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Random networks of crosslinked manifolds

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Abstract. We generalize the statistical mechanical theory of vulcanization to the case of D -dimensional polymerized manifolds. Starting from a continuum model of self-avoiding manifolds, we study the effects of introducing random crosslinks between monomers on (in general) different manifolds. As for the case of linear polymers, one observes a continuous phase transition from a fluid to an amorphous solid state, characterized by a finite fraction of localized monomers. We compute this fraction, as well as the typical localization length near the transition.

1. Introduction

A melt or solution of linear macromolecules undergoes a thermodynamic phase transition from a fluid state to an amorphous solid state, if a sufficient number of permanent crosslinks between randomly chosen monomers are formed. This phase transition can be described within the framework of equilibrium statistical mechanics and, in particular, with methods that have been developed for random systems having quenched disorder [1, 2]. Recently, a statistical mechanical theory of the equilibrium phase transition has been presented [3–5]. It is the purpose of this paper to extend the analysis to the case of D -dimensional polymerized manifolds. We show that there is also, in general, a vulcanization transition for D -dimensional manifolds, if a sufficient density of permanent random crosslinks is introduced. Within mean-field theory, the critical behaviour is independent of the dimension D of the manifold. In particular, the gel fraction and the localization length (measured in units of the radius of gyration) are universal.

Polymerized membranes (i.e. manifolds with $D = 2$) have attracted a lot of theoretical interest [6], since they were first introduced by Kantor *et al* [7]. A variety of potential experimental realizations have been investigated:

- the spectrin network of red blood cells [8];
- the two-dimensional carbon networks in graphite oxide [9, 10];
- two-dimensional B_2O_3 glasses that have been nucleated under appropriate conditions [11];
- superstructures generated by the chemical crosslinking of macromolecules [12].

Scattering experiments on graphite oxide and spectrin networks have been interpreted as evidence for crumpled states. However the experimentally-observed directionally-averaged structure function is also compatible with flat and rough membranes, as discussed by Abraham and Goulian [13].

Extensive Monte Carlo simulations have been performed in order to understand the phase structure of polymerized membranes, and to resolve the question of a crumpling transition. Most simulations for two-dimensional tethered membranes, with excluded-volume interactions only, find no crumpled phase in three space dimensions [14–18]. There have also been studies of collections of manifolds to investigate the effects of screening [19,20]. We are not aware of studies—experimental or theoretical—of networks of D -dimensional manifolds.

2. Model of crosslinked manifolds

2.1. Hamiltonian for a polymerized membrane

A polymerized membrane is characterized by fixed connectivity of neighbouring monomers. Nearest neighbours are, for example, connected by a covalent bond. The connectivity can be modelled by a nearest-neighbour interaction of the form

$$H_{\text{int}} = \sum_{(\sigma, \sigma')} V(\mathbf{R}(\sigma) - \mathbf{R}(\sigma')) \quad (1)$$

where the summation runs over all nearest-neighbour pairs on the membrane. The position of a monomer on the membrane is characterized by a two-dimensional internal cartesian coordinate $\sigma = (\sigma_1, \sigma_2) \in S$, where S denotes a set of indices in \mathcal{R}^2 . The position of the monomer in the d -dimensional embedding space \mathcal{R}^d is specified by the external coordinate $\mathbf{R}(\sigma)$.

If no other interactions are considered then the model is called a phantom model. All interactions between monomers that are widely separated on the membrane have been ignored and, hence, nothing prevents the membrane from passing through itself. A tethered membrane can be modelled by $V(r) = 0$ for $a_1 < r < a_2$, and is infinite otherwise. If one is interested in length scales much larger than the typical distance b between monomers, $a_1 < b < a_2$, then one commonly replaces the potential by a harmonic one:

$$\beta H_{\text{int}} = \frac{d}{2b^2} \sum_{(\sigma, \sigma')} |\mathbf{R}(\sigma) - \mathbf{R}(\sigma')|^2. \quad (2)$$

(For a discussion see [7].)

It is well known that excluded-volume interactions are much more important for membranes (i.e. $D = 2$ manifolds) in $d = 3$ than for linear polymers (i.e. $D = 1$ manifolds). These interactions act between pairs of monomers that are close in \mathcal{R}^d but arbitrarily far apart on the membrane, and can be modelled, following Edwards [21], by using

$$\beta H_0 = \frac{d}{2b^2} \sum_{(\sigma, \sigma')} |\mathbf{R}(\sigma) - \mathbf{R}(\sigma')|^2 + \frac{1}{2} \sum_{\substack{\sigma, \sigma' \\ |\sigma - \sigma'| > b}} v_0 \delta^{(d)}(\mathbf{R}(\sigma) - \mathbf{R}(\sigma')) \quad (3)$$

where v_0 characterizes the strength of the (repulsive) excluded-volume interaction. It will be more convenient to use a continuum description, having in mind a large membrane consisting of many monomers, and focusing on length scales $\gg b$. Furthermore, we shall consider the general case of D -dimensional manifolds of ‘area’ S . We adopt units of energy such that $\beta^{-1} \equiv k_B T = 1$, and introduce dimensionless internal coordinates $s = \sigma/L$ and external coordinates $\mathbf{c} = (L^{2-D} b^D/d)^{-1/2} \mathbf{R}$, with $L \equiv S^{1/D}$. In terms of these coordinates the model Hamiltonian for a single membrane is expressed as

$$H_0(\{\mathbf{c}(s)\}) = \frac{1}{2} \int d^D s \sum_{a=1}^D \sum_{v=1}^d \left(\frac{\partial c_v}{\partial s_a} \right)^2 + \frac{\lambda^2}{2} \int d^D s \int d^D s' \delta^{(d)}(\mathbf{c}(s) - \mathbf{c}(s')). \quad (4)$$

The above Hamiltonian has been discussed extensively in the literature. In our approach, H_0 specifies the statistical properties of the elements that are then used to build up a network, i.e. the building blocks. In the following section we shall discuss the statistical mechanics of an ensemble of building blocks, and the construction of a network by pointwise crosslinking of randomly chosen pairs of monomers.

2.2. Networks of polymerized membranes

The degrees of freedom of a system of N membranes (or, in general, D -dimensional manifolds) are denoted by $\{c_i(s)\}$ with $i = 1, \dots, N$ and are confined to a large hypercube of volume V . The system is characterized by the Hamiltonian

$$H = \sum_{i=1}^N H_0(\{c_i(s)\}) + \frac{\gamma^2}{2} \sum_{i,j=1}^N \int d^D s d^D s' \delta^{(d)}(c_i(s) - c_j(s')). \quad (5)$$

The first term is just the sum of one-membrane Hamiltonians and the second term accounts for excluded-volume interactions between monomers on different membranes. These are characterized by γ^2 , which can in principle be different from the intramanifolds interactions[†]. We take the thermodynamic limit such that $N \rightarrow \infty$ and $V \rightarrow \infty$ with $n_0 = N/V$ fixed. Alternatively one may consider one extensive manifold, as discussed in appendix A.

Crosslinks are introduced into the system by randomly choosing pairs of monomers, and constraining these pairs to occupy common spatial locations. If M pairs (monomer s_e on manifold i_e and monomer s'_e on manifold i'_e , with $e = 1, \dots, M$) have been chosen, the configurations of the system must respect the M random constraints

$$c_{i_e}(s_e) = c_{i'_e}(s'_e) \quad (\text{for } e = 1, \dots, M). \quad (6)$$

The partition function of the crosslinked system, relative to that of the uncrosslinked system, is given by

$$Z(\{i_e, i'_e, s_e, s'_e\}) = \left\langle \prod_{e=1}^M \delta^{(d)}(c_{i_e}(s_e) - c_{i'_e}(s'_e)) \right\rangle_H. \quad (7)$$

Here, the expectation value is taken with respect to the statistical weight $\exp(-H)$.

Once a crosslink is formed, it is not allowed to break up and reconnect, but instead is assumed to be permanent. Hence, the indices $\{i_e, i'_e, s_e, s'_e\}$, which specify a particular realization of the crosslinks, are quenched random variables. We only consider crosslinking processes in which crosslinks form rapidly, compared to the characteristic diffusion time of the building blocks, i.e. crosslinking is essentially instantaneous. Monomers that are nearby at the instant of crosslinking are connected with a certain probability. The statistics of such a process can be described by the Deam–Edwards form [1],

$$P(\{i_e, i'_e, s_e, s'_e\}) \propto \left\langle \prod_{e=1}^M \delta^{(d)}(c_{i_e}(s_e) - c_{i'_e}(s'_e)) \right\rangle_H \quad (8)$$

of the probability distribution $P(\{i_e, i'_e, s_e, s'_e\})$ of finding a particular realization of the crosslinks, in which monomer s_e on manifold i_e is linked to monomer s'_e on manifold i'_e

[†] Strictly speaking, one should only sum over $i \neq j$ in (5). This is equivalent to unrestricted summation, if λ^2 is replaced by $\lambda^2 - \gamma^2$. Since none of our results depends on the particular value of λ^2 , we find it convenient to include the term $i = j$ from the start.

(for $e = 1, \dots, M$). For technical reasons it is also convenient to allow the number of crosslinks to fluctuate, and take

$$P_M = \frac{1}{\mathcal{Z}_1} \frac{1}{M!} \left(\frac{\mu^2 V}{2N} \right)^M \left\langle \prod_{e=1}^M \delta^{(d)}(\mathbf{c}_{i_e}(s_e) - \mathbf{c}_{i'_e}(s'_e)) \right\rangle_H. \quad (9)$$

Here, \mathcal{Z}_1 ensures the proper normalization of P_M , and the mean number of crosslinks $[M]$ is controlled by μ^2 . As shown in appendix B, $[M] = \alpha \mu^2 N$, where the proportionality constant $\alpha = \mathcal{O}(1)$. Its precise value depends on the strength of the monomer–monomer interaction.

3. Calculations and results

To average $\ln Z$ over the disorder with the crosslink distribution P_M we use the replica technique. The average free energy per manifold f is given by $\lim_{n \rightarrow 0} f_n$ with $-N n f_n = [Z^n - 1]$. Averaging over the quenched disorder with the distribution P_M is denoted by $[\dots]$. Given the distribution of the quenched degrees of freedom P_M , we adopt the strategy of simultaneously computing the partition function and the distribution of disorder P_M . This can be achieved by introducing one additional replica (for details see [5]), so that the average free energy is given by

$$-N n f_n = \frac{\mathcal{Z}_{n+1} - \mathcal{Z}_1}{\mathcal{Z}_1}. \quad (10)$$

For integer n the disorder average can be explicitly performed, yielding

$$\mathcal{Z}_{n+1} = \left\langle \exp \left(\frac{\mu^2 V}{2N} \sum_{i,j=1}^N \int d^D s d^D s' \prod_{\alpha=0}^n \delta^{(d)}(\mathbf{c}_i^\alpha(s) - \mathbf{c}_j^\alpha(s')) \right) \right\rangle_H^{n+1}. \quad (11)$$

Here, the angular brackets $\langle \dots \rangle_H^{n+1}$ denote averaging with the $(n+1)$ -fold replicated Hamiltonian (5). It is convenient to simplify the notation by introducing hatted vectors for $(n+1)$ -fold replicated vectors, for example, $\hat{\mathbf{c}} \equiv (\mathbf{c}^0, \mathbf{c}^1, \dots, \mathbf{c}^n)$, and to use a Fourier representation for the δ -function in (11):

$$\mathcal{Z}_{n+1} = \left\langle \exp \left(\frac{\mu^2 N}{2V^n} \sum_{\hat{\mathbf{k}}} \left| \frac{1}{N} \sum_{i=1}^N \int d^D s e^{i\hat{\mathbf{k}} \cdot \hat{\mathbf{c}}_i(s)} \right|^2 \right) \right\rangle_H^{n+1}. \quad (12)$$

We aim at the decoupling of the membranes from one another, which interact due to crosslinks and the excluded-volume interaction in H . In order to achieve such a decoupling we first rewrite \mathcal{Z}_{n+1} in such a way as to explicitly display all intermembrane interactions: $\mathcal{Z}_{n+1} = \psi(\mu^2)/\psi(0)$, with

$$\begin{aligned} \psi(\mu^2) &= \left\langle \exp \left(-\frac{\gamma^2}{2} n_0 N \sum_{\alpha=0}^n \sum_{\hat{\mathbf{k}}} \left| \frac{1}{N} \sum_{i=1}^N \int d^D s e^{i\hat{\mathbf{k}} \cdot \mathbf{c}_i^\alpha(s)} \right|^2 \right) \right. \\ &\quad \left. \times \exp \left(\frac{\mu^2 N}{2V^n} \sum_{\hat{\mathbf{k}}} \left| \frac{1}{N} \sum_{i=1}^N \int d^D s e^{i\hat{\mathbf{k}} \cdot \hat{\mathbf{c}}_i(s)} \right|^2 \right) \right\rangle_{H_0}^{n+1}. \end{aligned} \quad (13)$$

Here, the average is taken with respect to the $(n+1)$ -fold replicated Hamiltonian for one manifold, i.e. with $\sum_{\alpha=0}^n \sum_{i=1}^N H_0(\{\mathbf{c}_i^\alpha\})$. All intermembrane interactions can now be

decoupled with the help of Gaussian transformations:

$$\begin{aligned} \psi(\mu^2) = & \int \mathcal{D}\Omega \mathcal{D}\rho \exp \left(-\frac{\mu^2 N}{2V^n} \overline{\sum_{\hat{k}} |\Omega(\hat{k})|^2} - \frac{\tilde{\gamma}^2 n_0}{2} N \sum_{\alpha=0}^n \sum_{\mathbf{k}}' |\rho_{\mathbf{k}}^\alpha|^2 - \frac{1}{2} n N \tilde{\gamma}^2 n_0 \right. \\ & + N \ln \left\langle \exp \left(i \tilde{\gamma}^2 n_0 \sum_{\alpha=0}^n \sum_{\mathbf{k}}' \operatorname{Re} \rho_{\mathbf{k}}^\alpha \int d^D s e^{-i\mathbf{k} \cdot \mathbf{c}^\alpha(s)} \right) \right. \\ & \left. \left. \times \exp \left(\frac{\mu^2}{V^n} \overline{\sum_{\hat{k}} \operatorname{Re} \Omega(\hat{k})} \int d^D s e^{-i\hat{\mathbf{k}} \cdot \hat{\mathbf{c}}(s)} \right) \right\rangle_{H_0}^{n+1} \right) \end{aligned} \quad (14)$$

and

$$\begin{aligned} \psi(0) = & \int \mathcal{D}\rho \exp \left(-\frac{\gamma^2}{2} N n n_0 - \frac{\gamma^2}{2} N n_0 \sum_{\alpha=0}^n \sum_{\mathbf{k}}' |\rho_{\mathbf{k}}^\alpha|^2 \right. \\ & \left. + N \ln \left\langle \exp \left(i \gamma^2 n_0 \sum_{\alpha=0}^n \sum_{\mathbf{k}}' \operatorname{Re} \rho_{\mathbf{k}}^\alpha \int d^D s e^{-i\mathbf{k} \cdot \mathbf{c}^\alpha(s)} \right) \right\rangle_{H_0}^{n+1} \right). \end{aligned} \quad (15)$$

Here, $\tilde{\gamma}^2 \equiv \gamma^2 - (\mu^2/V^n)n_0$ denotes the effective strength of the excluded-volume interaction, $\sum_{\mathbf{k}}'$ refers to the summation over \mathbf{k} (excluding $\mathbf{k} = \mathbf{0}$), and $\overline{\sum_{\hat{k}}}$ refers to the summation over $\hat{\mathbf{k}}$ vectors with at least two components different from zero. Functional integration over the fields $\Omega(\hat{\mathbf{k}})$ and $\rho_{\mathbf{k}}^\alpha$ is denoted by $\mathcal{D}\Omega$ and $\mathcal{D}\rho$. The expectation value of the field $\rho_{\mathbf{k}}^\alpha$,

$$\langle \rho_{\mathbf{k}}^\alpha \rangle = \frac{1}{N} \sum_{i=1}^N \int d^D s [\langle \exp(i\mathbf{k} \cdot \mathbf{c}^\alpha(s)) \rangle] \quad (16)$$

is simply the average density (assuming a replica symmetric state). The expectation value of the field $\Omega(\hat{\mathbf{k}})$

$$\langle \Omega(\hat{\mathbf{k}}) \rangle = \frac{1}{N} \sum_{i=1}^N \int d^D s [\langle \exp(i\hat{\mathbf{k}} \cdot \hat{\mathbf{c}}(s)) \rangle] \quad (17)$$

is the straightforward generalization of the order parameter for vulcanization to D -dimensional manifolds [5]. In the fluid phase, a flexible manifold can wander throughout the container, hence there are no static density fluctuations: $\langle e^{i\mathbf{k} \cdot \mathbf{c}_i(s)} \rangle = 0$ and $\langle \Omega(\hat{\mathbf{k}}) \rangle = 0$. Once an infinite network is built up, a finite fraction of manifolds are localized around fixed random positions, implying non-zero static density fluctuations $\langle e^{i\mathbf{k} \cdot \mathbf{c}_i(s)} \rangle \neq 0$. The amorphous solid preserves macroscopic translational invariance. Hence, this state is characterized by vanishing macroscopic density fluctuations, i.e. $\langle \rho_{\mathbf{k}}^\alpha \rangle = 0$, whereas higher moments of the local static density are non-zero, indicating that a finite fraction of monomers are localized. For example, the second moment of the static density fluctuations is the analogue of the Edwards–Anderson order parameter for spin glasses. It is given by

$$\langle \Omega(0, \mathbf{k}, -\mathbf{k}, 0, \dots, 0) \rangle = \frac{1}{N} \sum_{i=1}^N \int d^D s [\langle \exp(i\mathbf{k} \cdot \mathbf{c}(s)) \rangle \langle \exp(-i\mathbf{k} \cdot \mathbf{c}(s)) \rangle] \quad (18)$$

whereas $\langle \Omega(\hat{\mathbf{k}}) \rangle$ with more than two components of $\hat{\mathbf{k}}$ non-zero yields higher moments of the static density fluctuations. In general, we expect that $\langle \Omega(\hat{\mathbf{k}}) \rangle \neq 0$ in the amorphous solid state, provided all wavenumbers add up to zero, $\sum_{\alpha=0}^n \mathbf{k}^\alpha = \mathbf{0}$, as required by macroscopic translation invariance.

The representation of the average free energy in terms of the fields $\Omega(\hat{\mathbf{k}})$ and $\rho_{\mathbf{k}}^\alpha$ is exact. So far, the formal development is very similar to the case of linear polymers, which has been explained in detail in [5]. A field theoretic formulation of crosslinked manifolds can be derived from (14) and (15). The bare vertices of the resulting Ginzburg–Landau–Wilson free energy would be correlation functions of the uncrosslinked manifold system, which differ considerably from the polymer case. Here we shall only discuss the mean-field approximation, obtained by saddle-point integration of the functional integral. As it turns out, the dimension D of the manifold only features via the elementary length scale, and leaves the critical behaviour unaltered from the case of polymers.

Instead of solving the full saddle-point equation we use a simplified ansatz, and invoke a variational principle for the free energy at the saddle-point level. We are primarily interested in non-crystalline networks, and therefore choose the parameters of the Hamiltonian of the uncrosslinked system such that no instability to crystalline or collapsed states occurs. This is equivalent to choosing the parameter $\gamma^2 > \mu^2(V/N)V^n$, and implies for the saddle-point solution $\bar{\rho}_{\mathbf{k}}^\alpha=0$ for all \mathbf{k} . In the amorphous solid state we expect a non-zero fraction of monomers, denoted by q , to be localized at random positions and exhibit fluctuations over a finite length scale ξ . In the simplest ansatz

$$\bar{\Omega}(\hat{\mathbf{k}}) = \delta_{\sum_{\alpha=0}^n k^\alpha, 0} q \exp\left(-\frac{\xi^2}{2} \sum_{\alpha=0}^n |\mathbf{k}^\alpha|^2\right) \quad (19)$$

these fluctuations are modelled by Gaussian functions parametrized by a characteristic localization length ξ . This Ansatz implies that $\psi(0) = 1 = \mathcal{Z}_1$ and

$$-Nnf_n = -\frac{\mu^2 N}{2V^n} \sum_{\hat{\mathbf{k}}} |\bar{\Omega}(\hat{\mathbf{k}})|^2 + N \ln \left\langle \exp\left(\frac{\mu^2}{V^n} \text{Re} \sum_{\hat{\mathbf{k}}} \bar{\Omega}(\hat{\mathbf{k}}) \int d^D s e^{-i\hat{\mathbf{k}} \cdot \hat{\mathbf{c}}(s)}\right) \right\rangle_{H_0}^{n+1}. \quad (20)$$

Next, the ansatz for $\bar{\Omega}(\hat{\mathbf{k}})$ is inserted into (20), and the exponential in the second term is expanded, resulting in a Landau free energy in terms of $\bar{\Omega}(\hat{\mathbf{k}})$. The coefficients in this expansion are the correlations of the density, determined by the one-membrane Hamiltonian, for example

$$C_{\mathbf{k}}(s, s') \equiv \langle \exp(i\mathbf{k} \cdot (\mathbf{c}(s) - \mathbf{c}(s'))) \rangle_{H_0}. \quad (21)$$

Near to the transition from the amorphous to the liquid state we expect the localization length ξ to be much larger than any inherent length scale of a membrane. Given the form of the expansion of f_n , we notice that the one-membrane correlations are always multiplied by $e^{-\xi^2 k^2/2}$, thereby restricting the range of wavenumbers to $k \leq 1/\xi$. In that range the one-membrane correlations are well approximated by

$$C_{\mathbf{k}}(s, s') \approx \exp\left(-\frac{\mathbf{k}^2}{2d} \langle (\mathbf{c}(s) - \mathbf{c}(s'))^2 \rangle_{H_0}\right) \quad (22)$$

so that sufficiently close to the transition only the second moment of $(\mathbf{c}(s) - \mathbf{c}(s'))$ enters the calculation, even though we consider in general *non-Gaussian* manifolds.

These expectations are born out by the explicit calculation of f , which yields

$$f = f^{(1)} + f^{(2)} + f^{(3)} \quad (23a)$$

$$f^{(1)} = \left(\frac{\mu^2 q^2}{2} - \tilde{g}(\mu^2 q)\right) \ln V \quad (23b)$$

$$f^{(2)} = -\frac{d}{2} \left(\frac{\mu^2 q^2}{2} - \tilde{g}(\mu^2 q)\right) \ln \xi^2 + \tilde{g}(\mu^2 q) \frac{R_G^2}{2\xi^2} + \mathcal{O}(\xi^{-4}) \quad (23c)$$

where $f^{(3)}$ contains all terms that only depend on q and are intensive. (See [5] for a discussion of non-intensive terms arising owing to the neglect of the issue of distinguishability.) Here, $\tilde{g}(x) \equiv e^{-x} - (1 - x)$, and the radius of gyration R_G has been defined for a general D -dimensional manifold via

$$R_G^2 \equiv \frac{1}{2} \int d^D s d^D s' \langle (c(s) - c(s'))^2 \rangle_{H_0}. \quad (24)$$

As in section 6C of [5] we regard $f^{(1)}$ as dominant and make it stationary with respect to the gel fraction q . This leads to the equation

$$1 - q = e^{-\mu^2 q} \quad (25)$$

which is *independent* of the dimension D of the manifold. At first sight this result may be surprising. However, a non-zero gel fraction indicates the appearance of an infinite network, which is solely a question of geometry, and should not depend on the building blocks of the network.

As discussed in detail in [5], (25) always has the solution $q = 0$, corresponding to the liquid state. For $\mu^2 > \mu_c^2 = 1$ an additional root appears, which emerges continuously from $q = 0$: for $|\mu^2 - 1| \ll 1$ we have

$$q \simeq 2(\mu^2 - 1)^\beta \quad (26)$$

with $\beta = 1$, in agreement with mean-field percolation. This solution describes the fraction of monomers that are localized in the amorphous solid state. To obtain the localization length we demand that $f^{(2)}$ be stationary with respect to variations of ξ^2 . This leads to

$$\frac{1}{\xi^2} = \frac{\mu^2 - 1}{3R_G^2} d + \mathcal{O}((\mu^2 - 1)^2) \quad (27)$$

i.e. the length over which particles are localized in the solid phase diverges at the vulcanization transition. In particular, sufficiently near to the critical point this length far exceeds the linear dimension of the objects being connected. Therefore the characteristics of these objects feature only to the extent that they determine the semi-microscopic length scale R_G , which depends on D , as will be discussed in the next section. The critical behaviour, such as the exponent of the localization length, is not explicitly dependent on the dimension D of the manifold.

To summarize our results so far: we observe a sharp phase transition from a fluid phase to a localized state with macroscopic translational invariance. The critical singularities are independent of the dimension D of the manifold. The latter only determines the semi-microscopic length, which sets the scale for ξ^2 .

4. Statistics of one membrane

The simplest model for a polymerized membrane is the Gaussian model, in which excluded-volume interactions are ignored, i.e. $\lambda = 0$ in (4). For a Gaussian D -dimensional manifold one can easily calculate the generating function, from which all correlations follow by differentiation. We assume stress-free boundary conditions, i.e. the outward normal derivative of c vanishes on the boundary, $\partial c / \partial n = \mathbf{0}$ on ∂S . The generating function can be expressed in terms of the eigenvalues λ_ρ and eigenfunctions u_ρ of the negative Laplacian operator, $-\Delta u_\rho = \lambda_\rho u_\rho$, in the following way

$$\left\langle \exp \left(i \sum_\alpha \mathbf{p}_\alpha \cdot c(s_\alpha) \right) \right\rangle_{\text{Gauss}} = \delta_{\mathbf{0}, \sum_\alpha \mathbf{p}_\alpha} \exp \left(- \frac{1}{2} \sum_{\alpha, \beta} \mathbf{p}_\alpha \cdot \mathbf{p}_\beta G(s_\alpha, s_\beta) \right) \quad (28a)$$

with

$$G(s_\alpha, s_\beta) = \sum_{\substack{\rho \\ (\lambda_\rho \neq 0)}} \frac{1}{\lambda_\rho} u_\rho^*(s_\alpha) u_\rho(s_\beta). \quad (28b)$$

The average is taken with the Gaussian one-membrane Hamiltonian, i.e. with H_0 from (4) with $\lambda^2 = 0$. For a linear polymer (i.e. $D = 1$), the eigenfunctions and eigenvalues are given by

$$u_n(s) \propto \cos(\pi s n) \quad (n = 0, 1, 2, \dots) \quad (29a)$$

$$\lambda_n = \pi^2 n^2. \quad (29b)$$

We make use of the result $\sum_{n=1}^{\infty} n^{-2} = \pi^2/6$ to obtain the well known result for the radius of gyration: $R_G^2 = Lb/6$ and, hence,

$$\xi^2 = \frac{1}{\mu^2 - 1} \frac{bL}{2d} \quad (30)$$

where physical units have been restored. For a Gaussian membrane (i.e. $D = 2$) the eigenfunctions and eigenvalues depend on the shape of the membrane. Easily solvable are shapes that allow for a separation of coordinates, such as a disc or a square. In the latter, case one obtains

$$u_{nm}(s) \propto \cos(\pi s_1 n) \cos(\pi s_2 m) \quad (n, m = 0, 1, 2, \dots) \quad (31a)$$

$$\lambda_{nm} = \pi^2(n^2 + m^2). \quad (31b)$$

To perform the summation over inverse eigenvalues one has to introduce a short distance cutoff. We require that the zeros of the eigenfunctions be separated by a distance larger than the persistence length b . This requirement truncates the summation for large n and m , and yields $R_G = (b/\pi)^2 \ln(L/b)$, and hence

$$\xi^2 = \frac{3}{\pi^2} \frac{1}{\mu^2 - 1} \frac{b^2}{d} \ln(L/b). \quad (32)$$

In a similar way one can treat the general case of a D -dimensional hypercube. However, as noted previously, these results are not meaningful for $D \geq 2$. If one makes the ansatz

$$R_G \propto L^\nu \quad (33)$$

then one can easily derive the following bounds on ν , viz $(D/d) \leq \nu \leq 1$ [22]. The upper bound corresponds to a flat manifold, and the lower bound to a dense packing of the monomers. A Gaussian or phantom linear polymer does satisfy the bounds for $d \geq 2$, whereas a Gaussian membrane violates the bounds in all finite space dimensions d . It is intuitively clear that the process of folding back and passing through itself is much more likely for a membrane than for a linear polymer in $d = 3$. Unfortunately, the radius of gyration of a membrane in a good solvent is not known analytically. If the manifold were crumpled, a generalization of Flory theory [7] would predict a radius of gyration that scales as $R_G \propto L^{(D+2)/(d+2)}$, i.e. $\nu \propto \frac{4}{5}$ for $d = 3$ and $D = 2$, compatible with the lower bound. Computer simulations [14–18] indicate that membranes with excluded-volume interactions are flat in $d = 3$, implying $R_G \propto L$.

One may also consider a different one-membrane Hamiltonian, including, for example, a bending energy. We stress that our results for the critical behaviour are independent of the particular model used. The one-membrane Hamiltonian determines only the ‘internal’ length scale of the problem, i.e. the radius of gyration.

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Appendix A. A different thermodynamic limit

So far we have discussed a statistical ensemble of manifolds, each manifold being of finite extent. An alternative way to achieve the thermodynamic limit is to consider a single manifold, the linear extent $L = Kb$ of which tends to infinity. We want to ensure that the configurations of the manifold are determined by its own statistical properties and not by the walls of the container (see [23]). Hence we have to require that the box size $V^{1/d}$ is larger than the radius of gyration:

$$V^{1/d} \geq R_G \propto K^v. \quad (\text{A1})$$

This inequality restricts our discussion to dilute or semi-dilute solutions. The latter are characterized by $R_G^d \sim Vz$, i.e. a monomer density

$$\rho_{\text{monomer}} = \frac{K^D}{V} \propto K^{D-dv}. \quad (\text{A2})$$

In the thermodynamic limit, $K \rightarrow \infty$ and $V \rightarrow \infty$. For semi-dilute solutions one has to keep $K^v/V^{1/d}$ fixed, whereas for dilute solutions the above ratio goes to zero in the thermodynamic limit.

To simplify the discussion, we only consider one-dimensional manifolds, i.e. one linear polymer of length L . The partition function of the crosslinked system is given by

$$Z(\{s_e, s'_e\}) = \left\langle \prod_{e=1}^M \delta^{(d)}(\mathbf{c}(s_e) - \mathbf{c}(s'_e)) \right\rangle_{H_0}. \quad (\text{A3})$$

Crosslink realizations $\{s_e, s'_e\}$ are generated by the distribution

$$P_M(\{s_e, s'_e\}) = \frac{1}{Z_1} \frac{1}{M!} \left(\frac{\mu^2 V}{2L} \right)^M \left\langle \prod_{e=1}^M \delta^{(d)}(\mathbf{c}(s_e) - \mathbf{c}(s'_e)) \right\rangle_{H_0} \quad (\text{A4})$$

where Z_1 guarantees proper normalization of P_M . The analysis of the average free energy is completely analogous to that given in section 3 and yields, in the saddle-point approximation,

$$nKf_n = \frac{\mu^2 L}{2V^n} \overline{\sum_{\hat{\mathbf{k}}} |\bar{\Omega}(\hat{\mathbf{k}})|^2} - \ln \left\langle \exp \left(\frac{\mu^2 L}{V^n} \text{Re} \sum_{\hat{\mathbf{k}}} \bar{\Omega}(\hat{\mathbf{k}}) \int ds e^{i\hat{\mathbf{k}} \cdot \hat{\mathbf{c}}(s)} \right) \right\rangle_{H_0}^{n+1} \quad (\text{A5})$$

with

$$\bar{\Omega}(\hat{\mathbf{k}}) = \int d^D s [e^{i\hat{\mathbf{k}} \cdot \hat{\mathbf{c}}(s)}]. \quad (\text{A6})$$

Comparison with (20) shows that the free energy per monomer for one long chain is the same as the free energy per monomer for an ensemble of finite chains, provided we make the substitution $\mu^2 K \rightarrow \mu^2$. Hence we can take over the results of section 3:

$$q \simeq 2(\mu^2 K - 1) \quad (\text{A7a})$$

$$\frac{1}{\xi^2} \simeq \frac{1}{3}(\mu^2 K - 1) \frac{d}{R_G^2}. \quad (\text{A7b})$$

The mean number of crosslinks is related to μ^2 by $[M] = \alpha \mu^2 K$ with $\alpha = \mathcal{O}(1)$ as $K \rightarrow \infty$, so that $[M] = \mathcal{O}(1)$ crosslinks are sufficient to observe the transition to the amorphous solid state. This result seems puzzling at first sight, but can be understood intuitively. The first crosslink that is introduced into the system typically generates a loop of size $L/2$. After M crosslinks have been formed one typically has loops of size $L/2^M$. To achieve a loop size of order R_G one needs $M_c \propto \ln(L/R_G)$. Whether M_c is actually of $\mathcal{O}(1)$ or $\mathcal{O}(\ln K)$ is difficult to decide. The typical loop size of the critical network is presumably larger than R_G , favouring smaller values of M_c . One may also consider one long polymer as being constructed by the endlinking of $\mathcal{O}(K)$ small ones, so that already of $\mathcal{O}(K)$ crosslinks have been introduced into the system. This interpretation is consistent with the results of section 3.

Appendix B. Average number of crosslinks

In this appendix we derive an approximate relation between the mean number of crosslinks $[M]$ and the control parameter μ^2 . Our starting point is the exact expression for $[M]$,

$$[M] = \mu^2 \frac{d}{d\mu^2} \ln \mathcal{Z}_1 \quad (\text{B1})$$

in terms of

$$\mathcal{Z}_1 = \left\langle \exp \left(\frac{\mu^2 V}{2N} \sum_{i,j} \int d^D s d^D s' \delta^{(d)}(\mathbf{c}_i(s) - \mathbf{c}_j(s')) \right) \right\rangle_H = \frac{\phi(\mu^2)}{\phi(0)}. \quad (\text{B2})$$

As in section 3, we decouple interactions between different manifolds by Gaussian transformations. The numerator is rewritten with help of the Gaussian field ρ_k in the following way

$$\begin{aligned} \phi(\mu^2) &= \text{Tr}_{\mathbf{c}_i(s)} e^{-H} \exp \left(\frac{\mu^2 V}{2N} \sum_{i,j} \int d^D s d^D s' \delta^{(d)}(\mathbf{c}_i(s) - \mathbf{c}_j(s')) \right) \\ &= \text{Tr}_{\mathbf{c}_i(s)} e^{-H_0} \exp \left(-\frac{\tilde{\gamma}^2 N^2}{2V} \sum_k \left| \frac{1}{N} \sum_i \int d^D s e^{i\mathbf{k} \cdot \mathbf{c}_i(s)} \right|^2 \right) \\ &= e^{-\tilde{\gamma}^2 N n_0 / 2} \int \mathcal{D}\rho_k \exp \left(-\tilde{\gamma}^2 N n_0 \sum_k' \rho_k \rho_{-k} + N \ln \Xi(\{\rho_k\}) \right) \end{aligned} \quad (\text{B3})$$

with

$$\Xi(\{\rho_k\}) = \text{Tr}_{\mathbf{c}_i(s)} e^{-H_0} \exp \left(i 2 \tilde{\gamma}^2 n_0 \sum_{k>0} \text{Re} \left(\rho_k \int d^D s e^{i\mathbf{k} \cdot \mathbf{c}_i(s)} \right) \right). \quad (\text{B4})$$

The functional integral over $\{\rho_k\}$ cannot be done exactly. We evaluate it approximately by expanding $\ln \Xi$ up to quadratic order in the fields $\{\rho_k\}$:

$$\ln \Xi(\{\rho_k\}) \approx -(\tilde{\gamma}^2 n_0)^2 \sum_k' \rho_k \rho_{-k} S(k^2) \quad (\text{B5})$$

where $S(k^2)$ denotes the static structure factor, given by

$$S(k^2) = \int d^D s d^D s' \langle e^{i\mathbf{k} \cdot (\mathbf{c}(s) - \mathbf{c}(s'))} \rangle_{H_0}. \quad (\text{B6})$$

The resulting Gaussian integral over $\{\rho_k\}$ yields

$$\phi(\mu^2) \approx e^{(\tilde{\gamma}^2/2) N n_0} \left(\prod_{k>0} (1 + 2\tilde{\gamma}^2 n_0 S(k^2)) \right)^{-1} \quad (\text{B7})$$

and hence

$$\ln \mathcal{Z}_1 \approx \frac{\mu^2}{2} N + \frac{V}{2(2\pi)^d} \int d^d k \ln \frac{1 + 2\gamma^2 n_0 S(k^2)}{1 + 2\tilde{\gamma}^2 n_0 S(k^2)}. \quad (\text{B8})$$

The integral over wavenumbers is ultraviolet divergent, for example, for $D = 1$, $S(k^2)$ decays like k^{-2} for large k . This divergence is an artifact of our continuum model and can be taken care of by going back to the microscopic basis of the model. The excluded-volume interactions as well as the constraints owing to the crosslinks cannot be modelled by δ -functions, if one is interested in length scales which are comparable to the persistence length b . In a more realistic model the δ -functions are replaced by a potential $U(\mathbf{x})$, which can, for example, be taken as a Gaussian of width b . One then obtains

$$\frac{[M]}{N} = \frac{\mu^2}{2} + \frac{1}{2n_0} \int \frac{d^d k}{(2\pi)^d} \ln \frac{1 + 2\gamma^2 n_0 U(\mathbf{k}) S(k^2)}{1 + 2\tilde{\gamma}^2 n_0 U(\mathbf{k}) S(k^2)} \quad (\text{B9})$$

or, for α ,

$$\alpha = \frac{[M]}{\mu^2 N} = \frac{1}{2} + \frac{1}{n_0} \int \frac{d^d k}{(2\pi)^d} U(\mathbf{k}) S(k^2) + \mathcal{O}(\mu^2). \quad (\text{B10})$$

References

- [1] Deam R T and Edwards S F 1975 *Phil. Trans. R. Soc. London A* **280** 317
- [2] Goldbart P M and Goldenfeld N 1987 *Phys. Rev. Lett.* **58** 2676
Goldbart P M and Goldenfeld N 1989 *Phys. Rev. A* **39** 1402
Goldbart P M and Goldenfeld N 1989 **39** 1412
- [3] Goldbart P M and Zippelius A 1993 *Phys. Rev. Lett.* **71** 2256
- [4] Castillo H E, Goldbart P M and Zippelius A 1994 *Europhys. Lett.* **28** 519
- [5] Goldbart P M, Castillo H E and Zippelius A 1996 Randomly crosslinked macromolecular systems: vulcanization transition to and properties of the amorphous solid state *Adv. Phys.* **45** 393–468; cond-mat/9604062
- [6] Nelson D, Piran T and Weinberg S (ed) 1989 *Jerusalem Winter School for Theoretical Physics: Statistical Mechanics of Membranes and Surfaces* (Singapore: World Scientific)
- [7] Kantor Y, Kardar M and Nelson D R 1986 *Phys. Rev. Lett.* **57** 791
Kantor Y, Kardar M and Nelson D R 1987 *Phys. Rev. A* **35** 3056
- [8] Schmidt C F, Svoboda K, Lei N, Petche I B, Berman L E, Safinya C R and Grest G S 1993 *Science* **259** 952
- [9] Hwa T, Kokufuta and Tanaka T 1991 *Phys. Rev. A* **44** 2235
- [10] Spector M S, Naranjo E, Chiruvolu S and Zasadzinski J A 1994 *Phys. Rev. Lett.* **73** 2867
- [11] Aziz M J, Nygren E, Hays J F and Turnbull D 1985 *J. Appl. Phys.* **57** 2233
- [12] Stupp S I, Son S, Lin H C and Li S 1993 *Science* **259** 59
- [13] Abraham F F and Goulian M 1992 *Europhys. Lett.* **19** 293
- [14] Plischke M and Boal D 1988 *Phys. Rev. A* **38** 4943
- [15] Abraham F F, Plischke M and Rudge W E 1989 *Phys. Rev. Lett.* **62** 1757
- [16] Abraham F F and Nelson D R 1990 *Science* **249** 393
- [17] Grest G S 1991 *J. Physique I* **1** 1695
- [18] Kantor Y and Kremer K 1993 *Phys. Rev. E* **48** 2490
- [19] Muthukumar M 1988 *Phys. Rev. A* **37** 1032
- [20] Kawanishi K, Mori S and Wadati M 1994 *Phys. Lett.* **190A** 439
- [21] Edwards S F 1965 *Proc. Phys. Soc. London* **85** 613
- [22] Kantor Y 1989 *Jerusalem Winter School for Theoretical Physics: Statistical Mechanics of Membranes and Surfaces* ed D Nelson, T Piran and S Weinberg (Singapore: World Scientific)
- [23] Doi M and Edwards S F 1986 *Theory of Polymer Dynamics* (Oxford: Oxford University Press)