thermodynamic limit when N and M are sufficiently large *any* specific but random crosslink configuration C would produce the same result for S_0 if, for example, equation (23) could be evaluated analytically. In the literature this is well known as self-averaging. In fact for any self-averaging quantity like the free energy, structure factor or radius of gyration (these are the quantities we are mainly interested in) performing the quenched average at the end of the calculation is not an absolute necessity. To obtain S_0 for RCGNs it is therefore sufficient to pick one specific set of random numbers $0 \leq i_e, j_e \leq N$, $e = 1, \dots, M$, from a suitable distribution function and evaluate (23) for this specific but random connectivity. With the results from section 3 it is indeed very easy to obtain y_i and carry out the summation in (23) numerically (figure 2). To create a specific set of crosslink coordinates $C = \{i_e, j_e\}_{e=1}^M$ we have chosen an uniform distribution $P(C) = (1/N)^{2M}$ for simplicity [4]. Physically this means that the frozen crosslinks can, in principle, be anywhere along the chain without restrictions.

Self-averaging is demonstrated in figure 2 for two random networks with different crosslink configurations C and also different network sizes N and M . We find that self-

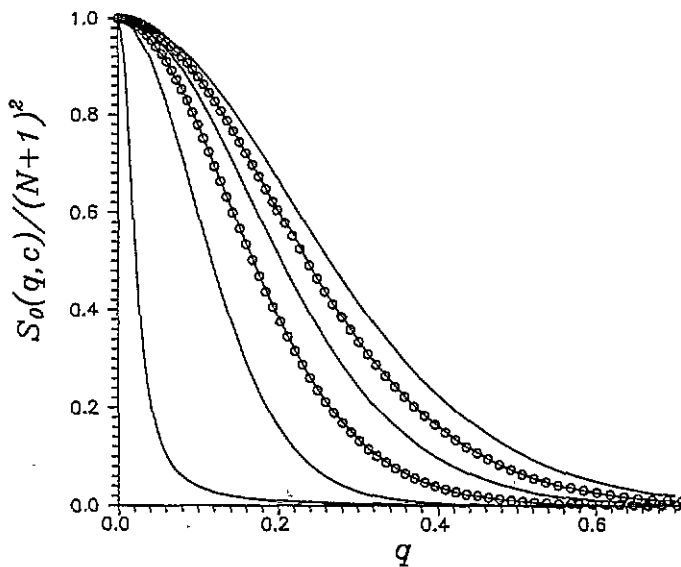


Figure 2. Scattering function $S_0(q, C)$ for two different RCGNs derived from (23). $q^2 = k^2 a^2 / 2d$; $c = M/N$; full curve $N = 10000$, $c = 0, 1, 2, 3, 4, 5\%$ (left to right); open circles $N = 5000$ (only shown for $c = 2, 4\%$). $C = \{i_e, j_e\}_{e=1}^M$ were picked from the interval $[0, N]$ at random. The orthonormalization of \mathcal{P} was performed with a standard singular value decomposition algorithm [16]. Due to self-averaging curves with same crosslink concentration (here $c = 2, 4\%$) are identical. For $c \rightarrow 0$ we recover the Debye function for linear polymers.

averaging is almost perfectly fulfilled even for relatively small networks with $N \gtrsim 5000$ and crosslink densities of a few percent. Small deviations between the two networks in figure 2 are due to finite-size effects. The structure function depicted in figure 2 is a universal function in a sense that any other RCGN with $N \gtrsim 5000$ led to identical curves. As one would have expected S_0 does only depend on the number of crosslinks M and monomers N and *not* on microscopic details of crosslink positions. In fact, our exact calculation shows that for RCGNs, $S_0(\mathbf{k}, \mathbf{C} = \{i_e, j_e\}_{e=1}^M) = S_0(\mathbf{k}, c)$ and that it depends only on crosslink concentration $c = M/N$. The important consequence is that for RCGNs the structure function $S_0(\mathbf{k}, c)$ can be viewed as the equivalent to the Debye function in the theory of linear polymers. By construction it is this complete analogy between the theory of linear polymers and our model that will allow us to approach the excluded volume problem in the next section very similarly to linear polymers.

As a by-product of equation (23) we obtain an exact expression for the radius of gyration R_g of a RCGN. It is easy to show [11] that in the limit $\mathbf{k} \rightarrow \mathbf{0}$, $S_0(\mathbf{k}, c)/N^2 = 1 - \mathbf{k}^2 R_g^2/d$, and from our numerical calculation we find that $R_g^2 = 0.26a^2/c$, where $c = M/N$. The latter result is also universal in a sense that the prefactor $0.26 \pm 0.01 \approx 1/f$ was found for all networks with functionality $f = 4$ which were modelled from a uniform crosslink distribution. Small fluctuations were mainly due to the finite size of the networks under investigation. Similar results have been suggested throughout the literature. However, these calculations had to rely upon various approximation schemes. For very large \mathbf{k} values of the order $1/a$, $S_0(\mathbf{k}, c)$ decays as $1/\mathbf{k}^2$ as expected for a non-interacting system. In the intermediate \mathbf{k} range no simple power-law decay could be found. From the semipositive definiteness of (20) and (23) it follows that the scattering function of any simply connected Gaussian structure is a monotonically decreasing function in \mathbf{k}^2 with a maximum at $\mathbf{k} = \mathbf{0}$. So far further analytic progress in (23) depends on simplifying assumptions or approximations about the form of \mathbf{y}_i 's in (24).

As another illustration of (20) we consider a generalized Gaussian structure in a homogeneous electric field \mathbf{E} when each monomer is randomly charged with $q_i = \pm q$. In this case the electric energy is given by $-\sum_i q_i \mathbf{E} \mathbf{R}_i$, and we can directly get the partition function from (20). Performing the quenched average over q_i which is analytically possible the free energy becomes $F(\mathbf{E}) = F(\mathbf{0}) - (a^2 q^2 \mathbf{E}^2 / 2dk_B T) \text{Tr } \mathcal{Y}$, where Tr means trace, and $\mathcal{Y} = \mathcal{D}(\mathcal{I} - \mathcal{X}\mathcal{X}')\mathcal{D}'$. Applying the definition in (24) we find that $\text{Tr } \mathcal{Y} = N(N-1)/2 - \sum_{i=1}^N \mathbf{y}_i^2$ and from a numerical calculation $\text{Tr } \mathcal{Y} \approx 0.5N/c$.

5. Random networks with excluded volume

5.1. Free energy

We want to outline how the free energy of a RCGN with excluded volume interaction can be obtained without resorting to replica methods. For the above considered network the partition function (8) is now expanded in terms of density fluctuations $\Phi_{-\mathbf{k}}$ up to second order. This approximation is known to be valid in dense systems when fluctuations about the mean density are small [11]. In the Gaussian approximation [11] it is straightforward to obtain the free energy density $F(v, c)$ of the interacting system in terms of $S_0(\mathbf{k}, c)$ of the non-interacting system

$$F(v, c) - F(0, c) = \frac{1}{2} k_B T \left(v \rho^2 + \int \frac{d^d \mathbf{k}}{(2\pi)^d} \log \left(1 + \frac{v}{V} S_0(\mathbf{k}, c) \right) \right) \quad (26)$$

where $\rho = N/V$ is the mean physical density. Note that no further averaging over the frozen crosslink positions is needed, since $S_0(\mathbf{k}, c)$ in (23) was already shown to be self-averaging. For further reference we also quote the result of the mean-field free energy in terms of mean density fluctuations $\langle \Phi_{\mathbf{k}} \rangle$. Up to an irrelevant constant it has been shown [11] that

$$F(v, c) = \frac{1}{2} k_B T \int \frac{d^d \mathbf{k}}{(2\pi)^d} S^{-1}(\mathbf{k}, c) \langle \Phi_{\mathbf{k}} \rangle \langle \Phi_{-\mathbf{k}} \rangle \quad (27)$$

where $S^{-1}(\mathbf{k}, c) = (v/V) + S_0^{-1}(\mathbf{k}, c)$ is the inverse structure function of the interacting system in Gaussian approximation. Higher order terms in the above Landau-type expansion are readily calculated from equation (20) by modifying c in (22) accordingly, but will be neglected in the following discussion.

5.2. Crosslinked polymer blends

Interpenetrating polymer networks (IPNs), semi-IPNs and crosslinked polymer blends have broad range of applications in polymer research and material sciences [19, 20]. There has been some effort to model these systems using a propagator originally proposed by de Gennes [21] which led to physically reasonable results and agreed widely with experiment [6]. However, these were semi-phenomenological models and a microscopic theory for multi-component networks is, to the best of our knowledge, still lacking.

We consider the case of a highly crosslinked two-component polymer blend. For sufficiently strong incompatibility between the network components we expect phase separation on a mesoscopic length scale in which A rich and B rich microdomains are formed. To model such a situation we start from a long A-B diblock copolymer with the following structure:

$$R_i = \begin{cases} \text{A monomer} & \text{if } 0 \leq i < \phi N \\ \text{B monomer} & \text{if } \phi N \leq i \leq N. \end{cases} \quad (28)$$

Here ϕ and $1 - \phi$ are the volume fractions of the A and B components. Crosslinks between monomers are introduced in the same fashion as in (4). The additional crosslink between the A and B chain has, of course, no severe consequences. The interaction is described by a proper generalization of H_I in (2)

$$\beta H_I = \frac{1}{2} \left(v_{AA} \sum_{i,j=0}^{\phi N-1} \delta(R_i - R_j) + v_{BB} \sum_{i,j=\phi N}^N \delta(R_i - R_j) + 2 v_{AB} \sum_{i=0}^{\phi N-1} \sum_{j=\phi N}^N \delta(R_i - R_j) \right). \quad (29)$$

Here we closely follow Leibler's derivation [12] for diblock copolymer melts. Using the more general expression (29) in the Hamiltonian (5), the free energy is calculated in terms of one-component density fluctuations $\Phi_{\mathbf{k}}^A = \sum_{i=0}^{\phi N-1} \exp(i\mathbf{k}R_i)$ up to second order. From this standard calculation [22] a free energy functional of the same form as (27) is obtained with a modified expression for the structure function S [12]. For an incompressible system of symmetric copolymers ($v_{AA} = v_{BB} = v$ and $v_{AB} = v + \Delta v$) S is given in terms of crosscorrelation functions of single component density fluctuations $S_0^{xy}(\mathbf{k}, c) = \langle \Phi_{\mathbf{k}}^x \Phi_{-\mathbf{k}}^y \rangle_0$ ($x, y = A, B$) and the Flory parameter $\chi_F = \rho \Delta v$ [12]

$$S^{-1} = \frac{S_0^{AA} + S_0^{BB} + 2S_0^{AB}}{S_0^{AA} S_0^{BB} - (S_0^{AB})^2} - 2 \frac{\chi_F}{N} \quad (30)$$

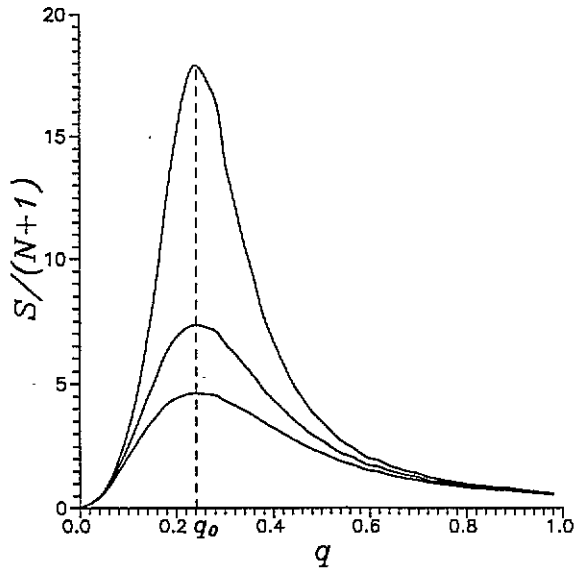


Figure 3. Structure function (30) of a symmetric crosslinked polymer blend for three different values of the Flory parameter $\chi_F = 0, 2c, 4c$ (upwards) with $c = M/N = 0.02$ ($M = 200$, $N = 10000$) and $\phi = 0.5$. We find that a maximum of S occurs at finite wavevector $q_0 = 0.23$ ($q^2 = k^2 a^2 / 2d$). For the above values of ϕ and c the disordered phase becomes unstable for $\chi_F \geq \chi_c \approx 4.3c$.

With the method described in section 4 it is straightforward to calculate $S_0^{xy}(k, c)$ by a proper generalization of (23) for arbitrary volume fraction $0 \leq \phi \leq 1$. In the disordered phase it is sufficient to consider quadratic terms of the order parameter (Φ_k^A) in the Landau free energy, equation (27). A complete understanding of microphase separation would require the study of the homogeneous phase as well as the ‘ordered’ mesophase. As a precursor for phase instability we analyse the behaviour of the structure function S , i.e. the correlation function of the local order parameter, at its maximum. From equation (30) it is clear that the position of the maximum can only depend on the magnitude of k and is independent of χ_F . From our calculation we find a maximum of S at finite wavevector k_0 (figure 3). Divergency of the structure function in (30) (i.e. $S^{-1} \rightarrow 0$) at its peak value k_0 indicates instability of the disordered phase and serves as definition for critical χ_c (figure 3). More calculational details will be presented elsewhere. For a lucid discussion of the above method, see [12].

6. Outlook and conclusion

There are many directions to extend this work and open problems in connection with macromolecular networks. Here we mention some of them mainly for completeness.

In this paper we have considered networks that were modelled from a single chain of macroscopic size. While this simplification is physically reasonable for highly crosslinked polymers [1–3], it completely fails to describe the correct physics of dilute systems. The problem of weakly crosslinked polymers is of special relevance in connection with the vulcanization transition, i.e. the transition from a liquid to an amorphous solid state. Upon increasing crosslink concentration the gel-fraction of the network grows until at the percolation threshold an infinitely large network cluster is formed. In this case it was shown

that a finite fraction of polymers spontaneously localizes [5] with respect to some reference frame (e.g., the centre of mass of the gel) and therefore can support applied stress. Although we are not dealing here with the vulcanization problem (*all* monomers are *a priori* localized via the harmonic potentials, equation (4)), it is instructive to see how the same issue arises in our formulation.

In a dilute network consisting of many unconnected or partially connected polymer chains, each network cluster has its own centre of mass mode. In this case it is no longer possible to integrate over each centre of mass coordinate separately as was done at the start of section 3. The simplifying feature there was, of course, simply connectedness of the object. Since any further progress required the matrix in (14) to be positive definite, a randomly crosslinked dilute network consisting of many chains poses additional mathematical problems. It is easy to see that for multiple chains, equation (A1) has to be replaced by the more general expression for a polymer melt

$$\mathcal{I}_n \otimes \begin{pmatrix} 0 & 0 & \cdots & 0 \\ 0 & 1 & \cdots & 0 \\ \vdots & \vdots & \ddots & \vdots \\ 0 & 0 & \cdots & 1 \end{pmatrix}. \quad (31)$$

Here \mathcal{I}_n is the n -dimensional unit matrix, n the number of polymer chains, and \otimes denotes a direct product. Equation (31) has a simple physical interpretation. The 1's represent the backbone of the chain and by removing one element from the diagonal, the chain is cut into two pieces, and so forth. It is interesting to note that even for this more general situation, it is still possible to 'invert' \mathcal{M} analytically, although it is no longer positive definite. This was proven in [14] by making use of the concept of pseudoinverse matrices which leads to a similar result as (18). However, the mathematics is more involved and will not be presented in this paper. In the framework of replica field theory the vulcanization problem was treated in [5] by invoking a variational ansatz for the localization length of monomers.

Finally, we want to make a short comment about the role of entanglements in polymeric networks. Up to now the systems considered were phantoms in the sense that the only topological restrictions on chain motion were permanent crosslinking junctions modelled by (4). In any realistic vulcanization process upon network formation a certain number of entanglements are permanently trapped, which can be viewed as another form of frozen constraint leading to reduction of entropy. However, up to now there are no topological invariants known to mathematicians that describe this phenomenon in a unique and rigorous fashion. A simplified version of the entanglement problem was proposed by Edwards and coworkers who have modelled entanglements in form of sliplinks [3, 23], i.e. crosslinks with the additional freedom to slide along the chain. Formally sliplinks are introduced by treating the crosslink coordinates as 'hot' variables. To see how equation (3) gets modified in the presence of sliplinks, we consider the simplest possible scenario in which all crosslinks in (3) are assumed to be sliplinks. To model a more realistic situation we had to consider both, crosslinks and sliplinks. Summing (3) over all i_e, j_e independently modifies the former crosslink term to $(\sum_{i,j=0}^N \delta(\mathbf{R}_i - \mathbf{R}_j))^M$. By invoking the well known identity $x^M = (M!/2\pi i) \oint d\mu e^{\mu x} \mu^{-(M+1)}$, it becomes clear that the sliplink contribution can be treated on a similar footing to the excluded volume interaction in (2). A mathematically similar but more involved problem arises in the replica formalism, and it has been shown [1] that the μ -integration is dominated by the steepest descent. Thus in the simple example considered the effective excluded volume is reduced by the presence of sliplinks to $v - \mu$. The above discussion is also valid for independently distributed crosslinks and sliplinks. Whereas the crosslinks modify the Wiener measure to (4), sliplinks renormalize the excluded

volume parameter. More sophisticated models can be formulated if the degrees of freedom of the sliplinks are, in addition, restricted by the permanent crosslink positions [3, 23].

In summary, we have proposed a microscopic model for RCGNs and its generalization to interacting networks and crosslinked polymer blends. As an extension of the Edwards Hamiltonian for linear polymers we introduced a similar Hamiltonian for RCGNs taking the excluded volume interaction into account. We developed a mathematical formalism which can solve the non-interacting RCGN exactly. By employing the idea of self-averaging we showed how to approach the excluded volume problem in a systematic, perturbative manner. Our method avoids the well known technical difficulties of replica theory like replica symmetry breaking or the $n \rightarrow 0$ limit. The theory presented provides a new perspective on various aspects and open questions of polymer networks with random and non-random connectivities that are of general interest.

Acknowledgment

Financial support of this work by the Deutsche Forschungsgemeinschaft, SFB 262, is gratefully acknowledged.

Appendix A.

To prove equation (14) we have to evaluate $\mathcal{D}'(z\mathcal{W} + \sum_{e=1}^M \mathcal{K}(i_e, j_e))\mathcal{D}$ in (9) with matrices defined via (10)–(12). First note that

$$\mathcal{D}'\mathcal{W}\mathcal{D} = \begin{pmatrix} 0 & 0 & \dots & 0 \\ 0 & 1 & \dots & 0 \\ \vdots & \vdots & \ddots & \vdots \\ 0 & 0 & \dots & 1 \end{pmatrix}. \tag{A1}$$

Let $e_i = (0, \dots, 0, 1, 0, \dots, 0)^t$ be the i th unitvector of the canonical basis in $N + 1$ -dimensional space. Then

$$\begin{aligned} \sum_{e=1}^M \mathcal{K}(i_e, j_e) &= \sum_{e=1}^M (e_{i_e} e_{i_e}^t + e_{j_e} e_{j_e}^t - e_{i_e} e_{j_e}^t - e_{j_e} e_{i_e}^t) \\ &= \sum_{e=1}^M (e_{i_e} - e_{j_e})(e_{i_e} - e_{j_e})^t \\ &= ((e_{i_1} - e_{j_1}), \dots, (e_{i_M} - e_{j_M}))((e_{i_1} - e_{j_1}), \dots, (e_{i_M} - e_{j_M}))^t. \end{aligned} \tag{A2}$$

From (A2) we obtain equations (14) and (15) by setting $p_e = -\mathcal{D}'(e_{i_e} - e_{j_e})$.

Appendix B.

We want to find the inverse of the matrix defined in equation (14),

$$\mathcal{M}(z) = z \left(\mathcal{I} + \frac{1}{z} \mathcal{P}\mathcal{P}^t \right) \tag{B3}$$

in the limit $z \rightarrow 0$. The difficulty with (B3) is that \mathcal{I} cannot be neglected against the $1/z$ term, since the crosslink contribution alone is highly singular with degeneracy $N - M$. We

proceed by writing the inverse of \mathcal{M} quite formally in terms of its Neumann series

$$\begin{aligned}\mathcal{M}^{-1}(z) &= \frac{1}{z} \left(\mathcal{I} + \frac{1}{z} \mathcal{P} \mathcal{P}^t \right)^{-1} = \frac{1}{z} \sum_{n=0}^{\infty} \left(-\frac{1}{z} \mathcal{P} \mathcal{P}^t \right)^n \\ &= \frac{1}{z} \left(\mathcal{I} - \frac{1}{z} \mathcal{P} \left(\sum_{n=0}^{\infty} \left(-\frac{1}{z} \mathcal{P}^t \mathcal{P} \right)^n \right) \mathcal{P}^t \right) \\ &= \frac{1}{z} \left(\mathcal{I} - \frac{1}{z} \mathcal{P} \left(\mathcal{I} + \frac{1}{z} \mathcal{P}^t \mathcal{P} \right)^{-1} \mathcal{P}^t \right).\end{aligned}\tag{B4}$$

With the definition in (15) it is easy to show that for tetrafunctional crosslinking junctions, the crosslink matrix \mathcal{P} is of full rank M . It is well known that in this case the normal form $\mathcal{P}^t \mathcal{P}$ is positive definite [13] and that therefore its inverse exists. Using this information we obtain equation (18) from (B4) by letting $z \rightarrow 0$. Convergency of the above manipulations is proved by multiplying the final result for \mathcal{M}^{-1} with \mathcal{M} in (B3) which gives identity. This also verifies the correctness of the result in (B4).

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