Universality of gelation: End-linking versus cross-linking and stiff rods versus flexible chains

Martin Huthmann,[1] Manuel Rehkopf,[1] Annette Zippelius,[1] and Paul M. Goldbart[2]

[1]*Institut für Theoretische Physik, Georg-August-Universität, 37073 Göttingen, Germany*
[2]*Department of Physics, University of Illinois at Urbana-Champaign, 1110 West Green Street, Urbana, Illinois 61801-3080*

End-linking is the process in which junctions that permanently connect l ends of polymers are introduced at random. Sufficient end-linking causes a system of polymers to undergo a continuous equilibrium phase transition from a liquid to an amorphous solid state, i.e., to gel. This gelation transition is explored for a variety of end-linked polymer systems, focusing on universal aspects, and is contrasted with that caused by cross-linking. The dependency of this phase transition on the single-chain statistics and on the functionality l of the junctions is investigated. As an example of a single-chain statistics, stiff rods with a finite bending energy are considered. The shear modulus and the distribution of localization lengths are calculated, and found to be universal near the transition. [S1063-651X(96)01910-1]

I. INTRODUCTION

Synthetic polymer networks consist of a great variety of building blocks, and are synthesized by many distinct chemical methods. One of these methods is to introduce a sufficient number of permanent cross-links between randomly chosen monomers in a solution or melt of linear polymers. A different way to build up networks is to prepare readily processible oligomers having reactive monomers at their ends. Under special treatment, these end monomers are able to react with one another so as to form permanent junctions between a certain number l of ends of polymers [1]. We shall refer to this process as *end-linking*. Both processes, cross-linking and end-linking, lead to a thermodynamic phase transition from a fluid to an amorphous solid state. Recently, a statistical mechanical theory of this equilibrium phase transition has been presented for the case of cross-linked flexible polymers [2–4], which has as its foundations the pioneering work of Deam and Edwards [5].

The aim of this paper is to extend the analysis reported in [2–4] to the case of polymers that are end-linked and have arbitrary stiffness. We investigate in detail the critical properties of the gelation transition. For $l=2$ we reproduce the results obtained previously for cross-linking: The equation for the gel fraction Q and the critical number of permanent random junctions μ_c are the same in both cases. Hence, for these quantities it does not matter whether the permanent junctions connect two monomers at the end of a chain (end-linking) or at arbitrary segments of the chain (cross-linking). For $l>2$ the critical density of permanent random end-links decreases with l, because each end-link represents a more efficient constraint on the system. For the gel fraction we find an equation, which—to the best of our knowledge—has not been derived previously in the context of percolation theory. The critical exponent of the gel fraction is, however, the same as for $l=2$ and for cross-linking. Q and μ_c are completely independent of the single-chain statistics. The latter does enter in our calculation of the localization length and the shear modulus. The single-chain statistics determines the radius of gyration R_g, which sets the length scale for the localization length. Apart from that, the single-chain statis-

tics turn out to be irrelevant. In particular, the critical exponents for the shear modulus and the localization length are the same for stiff rods and flexible chains, for end-linked and cross-linked networks. We also compute the distribution of localization lengths near the transition: it is found to be universal, i.e., the same for cross-linking and for end-linking.

II. MODEL OF END-LINKED POLYMERS

We consider a system of N identical linear polymers of arclength L. The degrees of freedom are the (three-dimensional) positions of the monomers $\mathbf{R}_i(s)$, with $i=1,\ldots,N$ and $s\in[0,L]$. Two types of interactions between the monomers will be considered. Short-range interactions among monomers are limited to a few neighbors along the chain, and characterize the type of bond connecting neighboring monomers. (In particular, the connectivity of the chain is guaranteed by the short-range interactions.) We do not specify the short-range interaction $H_{sr}(\mathbf{R}_i(s))$, and only assume that it preserves the rotational and translational invariance of the system. Later on, we shall compare flexible chains to stiff rods, and discuss in detail which of our results depend on the short-range interactions and which do not. Interactions between segments that are distant along the chain but close in (real) space are called long ranged. For these we take excluded-volume interactions, so that the system is characterized by the following Hamiltonian:

$$H = \sum_{i=1}^{N} H_{sr}(\mathbf{R}_i(s)) + \frac{1}{2}v_0 \sum_{i,j=1}^{N} \int_0^L ds\, ds'\, \delta(\mathbf{R}_i(s) - \mathbf{R}_j(s')).$$

(1)

Here, v_0 characterizes the strength of the excluded-volume interaction introduced by Edwards [9]. We find it convenient to use a continuum description, and we have chosen units of energy such that $\beta^{-1}=k_B T=1$.

An end-link of functionality l connects the ends of l polymers, so that they occupy common spatial locations. A realization of the end-linking process with M end-links, labeled by $e=1,\ldots,M$, is modeled by $(l-1)M$ constraints

$$\mathbf{R}_{i_{e,1}}(s_{e,1}) = \cdots = \mathbf{R}_{i_{e,l}}(s_{e,l}) \quad (\text{for } e = 1, \ldots, M), \quad (2)$$

where $\{i_{e,j}\}_{j=1}^{l}$ is the set of polymers participating in end-link e, and $\{s_{e,j}\}_{j=1}^{l}$ (with $s_{e,j} = 0$ or L) designate which end of each of the participating polymers is in end-link e. The partition function of the end-linked system, relative to that of the uncross-linked system, is given by [4]

$$Z(\{i_{e,1}, s_{e,1}; \cdots; i_{e,l}, s_{e,l}\})$$
$$= \left\langle \prod_{e=1}^{M} \int d\mathbf{x}_e \delta(\mathbf{x}_e - \mathbf{R}_{i_{e,1}}(s_{e,1})) \cdots \delta(\mathbf{x}_e - \mathbf{R}_{i_{e,l}}(s_{e,l})) \right\rangle_{1}^{H}.$$
$$(3)$$

The expectation value is taken with respect to the statistical weight $\exp(-H)$. The integration over $\mathbf{x}_e$ is a convenient way to express the constraints, which are symmetric in the indices.

Once an end-link has been established it remains permanently. Hence, the set of indices $\{i_{e,1}, s_{e,1}; \ldots; i_{e,l}, s_{e,l}\}$ are quenched variables. The end-linking process is a stochastic process. The monomers and polymers that participate in an end-link are chosen randomly according to a probability distribution $\mathcal{P}(\{i_{e,1}, s_{e,1}; \ldots; i_{e,l}, s_{e,l}\})$. We assume that all end-links are established in the fluid phase instantaneously. Ends of polymers that happen to be close immediately prior to the end-linking process are linked with a certain probability. Therefore the statistics of such a process reflects the correlations of the fluid phase. Following Deam and Edwards [5], we take for the probability distribution

$$\mathcal{P}(\{i_{e,1}, s_{e,1}; \cdots; i_{e,l}, s_{e,l}\}) \propto Z(\{i_{e,1}, s_{e,1}; \ldots; i_{e,l}, s_{e,l}\}).$$
$$(4)$$

For technical reasons we allow the number of cross-links M to fluctuate, controlled by the parameter μ^2

$$\mathcal{P}_M(\{i_{e,1}, s_{e,1}; \cdots; i_{e,l}, s_{e,l}\})$$
$$= \frac{1}{M! \mathcal{Z}_1} \left(\frac{\mu^2 V^{l-1}}{2N^{l-1}} \right)^M \left\langle \prod_{e=1}^{M} \int d\mathbf{x}_e \delta(\mathbf{x}_e - \mathbf{R}_{i_{e,1}}(s_{e,1})) \cdots \right.$$
$$\left. \times \delta(\mathbf{x}_e - \mathbf{R}_{i_{e,l}}(s_{e,l})) \right\rangle_{1}^{H}.$$
$$(5)$$

Here, $\mathcal{Z}_1$ is a normalization factor. The mean number of end links $[M]$ is a monotonic function of μ^2, and is approximately given by $[M] = (1/2)\mu^2 N$ (see [6]), and $[\cdots]$ denotes an average over the quenched disorder with the distribution $\mathcal{P}_M$.

III. VARIATIONAL CALCULATION

To calculate the disorder average of the free energy Nf we use the replica technique

$$-Nf = \lim_{n \to 0} \frac{[Z^n] - 1}{n}. \quad (6)$$

We follow the strategy of simultaneously calculating the partition function and the distribution of disorder $\mathcal{P}_M$. This can be achieved by introducing one additional replica, denoted by the replica index 0. To keep the notation simple we introduce $(n+1)$-fold replicated vectors $\hat{\mathbf{x}} \equiv (\mathbf{x}^0, \ldots, \mathbf{x}^n)$ and normalized sums $\overline{\Sigma}_i \equiv (1/N)\Sigma_{i=1}^{N}$ and $\overline{\Sigma}_s \equiv (1/2)\Sigma_{s=0,L}$. By performing the disorder average for positive integer n we get

$$-Nnf_n = \frac{\mathcal{Z}_{n+1} - \mathcal{Z}_1}{\mathcal{Z}_1} \quad (7)$$

with

$$\mathcal{Z}_{n+1} = \left\langle \exp\left\{ \frac{\mu^2 V^{l-1} N}{2} \int d\hat{\mathbf{x}} \left(\overline{\Sigma}_i \, \overline{\Sigma}_s \, \delta(\hat{\mathbf{x}} - \hat{\mathbf{R}}_i(s)) \right)^l \right\} \right\rangle_{n+1}^{H},$$
$$(8)$$

so that $f = \lim_{n \to 0} f_n$.

We introduce an order-parameter field $\Omega_{\hat{\mathbf{x}}}$ to decouple different polymers from each other

$$\mathcal{Z}_{n+1} = \left\langle \int \mathcal{D}\Omega_{\hat{\mathbf{x}}} \prod_{\hat{\mathbf{x}}} \delta\left(\Omega_{\hat{\mathbf{x}}} - \overline{\Sigma}_i \, \overline{\Sigma}_s \, \delta(\hat{\mathbf{x}} - \hat{\mathbf{R}}_i(s)) \right) \right.$$
$$\left. \times \exp\left(\frac{\mu^2 V^{l-1} N}{2} \int d\hat{\mathbf{x}} \Omega_{\hat{\mathbf{x}}}^l \right) \right\rangle_{n+1}^{H}. \quad (9)$$

The functional integral over the fields $\Omega_{\hat{\mathbf{x}}}$ is done in the saddle-point approximation, yielding

$$f_n^S(\overline{\Omega}_{\hat{\mathbf{x}}}) = \frac{\mu^2}{2} + \frac{\mu^2(l-1)V^{l-1}}{2} \int d\hat{\mathbf{x}} \, \overline{\Omega}_{\hat{\mathbf{x}}}^l$$
$$- \ln\left\langle \exp\left(\frac{\mu^2 l}{2} V^{l-1} \int d\hat{\mathbf{x}} \, \overline{\Omega}_{\hat{\mathbf{x}}}^{l-1} \overline{\Sigma}_s \, \delta(\hat{\mathbf{x}} - \hat{\mathbf{R}}(s)) \right) \right\rangle_{n+1}^{H_{sr}}.$$
$$(10)$$

The saddle-point equation for $\overline{\Omega}_{\hat{\mathbf{x}}}$ is

$$\overline{\Omega}_{\hat{\mathbf{x}}} = \frac{\left\langle \overline{\Sigma}_s \, \delta(\hat{\mathbf{x}} - \hat{\mathbf{R}}(s)) \exp\left(\frac{\mu^2 l}{2} V^{l-1} \int d\hat{\mathbf{x}} \, \overline{\Omega}_{\hat{\mathbf{x}}}^{l-1} \overline{\Sigma}_s \, \delta(\hat{\mathbf{x}} - \hat{\mathbf{R}}(s)) \right) \right\rangle_{n+1}^{H_{sr}}}{\left\langle \exp\left(\frac{\mu^2 l}{2} V^{l-1} \int d\hat{\mathbf{x}} \, \overline{\Omega}_{\hat{\mathbf{x}}}^{l-1} \overline{\Sigma}_s \, \delta(\hat{\mathbf{x}} - \hat{\mathbf{R}}(s)) \right) \right\rangle_{n+1}^{H_{sr}}}. \quad (11)$$

Here, the angular brackets denote an average with the $(n+1)$-fold replicated short-range interaction $H_{\rm sr}$. Within the saddle-point approximation $\overline{\Omega}_{\hat{\mathbf{x}}}$ gives the disorder-averaged static density fluctuations of the ends of the polymers

$$\overline{\Omega}_{\hat{\mathbf{k}}} = \overline{\sum_i} \; \overline{\sum_s} [\langle \exp(i\hat{\mathbf{k}} \cdot \hat{\mathbf{R}}_i(s)) \rangle], \qquad (12)$$

where we have made a (replicated) Fourier transform from $\hat{\mathbf{x}}$ to $\hat{\mathbf{k}}$. To obtain Eqs. (10) and (11) we replaced the δ functional in Eq. (9) by its (functional) Fourier integral representation, thus introducing the conjugate order-parameter field $\hat{\Omega}_{\hat{\mathbf{x}}}$. We then performed the functional integrals over $\Omega_{\hat{\mathbf{x}}}$ and $\hat{\Omega}_{\hat{\mathbf{x}}}$ in the saddle-point approximation. Finally, we used one of the saddle-point equations to eliminate $\hat{\Omega}_{\hat{\mathbf{x}}}$.

A nonzero value of the order parameter with at least two (replica) components of $\hat{\mathbf{k}}$ different from zero indicates the appearance of random static density fluctuations without long-range translational order. These issues have been discussed in detail in [4]. As in the case of cross-linking, the absence of long-range translational order shows up in a vanishing of the order parameter in the one-replica sector, i.e., $\overline{\Omega}_{\hat{\mathbf{k}}}$ with only one (replica) component of $\hat{\mathbf{k}}$ different from zero vanishes at the saddle point, provided the excluded-volume interactions have been chosen sufficiently strong to prevent collapse.

We postpone the solution of the saddle-point equation to Sec. VI, and first discuss a variational approximation based on a simple intuitive picture of the amorphous solid state. We expect that in the gel phase a nonzero fraction Q of polymers are localized at random positions. By assuming Gaussian fluctuations with a typical lengthscale ξ around the preferred positions, we are led to the following variational ansatz for $\overline{\Omega}(\hat{\mathbf{k}})$

$$\overline{\Omega}(\hat{\mathbf{k}}) = (1-Q) \, \delta_{\hat{\mathbf{k}}, \hat{\mathbf{0}}} + Q \, \delta_{\sum_{\alpha=0}^n \mathbf{k}^\alpha, \mathbf{0}} \exp\left(-\frac{\xi^2}{2} \sum_{\alpha=0}^n |\mathbf{k}^\alpha|^2 \right). \qquad (13)$$

The second term reflects the fraction of ends that are part of the infinite cluster. The δ function ensures macroscopic translational invariance. The first term in Eq. (13) accounts for those polymers that are still fluid.

The gel fraction Q and the localization length ξ are variational parameters, which are determined by a minimization of f_n^S. First, we insert the full ansatz, including both terms, into Eq. (10). Next, we expand the exponential of the second term, generating a Landau-Ginzburg free energy for the order-parameter field. The coefficients in this expansion are the density correlations of a single polymer, e.g., $\langle \exp(i\xi^{-1} \sum_{i=1}^r \mathbf{k}_i \cdot \mathbf{R}(s_i)) \rangle$. From translational invariance we know that $\langle \exp(i\sum_{i=1}^r \mathbf{k}_i \cdot \mathbf{R}(s_i)) \rangle \propto \delta_{\sum_i \mathbf{k}_i, \mathbf{0}}$. Rotational invariance is used to calculate the moments of $\xi^{-1}\mathbf{k}_i \cdot \mathbf{R}(s_i)$

$$\langle \mathbf{k}_i \cdot \mathbf{R}(s_i) \mathbf{k}_j \cdot \mathbf{R}(s_j) \rangle = \tfrac{1}{3} \mathbf{k}_i \cdot \mathbf{k}_j \langle \mathbf{R}(s_i) \cdot \mathbf{R}(s_j) \rangle_1^{H_{\rm sr}}. \qquad (14)$$

Near the transition, ξ^{-1} is expected to be small, and it is only necessary to calculate terms to order ξ^{-2}.

Stationarity of the free energy with respect to the gel fraction Q yields

$$1 - Q = \exp\left(\frac{\mu^2 l}{2} ((1-Q)^{l-1} - 1) \right). \qquad (15)$$

The gel fraction reflects the geometric character of the transition: a nonzero gel fraction indicates the appearance of an infinite network. This does not depend on the building blocks of the network, but only on the number of polymers that are connected at any end-link. For $l=2$, Eq. (15) was first derived in the context of graph theory by Erdős and Rényi (reprinted in [8]).

Equation (15) always has the solution $Q=0$, corresponding to the liquid state. For $\mu^2 > \mu_c^2 = 2/l(l-1)$ an additional solution appears, which emerges continuously from $Q=0$. For $|\mu^2 - \mu_c^2| \ll 1$ we have

$$Q \simeq l(\mu^2 - \mu_c^2). \qquad (16)$$

To obtain an equation for the localization length ξ we demand that f_n^S be stationary with respect to ξ^2, which gives, to leading order,

$$\frac{1}{\xi^2} = \frac{4(\mu^2 - \mu_c^2)}{(l-1)\mu_c^2} \frac{1}{R_g^2}, \qquad (17)$$

where R_g^2 $(\equiv \langle |\mathbf{R}(L) - \mathbf{R}(0)|^2 \rangle_1^{H_{\rm sr}})$ is the mean square end-to-end distance (proportional to the radius of gyration squared), which depends on the explicit form of $H_{\rm sr}$ and will be discussed in Sec. IV.

To summarize, for $l=2$ the equation for the gel fraction is identical for the cases of cross-linking and end-linking. For end-linking with $l>2$ we find an equation that reflects the altered connectivity. As expected, the gel fraction is independent of the chain statistics. The critical concentration of end-links μ_c^2 depends on l, whereas the critical exponents for Q and ξ depend neither on l nor on the chain statistics. The statistics of a single polymer determines only a semimicroscopic length that sets the scale for ξ^2.

It is tempting to enquire why a solidification transition should occur for the case of end-linking with $l=2$, in which case the end-links merely join pairs of polymers, end to end. However, our model of end-linking has no saturation, in the sense that there is no prohibition on polymer ends participating in more than one end-link. This is not anticipated to be significant for $l \geq 3$, for which saturation does not prohibit (nonlinear) network formation. However, it is crucial for the (physically less important) case of $l=2$, for which end-linking with saturation would permit only the formation of linear assemblies of macromolecules and, hence, would not allow for network formation.

IV. RODS WITH A FINITE BENDING ENERGY

To calculate the radius of gyration, one has to choose a particular short-range interaction. As an example, we review the wormlike chain model, which was introduced by Kratky and Porod [10]. We follow the approach of Saito, Takahashi, and Yunaki [7]. The wormlike chain is a simple model, but is rich enough to interpolate between the limit of totally stiff

HUTHMANN, REHKOPF, ZIPPELIUS, AND GOLDBART

chains, for which it yields the length of the rod L for R_g, and the limit of long flexible chains, for which it yields $R_g^2 \propto L$ in agreement with the Gaussian chain model. The polymer is represented by a curve $\mathbf{R}(s)$ in three-dimensional space that is parametrized by the arclength $s \in [0,L]$, such that $|\mathbf{u}(s)| \equiv |d\mathbf{R}(s)/ds| = 1$. This implies that the total arclength $S \equiv \int_0^L |\mathbf{u}(s)| ds = L$ is constant, modeling a thin rod that can be bent but not stretched. The configuration of a single chain $\mathbf{R}(s)$ is given by the location of one end vector, e.g., $\mathbf{R}(0)$, along with $\mathbf{u}(s)$ for all s, via

$$\mathbf{R}(s) = \mathbf{R}(0) + \int_0^s ds\, \mathbf{u}(s). \qquad (18)$$

We assume a bending energy that can be expressed in terms of derivatives of $\mathbf{u}(s)$: the straight configuration is the ground state, and bending the rod costs energy according to

$$H_{\text{bend}} = \frac{\Lambda}{2} \int_0^L ds\, |\dot{\mathbf{u}}(s)|^2, \qquad (19)$$

where $\dot{\mathbf{u}}(s) \equiv d\mathbf{u}(s)/ds$. The bending elastic constant of the chain is denoted by Λ. (Kratky and Porod use a discretized model. They consider a chain composed of many segments of fixed length b and with a fixed angle Θ between adjacent bonds. Then they perform the limit of small bond lengths and bond angles approaching π. The total polymer length is kept constant, as is the ratio $b/(1+\cos\Theta)$. Thereby they get the same result for R_g.) Higher-order derivatives of $\mathbf{u}(s)$ describe interactions between more than two neighboring monomers on a chain.

The probability for a conformation $\{\mathbf{u}(s)\}$ of a single polymer is given by the Boltzmann weight

$$\Psi(\{\mathbf{u}, \mathbf{R}(0)\}) = \frac{1}{z} \exp\left(-\frac{1}{4D} \int_0^L ds\, |\dot{\mathbf{u}}(s)|^2\right), \qquad (20a)$$

$$z = \int d\mathbf{R}(0) \int \mathcal{D}\mathbf{u}\, \exp\left(-\frac{1}{4D} \int_0^L ds\, |\dot{\mathbf{u}}(s)|^2\right) \qquad (20b)$$

$$D = \frac{k_B T}{2\Lambda}, \qquad (20c)$$

where we assume that the end vector $\mathbf{R}(0)$ is uniformly distributed over the volume. To obtain expectation values of physical quantities that depend only on tangent vectors $\mathbf{u}$ at different arclengths, one defines a transition probability

$$p(\mathbf{u}_1, s_1; \mathbf{u}_0, s_0) \equiv \frac{\int_{\mathbf{u}_0}^{\mathbf{u}_1} \mathcal{D}\mathbf{u}\, \exp\left(-\frac{1}{4D} \int_{s_0}^{s_1} ds\, |\dot{\mathbf{u}}(s)|^2\right)}{\int d\mathbf{u}_1 \int_{\mathbf{u}_0}^{\mathbf{u}_1} \mathcal{D}\mathbf{u}\, \exp\left(-\frac{1}{4D} \int_{s_0}^{s_1} ds\, |\dot{\mathbf{u}}(s)|^2\right)} \qquad (21)$$

that a chain that has tangent vector $\mathbf{u}_0$ at position s_0 has tangential vector $\mathbf{u}_1$ at position s_1. (A simple discussion for the case of Gaussian polymers is given in Chap. 2 of [11].) Then the expectation value of a quantity $A(\mathbf{u}(s_1))$ can be calculated from the transition probability via

$$\langle A(\mathbf{u}(s_1)) \rangle$$
$$= \frac{\int d\mathbf{u}_0 d\mathbf{u}_1 d\mathbf{u}_L\, p(\mathbf{u}_L, L; \mathbf{u}_1, s_1) A(\mathbf{u}_1) p(\mathbf{u}_1, s_1; \mathbf{u}_0, 0)}{\int d\mathbf{u}_0 d\mathbf{u}_L\, p(\mathbf{u}_L, L; \mathbf{u}_0, 0)}. \qquad (22)$$

The transition probabilities satisfy the Fokker-Planck equation for a diffusion process on a unit sphere ($|\mathbf{u}| = 1$)

$$\frac{\partial}{\partial s_1} p(\mathbf{u}_1, s_1; \mathbf{u}_0, s_0) = D\mathbf{L} \cdot \mathbf{L}\, p(\mathbf{u}_1, s_1; \mathbf{u}_0, s_0). \qquad (23)$$

The angular part of the Laplacian is denoted by $\mathbf{L} \cdot \mathbf{L}$, and acts on $\mathbf{u}_1$. Equation (23) is to be solved with the initial condition

$$p(\mathbf{u}_1, s_0; \mathbf{u}_0, s_0) = \delta(\mathbf{u}_0 - \mathbf{u}_1). \qquad (24)$$

In three dimensions the solution is given by

$$p(\mathbf{u}_1, s_1; \mathbf{u}_0, s_0)$$
$$= \sum_{l=0}^{\infty} e^{-l(l+1)D(s_1 - s_0)} \sum_{m=-l}^{l} Y_{lm}(\mathbf{u}_1) Y_{lm}^*(\mathbf{u}_0), \qquad (25)$$

where Y_{lm} are the spherical harmonics. The radius of gyration then follows from

$$\langle |\mathbf{R}(L) - \mathbf{R}(0)|^2 \rangle = \left\langle \int_0^L ds\, \mathbf{u}(s) \cdot \int_0^L ds'\, \mathbf{u}(s') \right\rangle$$
$$= 2 \int_0^L ds \int_0^s ds'\, \langle \mathbf{u}(s) \cdot \mathbf{u}(s') \rangle, \qquad (26)$$

in which $\langle \mathbf{u}(s) \cdot \mathbf{u}(s') \rangle$ can be calculated using the transition probability and the orthogonality of the spherical harmonics

$$\langle \mathbf{u}(s) \cdot \mathbf{u}(s') \rangle = \frac{1}{4\pi} \int d\mathbf{u}_L d\mathbf{u}_s d\mathbf{u}_{s'} d\mathbf{u}_0\, p(\mathbf{u}_L, L; \mathbf{u}_s, s)$$
$$\times p(\mathbf{u}_s, s; \mathbf{u}_{s'}, s') p(\mathbf{u}_{s'}, s'; \mathbf{u}_0, 0) \mathbf{u}_s \cdot \mathbf{u}_{s'} \qquad (27)$$

$$= \exp(-2D(s - s')). \qquad (28)$$

Inserting Eq. (27) into Eq. (26) we find

$$\langle |\mathbf{R}(L) - \mathbf{R}(0)|^2 \rangle = \frac{e^{-2DL} - 1 + 2DL}{2D^2}. \qquad (29)$$

This result has the expected asymptotics: short, stiff chains (for which $DL \to 0$) have $\langle |\mathbf{R}(L) - \mathbf{R}(0)|^2 \rangle \to L$, whereas long, flexible chains (for which $DL \to \infty$) have $\langle |\mathbf{R}(L) - \mathbf{R}(0)|^2 \rangle \to L/D$.

V. SHEAR MODULUS

The aim of this section is to calculate the free energy of elastic deformations within our variational approach. The partition function is invariant with respect to spatially uniform, replica-dependent displacements of the monomers: $\mathbf{R}_i^\alpha(s) \to \mathbf{R}_i^\alpha(s) + \mathbf{u}^\alpha$ (for $\alpha = 0, \ldots, n$). Hence, we expect that almost-uniform displacements are low lying excitations,

the energy of which goes to zero in the long wavelength limit. To calculate their spectrum, we consider nonuniform displacements of the thermodynamic degrees of freedom only: $\mathbf{R}_i^\alpha(s) \to \mathbf{R}_i^\alpha(s) + \mathbf{u}(\mathbf{R}_i^\alpha(s))$ (for $\alpha = 1, \ldots, n$). The $\alpha = 0$ replica generates the end-link distribution in the unstrained system and, hence, is not displaced.

Under this transformation $\bar{\Omega}_{\hat{\mathbf{k}}} \to \tilde{\Omega}_{\hat{\mathbf{k}}}$, with

$$\delta\Omega \equiv \tilde{\Omega}_{\hat{\mathbf{k}}} - \bar{\Omega}_{\hat{\mathbf{k}}}$$

$$= \overline{\sum_i} \ \overline{\sum_s} \left\langle \left(e^{i\sum_{\alpha=1}^n \mathbf{k}^\alpha \cdot \mathbf{u}(\mathbf{R}_i^\alpha(s))} - 1\right) e^{i\sum_{\alpha=0}^n \mathbf{k}^\alpha \cdot \mathbf{R}_i^\alpha(s)} \right\rangle, \quad (30\text{a})$$

$$= \frac{i}{V} \sum_{\mathbf{q}} \sum_{\alpha=1}^n \mathbf{k}^\alpha \cdot \mathbf{u}(\mathbf{q}) \bar{\Omega}(\mathbf{k}^0, \ldots, \mathbf{k}^\alpha + \mathbf{q}, \ldots, \mathbf{k}^n)$$

$$- \frac{1}{2V^2} \sum_{\mathbf{q}_1, \mathbf{q}_2} \sum_{\substack{\alpha, \beta=1 \\ \alpha \neq \beta}}^n \mathbf{k}^\alpha \cdot \mathbf{u}(\mathbf{q}_1) \mathbf{k}^\beta \cdot \mathbf{u}(\mathbf{q}_2)$$

$$\times \bar{\Omega}(\mathbf{k}^0, \ldots, \mathbf{k}^\alpha + \mathbf{q}_1, \ldots, \mathbf{k}^\beta + \mathbf{q}_2, \ldots, \mathbf{k}^n)$$

$$- \frac{1}{2V^2} \sum_{\mathbf{q}_1, \mathbf{q}_2} \sum_{\alpha=1}^n \mathbf{k}^\alpha \cdot \mathbf{u}(\mathbf{q}_1) \mathbf{k}^\alpha \cdot \mathbf{u}(\mathbf{q}_2)$$

$$\times \bar{\Omega}(\mathbf{k}^0, \ldots, \mathbf{k}^\alpha + \mathbf{q}_1 + \mathbf{q}_2, \ldots, \ldots, \mathbf{k}^n), \quad (30\text{b})$$

where $\mathbf{u}(\mathbf{R}_i^\alpha(s))$ is the elastic displacement field, and $\mathbf{u}(\mathbf{q})$ is its Fourier transform. We restrict ourselves to displacement fields $\mathbf{u}(\mathbf{R})$ that vary over lengthscales much larger than the localization length ξ, and calculate $\delta f_n \equiv f_n(\bar{\Omega} + \delta\Omega) - f_n(\bar{\Omega})$ to second order in $\mathbf{u}$. We find for the elastic free energy

$$\delta F\{\mathbf{u}\} = \frac{1}{2} \int d^3r \left(B(u^{aa})^2 + S(u^{ab} - \tfrac{1}{3}\delta^{ab}u^{cc}) \right), \quad (31)$$

where $u^{ab} \equiv \frac{1}{2}(\partial^a u^b + \partial^b u^a)$ is the (linearized) strain field, and summation is implied over repeated Cartesian indices $a = 1, 2, 3$. To lowest nontrivial order in Q and ξ^{-2} the shear modulus S is given by

$$S = \frac{N}{V} k_B T \frac{l^2(l-1)^2}{1152} \tilde{Q}^2 \frac{R_g^4}{\xi^4}. \quad (32)$$

Inserting Eqs. (16) and (17) we find

$$S \simeq \frac{N}{V} k_B T \frac{l^4}{72} \frac{(\mu^2 - \mu_c^2)^4}{\mu_c^4}. \quad (33)$$

This implies a critical exponent of 4, independent of the statistics of a single polymer. In Ref. [4] we obtained a critical exponent of 2 because the variational ansatz that was used in [4] did not take into account the fraction of delocalized monomers, $1 - Q$, in the amorphous solid state [see Eq. (13)]. There is also a singular contribution to the bulk modulus which is, however, dominated by regular contributions of the uncross-linked system (that we are unable to calculate from f_n).

Mechanical measurements have been performed on copolymerization (corresponding to cross-linking) and polycondensation (corresponding to end-linking). Whereas the experimental data reveal the same critical behavior for the viscosity in the two systems, the critical exponent t for the static shear modulus in the gel phase is different for copolymerization ($t \sim 2$) and polycondensation ($t \sim 3$) [12]. It is unclear why the two linking mechanisms should produce distinct modulus exponents [13]. One possible explanation is the size of the critical region (in which deviations from mean-field behavior may be observable [14]). The size of this region depends on the distance between links along the chain, and may possibly vary for different linking mechanisms.

VI. DISTRIBUTION OF LOCALIZATION LENGTHS

In this section we apply the idea of solving the saddle-point equation presented by Castillo, Goldbart, and Zippelius [3,4] to the case of end-linking. The improvement of this approach reflects the possibility that in the amorphous solid state the localization length is not unique but instead has a distribution.

The starting point of our calculation is the saddle-point equation (11). We are not able to find the general solution of Eq. (11), and instead proceed with an ansatz for the self-consistent $\Omega_{\hat{\mathbf{k}}}$, viz.,

$$\Omega_{\hat{\mathbf{k}}} = (1 - Q)\delta_{\hat{\mathbf{k}}, 0} + Q \delta_{\tilde{\mathbf{k}}, \mathbf{0}} \omega(\hat{\mathbf{k}}^2), \quad (34)$$

parametrized by the variable Q and the function $\omega(\hat{\mathbf{k}}^2)$. Here, we use the notation $\tilde{\mathbf{k}} = \sum_{\alpha=0}^n \mathbf{k}^\alpha$ and $\hat{\mathbf{k}}^2 = \sum_{\alpha=0}^n |\mathbf{k}^\alpha|^2$ for two permutation invariant combinations of $\{\mathbf{k}^\alpha\}_{\alpha=0}^n$.

Under fairly mild conditions, the technical restriction being that $\omega(z)$ must be analytic for $\text{Re}(z) \geq 0$ and vanish sufficiently fast at infinity, we can adopt a convenient alternative parametrization of $\Omega_{\hat{\mathbf{k}}}$ (see also Castillo, Goldbart, and Zippelius [3]):

$$\Omega_{\hat{\mathbf{k}}} = (1 - Q)\delta_{\hat{\mathbf{k}}, 0} + Q \delta_{\tilde{\mathbf{k}}, \mathbf{0}} \int_0^\infty d\tau \, p(\tau) \exp(-\hat{\mathbf{k}}^2/2\tau). \quad (35)$$

This ansatz (35) can be motivated as follows. As in the previous sections, we assume that each end of a polymer (i, s) is either delocalized (with probability $1 - Q$) or localized (with probability Q) at a random mean position. About this position it performs independent Gaussian thermal fluctuations, characterized by an inverse square localization length $\tau(i, s)$, which depends on (i, s) and is not unique, in contrast to the previous sections. The assumptions that (i) the mean positions are independently and uniformly distributed through the volume, (ii) the localization lengths are independently distributed with probability density $\tilde{p}(\tau) = 2\xi^{-3}p(\xi^{-2})$, and (iii) the replica symmetry is not broken together lead to the ansatz hypothesized in Eq. (35). Thus $p(\tau)$ can be interpreted as the distribution of inverse square localization lengths.

By inserting this ansatz into the self-consistency condition, Eq. (11), we obtain

$$(1-Q)\delta_{\hat{\mathbf{q}},\hat{\mathbf{0}}}+Q\,\delta_{\widetilde{\mathbf{q}},\mathbf{0}}\int_0^\infty d\tau\,p(\tau)\exp(-\hat{\mathbf{q}}^2/2\tau)$$

$$=e^{(\mu^2 l/2)[(1-Q)^{l-1}-1]}\delta_{\hat{\mathbf{q}},\hat{\mathbf{0}}}+e^{(\mu^2 l/2)[(1-Q)^{l-1}-1]}\sum_{M=0}^\infty\underbrace{\left(\sum_{j=\kappa}^M\frac{1}{j!}\left(\frac{\mu^2 l}{2}\right)^j\left\langle\overline{\sum_\sigma e^{i\hat{\mathbf{q}}\cdot\hat{\mathbf{R}}(\sigma)}a_{M,j}}\right\rangle_{n+1}^{H_{\mathrm{sr}}}\right)}_{=H_M}Q^M,\qquad(36)$$

where $\kappa=\kappa(M,l)$ is the integer satisfying $M/(l-1)\leqslant\kappa<(M/(l-1))+1$, and the $a_{i,r}$ are defined by the following recursive structure:

$$a_{k,1}=\sum_{i=1}^k(-1)^{k-i}\binom{l-1-(k-i)}{k-i}\binom{l-1}{i}V^i\widetilde{A}_i,\quad(37\mathrm{a})$$

$$a_{i,r}=\sum_{j=1}^{i-r+1}a_{j,1}a_{i-j,r-1},\qquad(37\mathrm{b})$$

$$a_{i,r}=0\quad(\text{for }r>i),\qquad(37\mathrm{c})$$

$$\widetilde{A}_m=\int\prod_{i=1}^m d\hat{\mathbf{k}}_i\,\delta_{\mathbf{0},\widetilde{\mathbf{k}}_i}\int d\tau_1\cdots d\tau_m p(\tau_1)\cdots p(\tau_m)$$

$$\times e^{-\hat{\mathbf{k}}_1^2/2\tau_1}\cdots e^{-\hat{\mathbf{k}}_m^2/2\tau_m}\overline{\sum_\sigma e^{i\sum_{j=1}^m\hat{\mathbf{k}}_j\cdot\hat{\mathbf{R}}(\sigma)}}.\qquad(37\mathrm{d})$$

It can be shown by explicit calculation that all terms included in H_M are proportional to $\delta_{\mathbf{0},\widetilde{\mathbf{q}}}$. So, by passing to the limit $\hat{\mathbf{q}}^2\to0$, via a sequence for which $\widetilde{\mathbf{q}}=\mathbf{0}$, we can identify from Eq. (36) the self-consistency condition for the gel fraction Q, viz.,

$$1-Q=\exp\left(\frac{\mu^2 l}{2}((1-Q)^{l-1}-1)\right),\qquad(38)$$

which is the same as that derived from the variational calculations in Eq. (15).

We now turn to the distribution of localization lengths, and restrict our attention to the vicinity of the transition regime in the solid state $[\epsilon\equiv2(\mu^2-\mu_c^2)/\mu_c^2\ll1]$, where the gel fraction is small (i.e., $Q\ll1$) and the localization lengths are large (i.e., typically $\xi\gg R_g$). Furthermore, we restrict ourselves to the case of a Gaussian polymer with persistence length ℓ, for which the short-range Hamiltonian is

$$H_{\mathrm{sr}}=\frac{3}{2\ell}\int_0^L ds\left|\frac{d\mathbf{R}(s)}{ds}\right|^2.\qquad(39)$$

We adopts units of length in which $\ell L/3=1$. We expect scaling near the critical point, and introduce a scaling function $\Pi(\theta)$ via $p_\epsilon(\tau)=(2/\epsilon)\Pi(2\tau/\epsilon)$. The hypothesized scaling form is motivated by the results from the variational calculations in the preceding section and, below, is shown actually to solve the saddle-point equation.

By expanding Eq. (36) to lowest order in ϵ, we arrive at an integro-differential equation for $\Pi(\theta)$:

$$\frac{\theta^2}{2}\dot{\Pi}(\theta)=(1-\theta)\Pi(\theta)-\int_0^\theta d\theta'\,\Pi(\theta-\theta')\Pi(\theta')+O(\epsilon).\qquad(40)$$

This is the same equation as that derived previously by Castillo, Goldbart, and Zippelius [3] for cross-linked polymers. We conclude that the distribution $\Pi(\theta)$ is a universal feature of systems of randomly linked polymers, independent of l and of whether the system is end-linked or cross-linked.

The asymptotics of $\Pi(\theta)$ are given by

$$\Pi(\theta)=\begin{cases}c\,\theta^{-2}e^{-2/\theta}&\text{if }\theta\ll1;\\3\left(a\theta-\dfrac{3}{5}\right)e^{-a\theta}&\text{if }\theta\gg1.\end{cases}\qquad(41)$$

The coefficients $a\simeq4.554$ and $b\simeq1.678$ can be obtained by the numerical solution of Eq. (40). Thus we find for the order parameter $\Omega_{\hat{\mathbf{k}}}$

$$\Omega_{\hat{\mathbf{k}}}=\left(1-\frac{\epsilon}{l-1}\right)\delta_{\hat{\mathbf{k}},\hat{\mathbf{0}}}+\frac{\epsilon}{l-1}\delta_{\widetilde{\mathbf{k}},\mathbf{0}}\omega(\sqrt{2}\hat{\mathbf{k}}^2/\epsilon),\quad(42\mathrm{a})$$

$$\omega(\hat{\mathbf{k}}^2)=\int_0^\infty d\theta\,\Pi(\theta)e^{-\hat{\mathbf{k}}^2/2\theta}.\qquad(42\mathrm{b})$$

The variational ansatz (13) is recovered by approximating the true distribution $p(\tau)$ by $\delta(\tau-\epsilon/2)$.

VII. CONCLUSIONS

We have addressed the equilibrium properties of systems of polymers that have been permanently end-linked at random, by developing appropriate techniques from the statistical mechanics of systems with quenched disorder. We have considered the general case in which each end-link brings together l ends of polymers. We have allowed for a broad class of polymeric systems, including flexible, semiflexible and rigid-rod molecules.

We have established that beyond a certain critical density of end-links, of order one per polymer, the system undergoes a continuous equilibrium thermodynamic phase transition, from a liquid state (in which all polymers are delocalized) to an amorphous solid state (in which a nonzero fraction of the monomers are localized about preferred positions, those positions being aperiodically distributed in space). For technical reasons, our results are restricted to the transition regime.

By using a simple variational hypothesis for the amorphous solid order parameter (in terms of the fraction of lo-

calized polymers and a single characteristic length that describes the thermal position fluctuations of the monomers), we have determined that the fraction of localized polymers (the so-called gel fraction) satisfies a simple equation. This equation constitutes the extension (to the case of end-linking) of a result first obtained in the context of random graph theory (i.e., mean-field percolation) and subsequently emerging from the replica-statistical mechanics of vulcanized polymer systems. From it, we demonstrate how the gel fraction vanishes, as the amorphous solidification transition is approached from the solid side.

Within the context of this variational hypothesis, we have also determined that the characteristic length (i.e., the localization length) diverges at the transition point coming from the solid side. In addition, by considering the free-energy cost of imposing a long-wavelength elastic shear strain, we have constructed the elastic shear free energy of the amorphous solid state, and calculated the shear modulus. The shear modulus is found to vanish at the transition from the amorphous solid state to the liquid state.

We find that the critical behavior of the gel fraction, the inverse localization length and the shear modulus are universal, in the sense that they are are independent of the end-link functionality and are the same as those found for the case of cross-linked polymer systems. On the other hand, the precise forms of the critical end-link density, the gel fraction, the localization length and the shear modulus do depend on the end-link functionality. Furthermore, the localization length depends on the nature of the constituent polymers, albeit in a simple way through the single-chain mean-square end-to-end distance.

Finally, by making a more refined hypothesis for the order parameter, which allows for a statistical variation in the degree to which the polymers are localized, we find an exact (replica-symmetric) solution of the order parameter self-consistency condition. As well as confirming the equation for the gel fraction obtained from the simpler variational hypothesis, this approach yields a self-consistent (nonlinear integro-differential) equation for the distribution of localization lengths. Upon suitably scaling the distribution with a (diverging) characteristic length, this equation is seen to be independent of the end-link functionality and, indeed, identical to that obtained (and solved) earlier for the case of cross-linked polymeric systems.

Our results reveal a broad universality to the phenomenon of amorphous solidification in polymeric systems: whether the random constraints are end-links of arbitrary functionality or cross-links, and whether the constituent polymers are flexible, semiflexible, or rigid, the essential features of the amorphous solid that emerges upon sufficient linking—the critical behavior of the gel fraction, the characteristic localization length, the distribution of localization lengths, and the shear modulus—are invariant.

[1] S. M. Aharoni and S. F. Edwards, Adv. Polym. Sci. **118**, 92 (1994).

[2] P. M. Goldbart and A. Zippelius, Phys. Rev. Lett. **71**, 2256 (1993).

[3] H. E. Castillo, P. M. Goldbart, and A. Zippelius, Europhys. Lett. **28**, 519 (1994).

[4] For a review, see P. M. Goldbart, H. E. Castillo, and A. Zippelius, Adv. Phys. **45**, 393 (1996); University of Illinois Report No. P-95-09-062-iii, 1995 (unpublished).

[5] R. T. Deam and S. F. Edwards, Philos. Trans. R. Soc. London A **280**, 317 (1975).

[6] C. Roos, A. Zippelius, and P. M. Goldbart, University of Illinois Report No. P-96-05-039-i, 1995 (unpublished).

[7] N. Saito, K. Takahashi, and Y. Yunoki, J. Phys. Soc. Jpn. **22**, 219 (1967).

[8] *P. Erdős: The Art of Counting*, edited by J. Spencer (MIT Press, Cambridge, MA, 1973).

[9] S. F. Edwards, Proc. Phys. Soc. London **85**, 613 (1965).

[10] O. Kratky and G. Porod, Rec. Trav. Chim. **68**, 1106 (1949).

[11] M. Doi and S. F. Edwards, *The Theory of Polymer Dynamics* (Oxford University Press, New York, 1986).

[12] For a review, see J. E. Martin and D. Adolf, Annu. Rev. Phys. Chem. **42**, 311 (1991).

[13] For a discussion of universality, see M. Adam, M. Delsanti, and D. Durand, Macromolecules **18**, 2285 (1985).

[14] P.-G. de Gennes, J. Phys. (Paris) **38**, L355 (1977).