the interstices of the lattice and that they were immobile in tungsten at 60, 61, 80, and 90 K.

The temperature at which the interstitial ^{4}He atoms became mobile in W was determined by implanting ^{4}He in an FIM specimen at different T_i's and then analyzing at $T_r = 60$ K. The ^{4}He integral profile determined at T_r was independent of T_i only if the ^{4}He was immobile at all values of T_i. However, when T_i was above the temperature at which the ^{4}He interstitials became mobile, the ^{4}He implanted during the irradiation diffused to the surface of the FIM specimen and entered the gas phase. Therefore a sharp decrease in the measured ^{4}He concentration was expected as T_i was increased (see Fig. 1). Since only T_i was varied, significant changes in the integral profile could only be attributed to a sharp increase in the mobility of the interstitial ^{4}He atoms at T_i. A dramatic change in the integral profile was observed upon increasing T_i from 90 to 110 K; thus indicating that interstitial ^{4}He atoms were immobile at 90 K but were highly mobile at 110 K. By employing a diffusion model, a value of the enthalpy change of migration ($\Delta h_{\mathrm{He}}{}^{m}$) of 0.24 to 0.32 eV was estimated.

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Site-Bond Correlated-Percolation Problem: A Statistical Mechanical Model of Polymer Gelation

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A new model for polymer gelation is presented that predicts new effects that can not be derived from the conventional theory of Flory and Stockmayer. An exact solution is obtained for the Bethe lattice, and is related to recent experimental results of Tanaka. Under certain conditions, the gelation curve terminates at the consolute point; at this point, both connectivity and concentration fluctuations are critical, just as in the random magnet at the percolation threshold.

Recently, there has been renewed interest in applications of critical-phenomena concepts to polymers.[1] The gelation transition is particularly intriguing, in part due to superficial resemblances to the bond percolation problem.

In 1941, Flory[2] proposed an elegant model of polymer gelation, which has the virtue of being amenable to closed-form solution for the special case in which one neglects the possibility of intramolecular binding. Flory's original model and its elaborations[3] have proved extremely versatile in providing a qualitative understanding of a wide range of gelation processes. In the following, we shall refer to this model as the Flory-Stockmayer (FS) model.

In this Letter, we propose a statistical mechanical model of polymer gelation that predicts new effects that cannot be derived from the classic FS model. First it is convenient to review the essential features of the FS model. For simplicity, consider the case of polyfunctional condensation in a system of identical monomers, each with functionality $f=4$ (cf. Fig. 1). The monomers are indicated by open circles and the chemical bonds between the monomers by wavy lines. The FS model assumes that for a given set of experimental conditions, the presence or absence of a bond between any given pair of monomers is a random event, characterized by a probability p_B. When p_B is small, the system consists of only finite polymers (monomers, dimers, trimers, ...); this is the sol phase of Fig. 1(a). However, when p_B exceeds some critical or "threshold" value p_c, there exists in addition to the finite molecules a single molecule that is infinite in spatial extent; this is the gel phase of Fig. 1(b). The weight fraction of monomers belonging to the gel molecule (the "order parameter") is zero for $p_B \leqslant p_c$ and nonzero for $p_B > p_c$. Today, of course, we recognize the FS model as being equivalent to the bond-percolation problem.[4]

In the FS theory two simplifying assumptions, which might leave out certain features at least in reversible gelation, are (i) the absence of solvent molecules, and (ii) the absence of correlations between the molecules. The model we propose does not assume (i) and (ii).

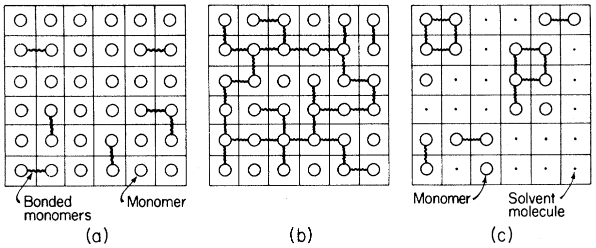

FIG. 1. (a), (b) All sites are occupied by a monomer (open circle), as in the Flory-Stockmayer model of gelation. The wavy lines correspond to chemical bonds between two monomers, while p_B is the probability of such a bond being present. (c) The model of gelation proposed here. Each site can be occupied by either a monomer (circle) or a solvent molecule (dot). The wavy line corresponds to a chemical bond. We find p_B, given by Eq. (3), is a function of the temperature.

Specifically, we associate an "A site" with a solvent molecule and a "B site" with a monomer. Moreover, we assume that the sites are correlated as in the lattice-gas or Ising model. In specifying the interactions, we must consider that the monomers can interact with each other in two ways. One is the usual van der Waals interaction, and the other is a directional interaction that leads to chemical bonds. The particle-particle interactions of this system are reasonably approximated by the following nearest-neighbor interactions:

$$\begin{aligned} -W_{AA} &= \text{solvent-solvent}, \\ -W_{AB} &= \text{monomer-solvent}, \\ -\epsilon_{BB} &= \text{monomer-monomer} \\ &= \begin{cases} -W_{BB} \text{ (van der Waals) with weight } \rho_u \\ -E \text{ (bonding energy) with weight } 1-\rho_u . \end{cases} \end{aligned} \tag{1}$$

The Hamiltonian for a system of N_A molecules of solvent and N_B monomers can be written as

$$H = -W_{AA} \sum_{\langle ij \rangle} \pi_i{}^A \pi_j{}^A - \epsilon_{BB} \sum_{\langle ij \rangle} \pi_i{}^B \pi_j{}^B - W_{AB} \sum_{\langle ij \rangle} \pi_i{}^A \pi_j{}^B , \tag{2}$$

where the sums are over all nearest-neighbor pairs of sites. Here $\pi_j{}^A$ is 1 if site j is occupied by a molecule of species A and zero otherwise; a similar definition holds for $\pi_j{}^B$. Clearly $\pi_j{}^A + \pi_j{}^B = 1$. For a given configuration of bonds, we can calculate the partition function from (2), and then take the average overall bond configurations.

While the thermodynamic properties can be derived from the free energy, the connectivity properties, which are related to the question of gelation, cannot. We define the "gel" phase to be the phase where a nonzero finite fraction of monomers are bonded together via chemical bonds to form a macroscopic molecule.

In order to calculate the gelation threshold $\varphi_g(T)$, we must specify when a pair of monomers are chemically bonded. We require that (i) they be nearest neighbors and (ii) their relative interaction energy be $-E$. When two nearest-neighbor monomers satisfy (ii), we say that a bond is present between two monomers.

The probability p_B that such a bond is present between two nearest-neighbor monomers is[5]

$$p_B = \frac{(1-\rho_u)\exp(\beta E)}{\rho_u \exp(\beta W_{BB}) + (1-\rho_u)\exp(\beta E)} . \tag{3}$$

Here $\beta \equiv 1/kT$; k is the Boltzmann constant.

The problem of calculating $\varphi_g(T)$ is in some respects similar to the usual site- or bond-percolation problem. However, it is more complex for the following two reasons: (a) In the "pure" site-percolation problem, the particles are *randomly* distributed, while here they are *correlated* according to the Hamiltonian (2) ("correlated" percolation). (b) In site percolation, the vertices can be occupied or not and the bonds are always present. In bond percolation the vertices are all occupied by the particles and the bonds may be present or absent. In our model the vertices may be occupied or not and *also* the bonds may be present or absent ("site-bond" percolation). While both the correlated-percolation problem[6-8] and the site-bond–percolation problem[9] have been treated separately, here we treat both problems simultaneously.

From the above considerations, it follows that if $p_B < p_c$ (pure bond-percolation threshold), there is no gelation no matter how high the monomer density φ. Therefore there exists a limiting value of the temperature, $T_{\max}$, with $p_B(T_{\max}) = p_c$, above which there is no gelation (see Fig. 2). $T_{\max}$ does not depend on the nature of the solvent.

The previous discussion was restricted for simplicity to a system of monomers. We have also extended the model to a system of polymer chains of M monomers embedded on the lattice[10] (cf. Fig. 2). The monomer-monomer interaction is still assumed to be given by (1). Two chains are bonded via monomers and the probability that two monomers are bonded is given by (3).

Next we calculate the equation of state and the gelation threshold $\varphi_g(T)$ for the interior of the Bethe lattice (see Fig. 2) with coordination number $f = \sigma + 1$ for such a system of chains. The most interesting case is $\sigma = 2$.

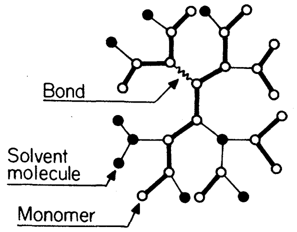

FIG. 2. Polymer chains (heavy line) embedded on a Bethe lattice of coordination number $f = \sigma + 1 = 3$. The open circles are the monomers. The dots are the solvent molecules. The wavy lines are the bonds between monomers of different chains.

Following closely the derivation for the pure site model[11,12] we find that the volume fraction of monomers is

$$\varphi = \frac{R(\mu_1^2 + \mu_1 z)}{R\mu_1^2 + (1+R)\mu_1 z + 1}, \tag{4}$$

where $R \equiv M\sigma(\sigma+1)/[M\sigma(\sigma-1) + 2\sigma]$ and

$$z \equiv \{\rho_u \exp[\beta(W_{BB} + W_{AA} - 2W_{AB})] + (1-\rho_u)\exp[\beta(E + W_{AA} - 2W_{AB})]\}^{-2}.$$

Here μ_1 is given implicitly in

$$\mu = \mu_1 \frac{(\mu_1 z + 1)^{M\sigma}}{(\mu_1 + z)^{M(\sigma-1)+1}} \tag{5}$$

where $\mu \equiv \exp(\beta\{\mu_A - \mu_A(0) - M[\mu_B - \mu_B(0)]\})$. Here μ_A is the chemical potential of species A, $\mu_A(0)$ is its value in the absence of species B; μ_B and $\mu_B(0)$ are defined analogously.

We have calculated, applying the "equal-area" rule, the coexistence curve for three different solvents (Fig. 3). Following the procedure for the site-correlated percolation problem,[11] we find the gelation threshold

$$\varphi_g = \frac{Rz^2\tilde{\sigma}}{[(1+R)\tilde{\sigma} - 1]z^2 + (\tilde{\sigma} - 1)^2}, \tag{6}$$

where $\tilde{\sigma} = [M(\sigma-1) + 1]p_B$ and p_B is given by (3).

In Fig. 3 the sol-gel phase boundary is given schematically, together with the coexistence curve for the binary mixture of monomers and solvent, for three different solvents. We have also continued the gelation curve (broken line) into the two-phase region. The solvent parameters have been chosen in such a way that the consolute point is in the sol region [Fig. 3(a)], on the gelation curve [Fig. 3(b)], and in the gel region [Fig. 3(c)]. We stress two interesting features:

(i) For all the solvents there is a temperature T_p (below the consolute temperature T_c) at which the coexistence curve crosses the gelation curve. For $T < T_p$ we have coexistence between sol phase and gel phase. In addition, in Fig. 3(c), for $T_p < T < T_c$ we have two possible gel phases.

(ii) By changing the solvent properties it is possible to realize the interesting case in which the consolute point lies on gel-sol phase boundary, as shown in Fig. 3(b). This particular point Q is characterized by the divergence of two lengths. One is the usual correlation length ξ which diverges at the consolute point, and the other is the characteristic linear dimension of the finite clusters (the "connectedness length") ξ_p which

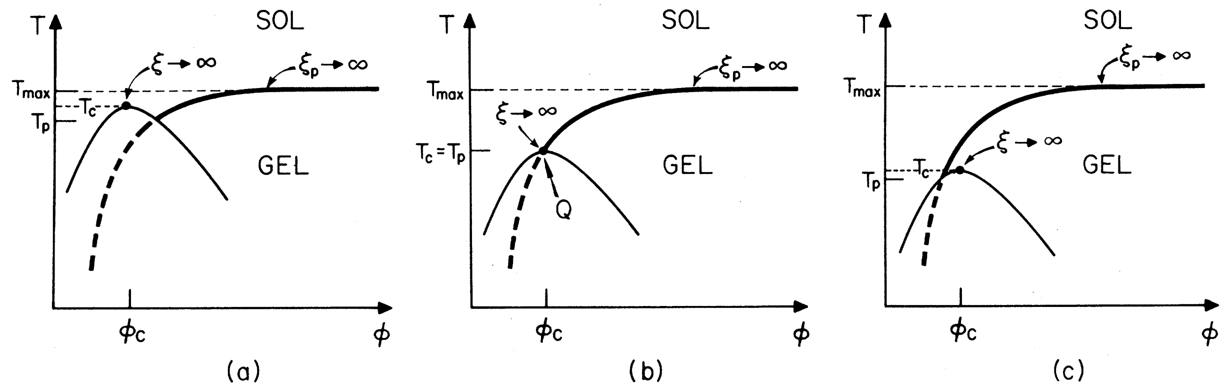

FIG. 3. Coexistence curve for the polymer-solvent binary mixture and sol-gel phase boundary for three different solvents. The broken curve is the continuation of the gelation curve into the two-phase region. The solvents have been chosen in such a way that the consolute point is (a) in the sol phase, (b) on the gelation curve, and (c) in the gel phase. T_p is the temperature at which the gelation curve crosses the coexistence curve.

diverges on the sol-gel phase boundary. It is interesting to study the nature of point Q, which in some respects is analogous to the point $(T=0, p=p_c)$ in the T-p phase diagram of a randomly dilute ferromagnet [cf. Fig. 1(c) of Ref. 13].

We find that the usual mean-field type of behavior occurs all along the sol-gel phase boundary, including the consolute point (T_c, φ_c). However at the point Q we find that $(T-T_c)/T_c$ is not a scaling variable. It would be interesting to test this prediction experimentally on a real polymer system.

We note that our results reduce to the FS theory in the particular case in which the monomer density $\varphi = 1$ (all sites occupied). But in this case, of course, there is no phase separation, consequently the new effects described in Fig. 3 vanish.

The results presented thus far are for the Bethe lattice, which corresponds to the physical approximation of neglecting intramolecular interaction ("loops"). It is known that the neglect of loops does not affect critical properties in the limit of high system dimensionality d. Hence the question is basically whether the results presented thus far can be expected to be useful in a system of low dimensionality.

Several points are worth making in this connection:

(i) *Experiments on three-dimensional systems.*—The results presented thus far are in close (qualitative) agreement with recent experimental data on calf gelatin suspended in alcohol-water solvents.[14]

(ii) *$d=3$ model systems.*—For the three-dimensional lattice-gas model, we know[6,7] that the percolation point for the correlated-site problem in zero magnetic field occurs at a temperature T_p which is smaller than T_c, as in the Bethe lattice. Thus, we would expect to find a phase diagram of the sort shown in Fig. 2.

(iii) *$d=2$ lattice gas.*—For the two-dimensional lattice-gas model with no bond dilution $(p_B=1)$, we know[7,15] that the line of percolation points terminates at T_c (i.e., $T_p = T_c$). Hence, the situation shown in Fig. 3(c) cannot occur for $d=2$.

In summary, we have presented a model for polymer gelation which predicts new effects which could not be derived from the original FS theory. A closed-form solution is obtained for this model for the Bethe lattice. The phase diagram so obtained is in qualitative agreement with recent experimental results. In particular, under certain conditions the gelation curve terminates at the consolute point (T_c, φ_c).

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