The Immunity of Polymer-Microemulsion Networks

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The concept of network immunity, i.e., the robustness of the network connectivity after a random deletion of edges or vertices, has been investigated in biological or communication networks. We apply this concept to a self-assembling, physical network of microemulsion droplets connected by telechelic polymers, where more than one polymer can connect a pair of droplets. The gel phase of this system has higher immunity if it is more likely to survive (i.e., maintain a macroscopic, connected component) when some of the polymers are randomly degraded. We consider the distribution $p(\sigma)$ of the number of polymers between a pair of droplets, and show that gel immunity decreases as the variance of $p(\sigma)$ increases. Repulsive interactions between the polymers decrease the variance, while attractive interactions increase the variance, and may result in a bimodal $p(\sigma)$.

I. INTRODUCTION

The immunity of networks refers to the ability of a network to preserve its function, even when a certain number of edges or vertices is removed. This attribute is of interest in many types of networks \[1\]. The immunity of a network is the number of polymers that can be removed (by chemical degradation or from shear forces) from the network while the gel maintains its macroscopic characteristics, and does not transform into the fluid phase. That is, a gel is immune if the physical network that comprises the gel retains a macroscopically connected component even though a relatively high fraction of the polymers that form the network have been deleted.

A simple polymer gel is a network of connected polymers in which each edge (i.e., bond) of the network consists of one polymer; in this case, the concept of immunity is identical with that of percolation \[2\]. However, in the system of polymers that join microemulsion droplets, each edge (i.e., bond) that connects two oil droplets may contain more than one polymer – and sometimes many polymers. The percolation problem deals with the removal of entire edges from the network, while immunity refers to the removal of individual polymers from a given edge in systems where there can be many polymers in an edge.

Examples of equilibrium, network-forming systems include surfactant solutions, gels of biological molecules or synthetic polymers. A particularly elegant experimental realization of a transient, self-assembling, physical network has been reported in \[3\]. The system consists of oil-in-water microemulsion droplets connected by telechelic polymers; the latter have a hydrophilic backbone with a hydrophobic group at each chain end. The insolubility of these groups in the continuous water phase and their solubility in the oil droplets result, in some cases, in a network of droplets connected by the polymers. Mixtures of telechelic polymers and microemulsions have a wide range of technological applications, including paints, cosmetics and enhanced oil recovery. Precise control of the structural and rheological properties of such materials is essential for effective and reliable performance. Such control is possible using the telechelic additives, that form a transient network with controlled rheological and structural properties that depends only on the physical properties of the system such as the size and concentration of the polymers and the droplets \[3\].

Apart from its applied interest, the telechelic-microemulsion mixtures serve as model systems for the understanding of a more general class of transient networks. The advantage of this particular system is that the parameters that control the thermodynamics and structure can be easily identified and independently controlled: the concentration of possible vertices (the droplets) and the connectivity of the network (the number of polymers per droplet).

The experimental systems \[3\] exhibit a phase transition from a single phase to coexisting high density and low density network phases. Zilman et al. \[7\] showed that this transition is expected from entropic considerations alone, and occurs even without any particular energetic interactions between the droplets and polymers. In this paper, we extend the analysis of \[7\] and examine the immunity of such polymer gels to random degradation of the polymers such as those that can result from chemical degradation or from shear forces. As the polymers are removed, the macroscopic network becomes disconnected and the gel reverts to a liquid. We show the interactions between the hydrophobic groups at the ends of the poly-
mers have an important affect on the immunity and the phase behavior of the system.

The relation between the degradation of the polymers and the breakdown of the network is not trivial. Each edge in the network may contain several polymers, each of which connect one pair of droplets. The fraction of polymers that must be degraded in order for the network to lose its connectivity depends on the distribution, \( p(\sigma) \), of the number of polymers in an edge. As the variance of the distribution increases, the network becomes more sensitive to polymer degradation, and will lose its connectivity when a smaller fraction of polymers is degraded.

We consider the distribution, \( p(\sigma) \), for various physical situations. Since we are treating relatively rigid and short polymers, we do not consider the interactions between the chains, but focus on the interactions between hydrophobic groups at the end of the polymers, which we denote as stickers. In particular, we predict the effect of both repulsive and attractive interactions between the stickers within a droplet. Repulsive interactions are expected from entropic and excluded volume considerations, while attractive interactions can arise from Van der Waals forces, or from the local change of curvature that the hydrophobic ends induce on the droplet surface. We find that repulsive interactions decrease the variance of \( p(\sigma) \) while attractive interaction increase the variance.

Attractive interactions between the stickers may lead to the co-existence of dense edges, with high density of polymers, with dilute edges, with low polymer density. In that case, the distribution of the edge occupation number, \( p(\sigma) \), is bimodal, and its width is of the order of its average. As the system approaches the critical point associated with the emergence of this two-phase behavior, the fluctuations in the number of polymers in an edge as well as the variance of \( p(\sigma) \), increase. Thus, as we increase the strength of the interaction between the stickers toward its critical value, local concentration fluctuations increase, and the immunity decreases.

In Sec. II, we describe the underlying physical model for the network forming systems of interest, and the simplified theoretical model we use in our calculations. Next, in Sec. III, we examine some simple distributions for \( p(\sigma) \) and demonstrate the dependence of the immunity of the gel on the variance of the distribution. The effects of repulsive and attractive interactions between the polymer ends on or in a droplet are presented in Sec. IV. We use an expression for the Landau free energy of the system of both interacting polymers and droplets to obtain the effect of the interactions on the variance of \( p(\sigma) \), and we predict the phase diagram of this system.

II. THE MODEL

We map the physical space to a discrete regular lattice \( \mathbb{Z}^2 \), where each site can be occupied by an oil droplet. Each pair of neighboring droplets may be connected by polymers. The set of polymers that connect such a pair is referred to as an edge of the network, whose vertices are the droplets.

From the applications of percolation theory to gelation we know that if the fraction, \( \kappa \), of occupied edges exceeds the percolation threshold, \( \kappa_c \), of the lattice, the system is in the gel phase. In the usual discussions of gel connectivity and percolation, each edge is occupied by one polymer. After the degradation of a fraction \( q \) of the polymers, the condition for the survival of the gel phase is \( \kappa(1 - q) > \kappa_c \).

However, the system we discuss here has two important and interesting differences from the usual percolation models:

1. The vertices of the polymer network only exist at those lattice sites at which the oil droplets are present, so only two neighboring vertices of the lattice that are each occupied by droplets can be connected by an edge. In the following, we refer to such a pair as an edge even it is not connected by polymers, in which case we consider it as a disconnected edge. If a given droplet has a neighboring vacant lattice site, we refer to the the droplet surface that face this site as a free face.

2. An edge may be occupied by a number, \( \sigma \), of polymers, whose value is determined by volume limitations (in the case of excluded volume interactions), explicit interactions between the polymers or between the stickers, and the polymer chemical potential - which is fixed by their concentration in the solution. The polymer chemical potential determines the average number of polymers in an edge, \langle \sigma \rangle .

III. NETWORK IMMUNITY AND EDGE OCCUPATION DISTRIBUTION

In this section, we concentrate on the effect of the edge occupation distribution, \( p(\sigma) \), on the immunity. We do not consider here the droplet-related degrees of freedom, but rather assume that they are fixed in a given (static) configuration. The following section considers the droplet-related degrees of freedom. The only degrees of freedom we relate to in this section are occupation, \( \sigma \), of the edges between neighboring droplets.

If the droplets are dense enough, and most of the edges are connected by one or more polymers, then the system has a connected component that spans its entire volume, and the system is in the gel phase. If the fraction of disconnected edges (i.e., those that contain no polymer), is large, the system is in the fluid phase. A system in the gel phase that undergoes a degradation of a fraction of its polymers, has higher immunity if fewer edges are completely disconnected by the degradation process. This will depend on the number of polymers per edge and on the variation of this number throughout the network.
For example, if the system has a distribution of edges in which some edges have large numbers of polymers and some have very few, it will have lower immunity than a system in which the number of polymers in each edge is the same. This is because the random removal of polymers from edges with lower than average occupancy more readily leads to the complete disconnection of that edge, as demonstrated in Fig. 1.

The probability for a given edge to be occupied by $\sigma$ polymers is $p(\sigma)$; the fraction of unoccupied, disconnected, edges is given by $p(0) -$ the probability of a pair of neighboring droplets to have no polymers linking them.

After a fraction $q$ of the polymers is degraded, the new occupation of an edge which had $\sigma$ polymers is proportional to the product of the probability of a number, $\sigma'$ of polymers to remain in the edge, $(1-q)^\sigma$ and the probability of the remaining polymers to be removed, $q^{\sigma-\sigma'}$. The resulting distribution can be written

$$\tilde{p}(\sigma') = \sum_{\sigma=\sigma'}^{\infty} p(\sigma) q^{\sigma-\sigma'} (1-q)^\sigma . \quad (1)$$

The new fraction of unoccupied edges is $\tilde{p}(0) = \sum_{\sigma} p(\sigma) q^\sigma$. The higher this quantity for a given initial average edge occupation, $\langle \sigma \rangle$, and a given degradation probability, $q$, the lower the immunity of the system.

A. Simple distributions

In order to elucidate relation between the variance of the edge occupation distribution $p(\sigma)$ and the immunity of the gel, we first study two simple distributions. The first is a uniform distribution,

$$p(\sigma) = \begin{cases} \frac{1}{2s+1} & m - s \leq \sigma \leq m + s \\ 0 & \text{otherwise} \end{cases} , \quad (2)$$

with an average $m$ and variance $\sigma^2 = (s^2 + s)/3$.

If we randomly delete a fraction $q$ of the polymers, then the fraction of unoccupied edges is

$$\tilde{p}(0) = q^{m-s} \cdot \frac{1 - q^{2s+1}}{1 - q} , \quad (3)$$

which is an increasing function of $s$ for any value of $q$. Thus, in a distribution with a larger variance, the probability of an edge to remain connected is smaller, and it is less immune to random polymer degradation.

The second distribution we would like to consider is the bimodal distribution depicted in Fig. 1.

$$p(\sigma) = \begin{cases} 1/2 & \sigma = m \pm s \\ 0 & \text{otherwise} \end{cases} , \quad (4)$$

with an average $m$ and variance $s^2$. After a deletion of a fraction $q$ of the polymers, the fraction of disconnected edges is

$$\tilde{p}(0) = q^m \cosh(s \log q) . \quad (5)$$

As the variance $s$ increases, the system becomes less immune to random polymer degradation, as demonstrated in Fig. 1. This is relevant to polymer-microemulsion systems with a bimodal distribution of the number of polymers in an edge, as expected when the attractive interactions between the hydrophobic stickers at the polymer ends are large (see Sec. IV).

In the following sections we consider several physical models corresponding to different physical interactions between the polymers and stickers, that yield different edge occupation distributions, $p(\sigma)$. We calculate the variance for each situation to estimate the gel immunity and how it depends on the interactions.

B. Non-interacting polymers

We first examine a naive, but instructive, model where any edge can accommodate an infinite number of polymers. In order to compare it with other models, we express the variance as a function of the polymer concentration, which is the control parameter in most of the experiments. First, we calculate the distribution in the grand canonical ensemble, in which the chemical potential, $\mu_p$, of the polymers is fixed. We then calculate the dependence of $\mu_p$ on the polymer concentration, to determine $\mu_p$. 

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Fig. 1: Models of polymer-microemulsion systems with different distributions, $p(\sigma)$, of the number of polymers in an edge. We compare a homogeneous system (a) with 11 polymers in each edge (mean $n = 11$ and distribution width $s = 0$) vs. a system with bimodal $p(\sigma)$ (b), as given by Eq. (4) ($m = 11$, $s = 9$). After a random deletion of a fraction, $q = 0.85$, of the polymers, most of the edges in the homogeneous system (c) survive, and it still retains a macroscopically connected component. In the inhomogeneous system, most of the dilute edges are eliminated by the deletion (d) and the system no longer has a macroscopically connected component.
The distribution is given by

\[ p(\sigma) = e^{-e^{-\mu_p} \frac{e^{-\sigma \mu_p}}{\sigma!}}, \tag{6} \]

where the factorial in the denominator comes from the fact that the polymers are indistinguishable. This distribution has an average and a variance \( \langle \sigma \rangle = S^2_\sigma = e^{-\mu_p}. \)

### C. Excluded volume interactions

In a more realistic model, the excluded volume interactions limit the maximum number of polymers that can reside in a given droplet. There is thus a finite, maximal number of polymers, \( \sigma_M \), associated with one edge. The volume restriction may arise from Helfrich-like, excluded volume interactions between the polymer chains, or from the finite area occupied by each sticker in or on the surface of a droplet.

If the only interactions between the polymers and between the stickers are short range excluded volume interactions, we can assume that there are \( \sigma_M \) sites in an edge, that can each be occupied by one polymer. The distribution of the edge occupation is

\[ p(\sigma) = Z^{-1} \left( \frac{\sigma_M}{\sigma} e^{-\sigma \mu_p} \right), \tag{7} \]

where \( Z = (1 + e^{-\mu_p})^{\sigma_M} \) is the partition function.

The free energy per site (we take all energies in units of \( k_B T \)) is \( f_e = - \log(Z)/\sigma_M \). The average edge occupation is

\[ \langle \sigma \rangle = \sigma_M \frac{\partial f_e}{\partial \mu_p} = \frac{\sigma_M}{1 + e^{\mu_p}}, \tag{8} \]

and the variance of the distribution \( p(\sigma) \) is

\[ S^2_\sigma = -\sigma_M \frac{\partial^2 f_e}{\partial \mu_p^2} = \frac{\sigma_M}{4 \cosh^2(\mu_p/2)} \langle \sigma \rangle \left( 1 - \frac{\langle \sigma \rangle}{\sigma_M} \right). \tag{9} \]

The variance here is smaller than in the case of non-interacting polymers (Eq. 9). In the non-interacting case, the variance was equal to \( \langle \sigma \rangle \), where in the present case it is smaller by a factor of \( 1 - \langle \sigma \rangle/\sigma_M \). As expected, the difference between the distributions vanishes for the case \( \sigma_M \gg \langle \sigma \rangle \). The narrowing of the distribution by the excluded volume interactions increases as the average number of polymers per edge approaches \( \sigma_M \), where the variance vanishes and the distribution approaches a delta function as \( \sigma \to \sigma_M \). This suggests that repulsive interactions between the polymers or the stickers increase the immunity of the gel under a random degradation of the polymers.

### IV. INTERACTING STICKERS

We now calculate the free energy of a system of droplets and polymers in which the polymers show attractive or repulsive interactions in the multi-canonical ensemble, where the number of polymers and droplets is not fixed, and is determined by the chemical potentials \( \mu_p \) and \( \mu_d \), respectively. We shall consider the possibility of polymers that connect neighboring droplets as well as polymers that form loops, in which both sticker ends reside in the same droplet.

The physical model can be associated with the vertices (droplets) and edges of an underlying graph. The vertices are given by the sites of the underlying lattice which are occupied by the droplets. The edges of the graph connect pairs of neighboring occupied vertices on the lattice. Since each site may be occupied by a droplet, the statistical ensemble we consider here includes the sub-graphs of the lattice (though most of them have negligible weight).

We divide each droplet into faces, one for each edge of the graph that emerges from its vertex. If another droplet occupies a vertex that is connected to the same opposite edge, then the corresponding face is associated with the edge between the two droplets, and we call it a linked face. If there is no neighboring droplet at the vertex connected to a given edge, we term it a free face.

We consider systems in which the radius of gyration of a polymer is smaller than the radius of a droplet. Thus, we treat each edge and each free face as a separate system. In an experiment, where the total number of polymers is fixed, the edges and faces interact through this constraint. In the multi-canonical ensemble, however, they do not interact. We can thus treat each edge or free face as an independent system and write its partition function explicitly.

As discussed above, excluded volume interactions imply that a face can contain a maximum of \( \sigma_M \) stickers. This means that an edge has a maximal occupation of \( \sigma_M \) polymers. These polymers can be links - with the two telechelic stickers of a given polymer attached to the two opposing faces of adjacent droplets, or loops - with both stickers of a given polymer attached to the same face of a single droplet. A face can contain a maximum of \( \sigma_M/2 \) such loops.

#### A. Polymer free energy

We consider a model in which, except for the excluded volume interactions that determine the maximal number of polymers per droplet, \( \sigma_M \), polymers interact only through their stickers (telechelic ends). The interactions between the polymer chains have a negligible contribution for the case of relatively short and stiff chains that we consider here. Thus the energy difference between an edge that has two loops on the opposite faces of two neighboring droplets, and an edge in which these faces are linked by two polymers, is simply \( 2e_{\text{loop}} - 2e_{\text{link}} \), where \( e_{\text{loop}} \) is the configurational free energy of a loop, and \( e_{\text{link}} \) is that of a link. We thus define an effective thermodynamic potential of a polymer in an edge

\[ \mu = \mu_p - \log(e^{-e_{\text{loop}}} + e^{-e_{\text{link}}}). \tag{10} \]
An edge where all the polymers have a thermodynamic potential $\mu$ is equivalent to a one in which loops have a potential of $\mu_p + \epsilon_{\text{loop}}$ and links a thermodynamic potential of $\mu_p + \epsilon_{\text{link}}$, in the sense that both systems have the same partition function and hence yield the same distribution $p(\sigma)$. Thus, we assume that all polymers in the edge have a thermodynamic potential of $\mu$, whether they are loops or links.

In a free face, where the polymers are all in loop configurations, the thermodynamic potential of a polymer is $\mu_p + \epsilon_{\text{loop}} = \mu + \Delta$, where $\Delta = \log(e^{\epsilon_{\text{loop}}-\epsilon_{\text{link}}} + 1)$.

The free energy of an edge or a free face depends only on the effective thermodynamic potential of the polymers and the interaction between the stickers, which is similar in both the linked faces and free faces. We denote the free energy of an edge as $\sigma M f_e(\mu)$, where $f_e(\mu)$ is the free energy density (free energy per polymer site) of the face surface, or the free energy of one of the $\sigma M$ sites on the face. Since in our model a free face differs from within a mean field approximation, the free energy density of the polymers is $\frac{1}{2} \left( \sigma M / \mu \right) f_e(\mu + \Delta)$.

One can readily derive the free energy, $f_e$, of a system with only excluded volume interactions: $f_e = -\log(1 + e^{-\mu})$. We considered such a system in Subsection III C where we ignored the configurational free energy of the polymers.

The interactions between the stickers are accounted for within a mean field approximation. The total interaction energy for an edge with $\sigma M$ polymers is written as $-\alpha \sigma M / 2$. The number of stickers that occupy a given edge is $\sigma$. We therefore write the interaction free energy due to two-body interactions among the stickers using a virial-type term: $-(\alpha/2\sigma M)\sigma^2$. The partition function is

$$Z = \sum_{\sigma=0}^{\sigma_M} \left( \frac{\sigma_M}{\sigma} \right)^{\sigma M} \exp \left( -\mu \sigma + \frac{\alpha}{2\sigma M} \sigma^2 \right)$$

$$= \sqrt{\frac{\sigma M}{2\pi\alpha}} \int_{-\infty}^{\infty} d\phi \left[ e^{-\phi^2/2\alpha} (e^{\phi - \mu} + 1) \right]^{\sigma M}$$

(11)

We consider this expression for $Z$ as the partition function of an effective Hamiltonian, $H(\phi) = \sigma M \left[ \frac{1}{2\alpha} \phi^2 - \log(e^{\phi - \mu} + 1) \right]$, that has a minimum at $\phi_0$, given by:

$$\phi_0 = \frac{\alpha}{e^{\mu - \phi_0} + 1}.$$  

(12)

For $\sigma M \gg 1$ the distribution of $\phi$ tends to a sharp peak around $\phi_0$, and we can use the mean field approximation $\langle f(\phi) \rangle_\phi \approx f(\phi_0)$ to estimate the average fraction $\bar{\varphi} = \langle \sigma / \sigma M \rangle$ of sites occupied in an edge and its variance:

$$\bar{\varphi} = -\frac{\partial f_e}{\partial \mu} = \frac{1}{\sigma M} \left( \frac{\partial H(\phi)}{\partial \mu} \right)_\phi \approx \frac{\phi_0}{\alpha},$$

$$S^2_{\bar{\varphi}} = \frac{\partial^2 f_e}{\partial \mu^2} \approx \left( \frac{1}{\bar{\varphi}(1-\bar{\varphi})} - \frac{\alpha}{\bar{\varphi}} \right)^{-1}.$$  

(13)

This expression applies whether $\alpha$ is positive (attractive interactions), negative (repulsive interactions), or zero. Eq. (14) suggests a divergence of the variance for $\alpha \geq 4$.

In a macroscopic system ($\sigma M \rightarrow \infty$), this signifies an instability related to macroscopic phase separation. We do not expect such behavior for finite $\sigma M$ (which is more realistic), but we do observe a pronounced increase in the variance, as the interaction strength $\alpha$ increases (see Fig. 2).

The increase in the variance is due to a bimodal distribution of the polymer density in the bonds, as demonstrated in Fig. 3. For large values of $\alpha$, the distribution $p(\sigma)$ resembles the bimodal distribution in Eq. 4.

In such a system, when the interactions are strong enough, one may observe two kinds of edges connecting the droplets: dilute edges containing one or a few polymers, and dense edges, containing about $\sigma M$ polymers. Both kinds induce the same effective attraction between the droplets (see below). Under degradation, most of the dilute edges will break down, and the connectivity of the network may decrease dramatically, as depicted in Fig. 4. If the system was in the gel phase, and the connectivity is reduced below the percolation threshold, the gel will transform into a fluid phase.

We conclude by obtaining an analytical expression for the mean-field free energy of an edge, which is a good approximation for the case $\sigma M \gg 1$. Expansion of the effective Hamiltonian around its minimum yields $H(\phi) \approx H(\phi_0) + \frac{1}{2} H''(\phi_0) (\phi - \phi_0)^2$, where $H''(\phi) = \frac{1}{2} \partial^2 H / \partial \phi^2$. Plugging this approximation into the integral of Eq. 4 and taking the logarithm, we obtain the grand-canonical distribution of the polymer density in the bonds.
potential for a single edge:

\[ f_e(\mu) = -\log(Z) \approx \frac{1}{\sigma_M} \left[ H(\phi_0) - \frac{1}{2} \log \left( \frac{\alpha}{\sigma_M} H''(\phi_0) \right) \right] \]

\[ = \frac{\sigma}{2} \tilde{\phi}^2 + \log(1 - \tilde{\phi}) - \frac{1}{2} \sigma_M \log(1 - \alpha \phi(1 - \tilde{\phi})) , \]  

where \( \tilde{\phi} \) is determined by the value of \( \mu \), and the last equality is obtained using Equations 12 and 13.

B. Droplet free energy

Each vertex of the network in our model can occupy one oil droplet. We define \( s_i = 0,1 \) as the occupation number associated with vertex \( i \) in the lattice. The number of edges in a given configuration of the system is \( N_{E} = \sum (ij) s_i s_j \), where the sum is over pairs of neighboring sites. The number of free faces is \( N_{F} = \sum (ij) s_i (1 - s_j) + s_j (1 - s_i) \). The number of droplets is \( N_{d} = \sum s_i \).

FIG. 3: The distribution \( P(\sigma) \) of the number of polymers in a bond, for \( \sigma_M = 20 \) and \( \sigma_M = 200 \). The effective chemical potential \( \mu \) is such that \( \langle \sigma \rangle = \sigma_M/2 \). The values of \( \alpha \) are in units of \( k_B T \).

Each edge has a free energy, \( \sigma_M f_e(\mu) \), and every free face has a free energy, \( (\sigma_M/2) f_e(\mu + \Delta) \). The partition function of the system containing both polymers (which have both interactions and configurational entropy) and droplets (which have translational entropy) is given by the sum over all droplet configurations:

\[
Z = \sum_{\{s\}} \exp \left[ N_{d} \mu_{d} + N_{E} \sigma_M f_e(\mu) + N_{F} \frac{\sigma_M}{2} f_e(\mu + \Delta) \right]
\]

\[ = \sum_{\{s\}} \exp \left[ N_{d} \left( \mu_{d} + \frac{\zeta}{2} \sigma_M f_e(\mu + \Delta) \right) + N_{E} J(\mu, \Delta) \right], \]

(16)

where \( \mu_{d} \) is the chemical potential of the droplets, \( J(\mu, \Delta) = f_e(\mu) - f_e(\mu + \Delta) \) is the effective interaction between the droplets, mediated by the polymers, and \( \zeta \) is the number of nearest neighbors at each site. This is equivalent to the partition function of a lattice gas model [7].

We use a Landau type, coarse grained approximation for the free energy, as a function of the dimensionless concentration (volume fraction) of droplets, \( c = \langle s \rangle \), which is the average occupation per vertex:

\[
f = c \log c + (1 - c) \log(1 - c) + \frac{1}{2} \beta \sigma_M f_e(\mu + \Delta)c + \frac{1}{2} \beta \sigma_M J(\mu, \Delta)c^2 . \]  

(17)

The first two terms in Eq. 17 give the lattice gas entropy; the third term is obtained using \( N_{d}/V = c \), where \( V \) is the volume of the system; the fourth term is obtained from Eq. 16 using the mean-field approximation \( N_{E}/V \approx \zeta c^2/2 \). The dependence of \( f \) on the potential \( \mu_{d} \) is linear in the droplet concentration, and this term has no effect on the phase behavior of the system.

In the coexistence region, there is an equilibrium of droplet chemical potential, \( \mu_{d} = \partial f/\partial c \), and of the osmotic pressure, \( \pi_{d} = f - \mu_{c} c \), between the coexisting phases. In equilibrium, the polymer chemical potential must be the same in both phases; this is automatically ensured by working at constant \( \mu \). By solving these equalities we obtain the binodal curve in \( c \times \mu \) (droplet concentration-polymer thermodynamic potential) plane.

Since in experiment it is easier to control the polymer concentration \( \phi \) than the polymer chemical potential, \( \mu \), it is useful to predict the phase diagram in the \( c \times \phi \) plane. We perform this transformation using the identity

\[
\varphi = \frac{df}{d\mu} = \sigma_M \left[ f'_e(\mu + \Delta)c + J'(\mu, \Delta)c^2 \right], \]  

(18)

where the prime indicates a derivative with respect to \( \mu \). This fixes the polymer chemical potential, \( \mu \), as a function of the number of polymers, \( \varphi \). In the phase-coexistence region, above the binodal curve, the conditions of constant droplet chemical potential, \( \mu_{d} \), and osmotic pressure, \( \pi_{d} \), for fixed polymer chemical potential, \( \mu \), yield values of the droplet density, \( c \), for the coexisting dilute and dense phases respectively. From Eq. 18
existing phases. As the interaction, existence curve and of the concentrations in the two co-
interactions can markedly affect the shape of the coex-

\[ \alpha \]

for different values of the edge interaction

out explicit sticker interactions (\( \alpha \)). The number

dilute droplets and low polymer concentration that co-
ration is sharper, and characterized by a phase with very

polymer concentration. In fact, in Fig. 4 the curve for

We note that dilute edges (with one or a few polymers) can also exist in the dense droplet phase, since they in-
fluence the same effective interaction, \( J(\mu, \Delta) \), between the droplets as the dense edges, and their polymers have the
same thermodynamic potential, \( \mu \), as the polymers in the
dense edges. This scenario may change if we consider interactions between the edges.

\[ \pi \]

\[ \bar{\phi} \]

\[ \sigma \]

\[ 2 \]

\[ \Delta = 0.3k_{B}T, \ \zeta = 4 \] and \( \sigma_{M} = 20 \).

this implies that each phase has a different value of the
polymer concentration, \( \varphi \).

The critical point in the \( c \times \mu \) (droplet concentration-
polymer concentration) plane occurs at \( c = 1/2 \), with \( \mu \)
given by

\[ J(\mu, \Delta) = \frac{-4}{\zeta \sigma_{M}}. \]  

(19)

The binodal curve of the system is presented in Fig. 4
for different values of the edge interaction \( \alpha \). The max-
imal number of stickers that can reside in one droplet is
\( \zeta \sigma_{M} \). Thus, the number of stickers per unit volume is
\( c \zeta \sigma_{M} \), and the maximal number of polymers per unit vol-
ume is \( c \zeta \sigma_{M}/2 \) (assuming a prohibitively high energetic
cost of a hydrophobic sticker in the water). The number
of polymers per available site in the system is then

\[ \bar{\phi} = \frac{2\varphi}{\zeta \sigma_{M}c}. \]  

(20)

A phase co-existence region is present in a system with-
out explicit sticker interactions (\( \alpha = 0 \)). However, the
interactions can markedly affect the shape of the coex-
istence curve and of the concentrations in the two co-
eexisting phases. As the interaction, \( \alpha \), increases, the ef-
effective interaction between the droplets, induced by the
edges, increases and becomes more sensitive to the poly-
mer concentration. As a result, the onset of phase sepa-
ration is sharper, and characterized by a phase with very
dilute droplets and low polymer concentration that co-
exists with a phase with high droplet density and high

V. DISCUSSION

In this paper, we have predicted the immunity of the
gel phase of a polymer-microemulsion system to random
degradation of polymers. The gel in this system consists of
doil droplets connected by telechelic polymers. The set
of polymers that link a given pair of droplets is defined
as an edge (i.e., bond) of the gel network. We consider
the distribution, \( p(\sigma) \), of the number of polymers in one
such edge, and argue that immunity of the gel is inversely
related to the variance, \( S_{\sigma}^{2} \), of this distribution.

Repulsive interactions between the stickers (the
telechelic ends of the polymers) reduce the variance \( S_{\sigma}^{2} \),
thus contributing to the gel immunity. Attractive inter-
action, which increase \( S_{\sigma}^{2} \), reduce the immunity of the
gel.

Attractive interactions may give rise to a bimodal dis-
tribution of the edge occupation, which can give rise to
the co-existence of dense and dilute edges in the same
macroscopic sample. A dilute edge contains a small num-
ber of polymers, and is likely to vanish under a random
degradation of the polymers. When a finite fraction (say,
1/2) of the edges are dilute, the fraction of edges surviv-
ing a degradation will be lower, and the system is more
likely to transform from the gel to the fluid phase.

This reasoning is particularly applicable to the case of
a dense phase that coexists with a dilute phase (as-
suming the dilute phase is not a gel). Since the polymer
density within the dense droplet phase is high, we ex-
pect – if the attractive interactions are large enough – to
find a bimodal distribution of the edge occupation within
the dense droplet phase. In that case, we are interested
in the immunity of the dense phase, and therefore must
take into account the distribution, \( p(\sigma) \), within the dense
droplet phase.

To test our predictions for the immunity of a system
with attractive interactions among the polymers, we sug-
gest comparing the elastic stability (gel-like nature) with
respect to polymer degradation of two systems (both in
the dense phase): one with no sticker interactions (\( \alpha = 0 \))
and one with strong interactions (say, \( \alpha = 10 \)). Accord-
ing to our predictions, the system with no interactions
will be characterized by edges each of which has approx-
imately the same number of polymers, while the system
with strong interactions will show a bimodal distribution
for the edge occupancy. We predict that after polymer
degradation the fraction of surviving edges will be larger
in the non-interacting system (see Fig. 1), and that this system is more likely to remain in the gel phase.

In order to investigate the immunity of such gels experimentally, it is necessary to devise a method to degrade the polymers at random and in a homogeneous manner throughout the system. It may be difficult to do this using molecules in a solvent, since a solvent added to the system will initially have a much higher concentration at the surface of the gel (penetrating the bulk by slow diffusion); thus the polymers near the surface are much more likely to be degraded.

One way to achieve random degradation may be to use polymers that have been synthesized with a photosensitive molecule in the middle of each chain. Optical methods might be used to cause these molecules to change their conformation and depolymerize. The intensity and duration of the optical beam can be used to control the fraction of polymers broken.

Acknowledgments

The authors thank L. Chai, M. Gottlieb, S. Havelin, J. Klein, C. Ligoure, G. Porte, and A. Zilman for useful discussions. This work has been supported by the German Israeli Foundation and by an EU Network Grant.

[1] R. Albert and A. L. Barabási, Rev. Mod. Phys. 74, 47 (2002).
[2] A. Wagner, Nature Genetics 24, 355 (2000).
[3] R. Albert, H. Jeong and A. L. Barabási, Nature 406, 378 (2000).
[4] R. Cohen R, S. Havlin and D. Ben-Avraham, Phys. Rev. Lett. 91, 247901 (2003).
[5] E. Michel, J. Appell, F. Molino, J. Kieffer and G. Porte, J. Rheol. 45, 1465 (2001); M. Filali, M. J. Ouazzani, E. Michel, R. Aznar, G. Porte and J. Appel, J. Phys. Chem. B 105, 10528 (2001).
[6] M. Adam, D. Laierez, M. Karpasas and M. Gottlieb, Macromolecules 30, 5920 (1997).
[7] A. Zilman, J. Kieffer, F. Molino, G. Porte and S. A. Safran, Phys. Rev. Lett. 91, 015901 (2003).