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Estimation of critical points of branched polymers

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The authors' theory of the gel point is applied to the gelation experiments in nonstoichiometric systems of Gordon and Scantlebury. Agreement between the theory and the observations is found to be excellent in every region examined, confirming the mathematical soundness of the theory. The theory is transposed to the site-bond problem. With the aid of a high dimension expansion of the ring distribution function, we derive an analytic expression for the bond percolation threshold. The resultant equation is in good conformity with the site-bond percolation simulation of Stauffer. The present theory is scrutinized over a wide range of dimensions for pure bond percolation; the result shows that the theoretical line abruptly merges with the observed points at $d=8$, consistent with the Lubensky-Isaacson excluded volume theory which predicts the critical dimension $d_c=8$ for sol clusters on lattices.

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I. INTRODUCTION

Estimation of gel points has been a long-standing problem in polymer physics [1,2]. In his first paper on gelation, Flory [1] showed that there exists a critical value for the extent of reaction, $D_{co}=1/(f-1)$ (the subscript o denotes the critical value based on the tree model), above which an infinite branched molecule emerges. For the purpose of comparing his theoretical consideration with observed gel points, he carried out experiments himself with branched polyesterifications: According to his paper, ''there is no difficulty in locating the gel point. ... Samples removed just prior to gelation are completely soluble in chloroform or chloroform-dioxane mixture. Samples removed two or three minutes after gelation do not dissolve completely in such solvents, a small amount of very gelatinous precipitate remaining suspended in the solution.'' The observed gel points showed that the reactions proceeded appreciably beyond the above theoretical point D_{co}. He reasoned that the discrepancy between the theoretical values and the observed values can be ascribed to the occurrence of intramolecular reaction.

Since Flory's memorable paper, numerous attempts have been made to formulate the theoretical gel point. Because of insufficient knowledge about cyclization frequency in branching media, however, none of those were quantitatively successful. Thus, despite its immense importance in gelation physics, so far the gel point problem has not been in the main stream of polymer physics.

The gel point is defined as a point at which (i) an infinitely large molecule emerges, so that (ii) the average molecular weight diverges, and (iii) solution viscosity becomes infinite; from a physicochemical point of view, even more important is that (iv) above this point there appears elastic material insoluble in any solvents. According to experiments carried out along these lines, it has been pointed out by experimentalists [3] that considerable uncertainty arises in estimating the gel point. At present, we can evaluate the experimental errors arising from the classical technique on the basis of the experiments by Flory [1], Wile [4], and Gordon and Scantlebury [5]. Using exactly the same system comprising a mixture of pentaerythritol (R-A_4) and an equivalent quantity of adipic acid (R-B_2), they observed, independently, $D_c=0.606$ (Flory), 0.630 (Wile), and 0.623 (Gordon and Scantlebury); the deviation from the mean, 0.620, is less than 2.3%. Considering their experimental techniques, based on solution viscosity and solubility tests alone, the precision is rather striking.

In turn, with respect to the percolation model, highly technical methods have been devised to estimate the threshold: (i) the series expansion method based on the d'Alembert theorem [6], (ii) the $1/(2d-1)$ expansion [7], and (iii) Monte Carlo methods, together with rigorous solutions. Making full use of these methods, physicists have calculated, with high precision, threshold values for various lattices and dimensions. Early in 1961, Vyssotsky *et al.* [8] found that the threshold appears to be little affected by differences of lattice type, but depends only on dimension and coordination number z; they showed that the empirical correlation $zD_c \cong d/(d-1)$ holds to good approximation, although they were aware, from examples in two dimensions, that this is not rigorously true. The predicting power of this empirical correlation has been repeatedly confirmed, leading physicists to the notion of the dimensional invariance of the percolation threshold [9]. These findings spurred the search for a general formula that explains observed values over wider dimensions [10]. Meanwhile, van der Marck [11] could show some exceptional lattice types incommensurate with the known empirical formulas. He claimed that d and z are not sufficient to predict percolation thresholds, implying that an additional factor is needed to determine the threshold. Van der Marck investigated, with higher precision, extensive threshold values for various lattices; his results revealed that there are many examples with equal d and z, but with different thresholds [12]. He concluded that one cannot predict the percolation threshold on the basis of dimension and coordination number alone.

We have taken an independent approach to this problem, from a purely chemical point of view [13]. Our central idea is the unification of the tree model and cyclization; i.e., we note that the critical point D_c is separable into the two terms of intermolecular reaction and cyclization: $D_c=D(\text{inter})+D(\text{ring})$. In principle, one can thus theoretically estimate

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D_c by calculating $D(\text{inter})$ and $D(\text{ring})$ independently. This simple additive law is our starting point, from which analytic expressions for the critical point can be deduced.

In this paper we present some advances on the critical point problem recently developed in our laboratory. We begin with a minor generalization of the previous theory along with a correction. The theoretical result is then subjected to test by the experiments of Gordon and Scantlebury [5] and Muller *et al.* [3]. Second, we transpose our theory to the percolation problem. Taking account of the specificity of the lattice model [14], we derive a formula that estimates the site-bond threshold; the result is examined with the corresponding simulation experiments in three to six dimensions by Stauffer [15,16], and with bond percolation simulations over a wider range of dimension. Finally, our theory is scrutinized in light of the Lubensky-Isaacson excluded volume theory [17] and marginal dimensionality [9,18]. Although we push forward with our discussion taking the $R\text{-}A_f$ and the $R\text{-}A_g+R\text{-}B_{f-g}$ models as examples, the same argument applies to other models as well.

II. ESTIMATION OF CRITICAL POINT

A. Concept

Consider the $R\text{-}A_f$ branching reaction that allows progressive bond formation among A type functional units (FU's), where R represents a monomer unit and f the functionality. Given proper reaction conditions, an infinite molecule can appear at a definitely defined point called the gel point. In general, this point is mentioned in terms of the extent of reaction D_c. It is important to notice that D_c is separable into the following two terms:

$$D_c = D(\text{inter}) + D(\text{ring}). \tag{1}$$

$D(\text{inter})$ represents the extent of reaction of intermolecular reaction alone and $D(\text{ring})$ that of cyclization alone. Note that only two FU's (one bond) are wasted at every cyclization independently of ring size. Thus, it is convenient to define cyclic bonds as equivalent to excess bonds which, when broken, do not disconnect a polymer molecule. Let $[\Gamma]$ be the number concentration of total rings and $C(=M_0/V)$ the initial monomer number concentration of the system. One has the equality

$$D(\text{ring}) = \frac{2[\Gamma]}{fC} \quad (R\text{-}A_f).$$

Then let us proceed to the formulation of $D(\text{inter})$. Suppose an equilibrium branching process where some fraction p_R of all the FU's fM_0 is already occupied by cyclic bonds. The remaining FU's then form the equilibrium distribution $\{f_1M_1, f_2M_2, \ldots, f_iM_i, \ldots\}$, where M_i denotes the number of monomer units having f_i FU's. We write the gel point of this mixing system as

$$\frac{1}{\langle f\rangle - 1} \quad (R\text{-}A_f),$$

which is equal to the ratio of the number of FU's consumed by intermolecular reaction to the sum $\Sigma_i f_i M_i$ excluding the FU's wasted by cyclic bonds. $D(\text{inter})$ is the ratio as against all the FU's, fM_0, so, following the definition of the extent of reaction, therefore, it is necessary to multiply the factor

$$\frac{\Sigma_i f_i M_i}{fM_0} \equiv 1 - \frac{\text{Number of FU's wasted by cyclization}}{\text{Total number of FU's}}$$
$$= 1 - p_R,$$

where p_R is the probability of a FU being occupied by cyclic bonds, and is equivalent to $D(\text{ring})$. Thus $D(\text{inter})$ can be written in the form

$$D(\text{inter}) = (1-p_R)\left\{\frac{1}{\langle f\rangle - 1}\right\},$$

which leads Eq. (1) to the following analytic expression:

$$D_c = (1-p_R)\left\{\frac{1}{\langle f\rangle - 1}\right\} + \frac{2[\Gamma]}{fC} \quad (R\text{-}A_f). \tag{2}$$

In the same way, for the $R\text{-}A_g+R\text{-}B_{f-g}$ model where bond formation is permitted only between an A-type FU and a B-type FU, one has

$$D_c = (1-p_R)\frac{1}{\sqrt{(\langle g\rangle - 1)(\langle f-g\rangle - 1)}} + \frac{[\Gamma]}{gC_A}$$
$$(R\text{-}A_g + R\text{-}B_{f-g}) \tag{3}$$

for the equimolar case of the different functionalities $(g = f - g)$, where C_A represents the concentration for A-type monomer units. Hence the problem of estimating the gel point reduces to the problem of solving the above equalities. In our previous papers [13], the factor $(1-p_R)$ dropped out.

B. Solving basic equalities

To solve the basic equalities, we introduce the assumption that cyclic bonds distribute randomly over all monomer units: the *random distribution assumption of cyclic bonds*. By this, we mean that each FU has an equal chance to undergo cyclization.

Given the random distribution assumption, the mean functionality $\langle\cdots\rangle$ is simply given by the weight-average functionality defined by $\langle f\rangle = \Sigma_i f_i^2 M_i / \Sigma_i f_i M_i$, and the distribution of $\{M_i\}$ is binomial. Then it is an easy task to calculate the mean functionality $\langle\cdots\rangle$. Let $\overline{f_i^m}$ be the mth moment, and one has

$$\langle f\rangle = \frac{\overline{f_i^2}}{\overline{f_i}} = (f-1)(1-p_R) + 1.$$

Upon substituting this result into the foregoing equality (2), one gets

$$D_c = \frac{1}{f-1} + \frac{2[\Gamma]}{fC} \quad \text{for the } R\text{-}A_f \text{ model}, \tag{4}$$

and in the same way

$$D_c=\frac{1}{\sqrt{(g-1)(f-g-1)}}+\frac{[\Gamma]}{gC_A}$$

$$\text{for the } R\text{-}A_g+R\text{-}B_{f-g} \text{ model.} \tag{5}$$

These equations are exactly the independence model developed in our previous papers [13]. Now the problem of seeking analytic expressions for gel points has been reduced to finding the number concentration of cyclics $[\Gamma]$.

C. Real system

In this section we consider real branching reactions to which the $R\text{-}A_g+R\text{-}B_{f-g}$ model applies. Let M_0 be the number of A-type monomer units, N_0 that of B-type monomer units, and $(f-g)N_0/gM_0+\kappa$ the number ratio of B- to A-type FU's. For the purpose of comparing with experiments, it is often more convenient to introduce the concentration for total monomer units:

$$C=\frac{M_0+N_0}{V}=\left(\frac{f-g+g\kappa}{f-g}\right)C_A,$$

where $C_A=M_0/V$ as defined above. Now we begin with a stoichiometric system.

Stoichiometric system $(\kappa=1)$

To seek the general form of $[\Gamma]$, we introduce the mathematical technique of the high concentration expansion of the limiting solution $[\Gamma]_{C\to\infty}$. Prior to applying the expansion method, we note that (i) the ring distribution function

$$[\Gamma]_{C\to\infty}=\sum_{j=1}^{\infty}\varphi_j[(g-1)(f-g-1)D^2]^j/2j$$

$$(R\text{-}A_g+R\text{-}B_{f-g}) \tag{6}$$

is physically meaningful only if we are below the classical gel point D_{co}, and (ii) the classical gel point is realized only in the limit of $C\to\infty$ (φ_j denotes the relative frequency of cyclization of j chains to intermolecular reaction, defined by $\varphi_j=\mathcal{P}/v$, where $\mathcal{P}$ is the probability of one end of a chain entering into a small volume v around the other end). With these restrictions in mind, we set up the imaginary equality (Appendix A)

$$[\Gamma]=\sum_{j=1}^{\infty}\varphi_j[(g-1)(f-g-1)D_c^2]^j/2j, \tag{7}$$

the left hand side representing the general expression of the number concentration of rings and the right hand side remaining the limiting case of $C\to\infty$. Experiments have shown that sol-gel lines are monotonic and continuous functions of D_c and C. Thus, regarding Eq. (7) as a function $Z(D_c)$ of D_c, we expand the equation with respect to $D_c=D_{co}$, manipulation of which justifies the equality (7). Collecting the leading two terms in the resultant series,

$$[\Gamma]=Z(D_c)\cong Z(D_{co})+Z^{(1)}(D_{co})(D_c-D_{co}),$$

and substituting into Eq. (5), we recover the previous results: for $d\geqslant 3$ (Appendix A),

$$D_c=D_{co}\left\{\frac{1-[f/g(f-g)D_{co}]\sum_{j}^{\infty}(1-1/2j)\varphi_j\gamma}{1-[f/g(f-g)D_{co}]\sum_{j}^{\infty}\varphi_j\gamma}\right\}$$

$$(R\text{-}A_g+R\text{-}B_{f-g}) \tag{8}$$

where $\gamma=1/C$ and we have made use of the classical relation $(g-1)(f-g-1)D_{co}^2=1$.

Equation (8) is exact at high concentration. This is fortunate, because gelation is a phenomenon typical of concentrated systems.

Nonstoichiometric system $(\kappa\neq 1)$

Extension of Eq. (8) to a nonstoichiometric system ($\kappa\neq 1$) is achieved simply by the following transformation:

$$\frac{f}{g(f-g)D_{co}}\Rightarrow\frac{f-g+g\kappa}{g(f-g)D_{Aco}},$$

$$D_{co}=\frac{1}{\sqrt{(g-1)(f-g-1)}}\Rightarrow D_{Aco}=\frac{\kappa}{\sqrt{(g-1)(f-g-1)}}, \tag{8$'$}$$

where D_{Aco} is the corresponding quantity for A-type FU's.

Comparison to experiment

There are not many experimental determinations of gel points. Systematic work is even more scarce and can be found in only a few papers. Figure 1(a) shows some of such examples: the gelation in the pentaerythritol–adipic acid system studied by Flory (△), Wile (◇), and Gordon-Scantlebury (×: $\kappa=1.0$, 1.5, and 2.0). The theoretical lines (solid lines) of Eq. (8′) are superimposed on the observed points as functions of γ and κ. Consulting the observed values by Jones, Scales, and Semlyen in linear systems [19], and taking gem-substituent effects into consideration [13], the same φ_j values as evaluated in the preceding paper were employed.[1] The theoretical result is in good agreement with the experimental points for every region examined [Fig. 1(a)].

The theory is compared with another experiment with a different polymer mixture. Recent development of rheologi-

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[1] According to the Lubensky-Isaacson theory [17], branched molecules ($f\geqslant 3$) in concentrated solutions are expected to exert appreciable excluded volume effects in three dimensions. Martin, Sykes, and Hioe [20] showed that this may lead to reduction of the cyclization probability. As a result, the evaluation of φ_j based on linear systems ($f=2$) without excluded volume effects tends toward overestimation. This may appear to deprive the present examination of rigor. Now recall that we are dealing with perturbation from the hypothetical limit of $C\to\infty$ where all sorts of excluded volume effects are expected to vanish rigorously and φ_j takes Gaussian values in nature. There is a mathematical reason for using linear systems as a measure of φ_j.

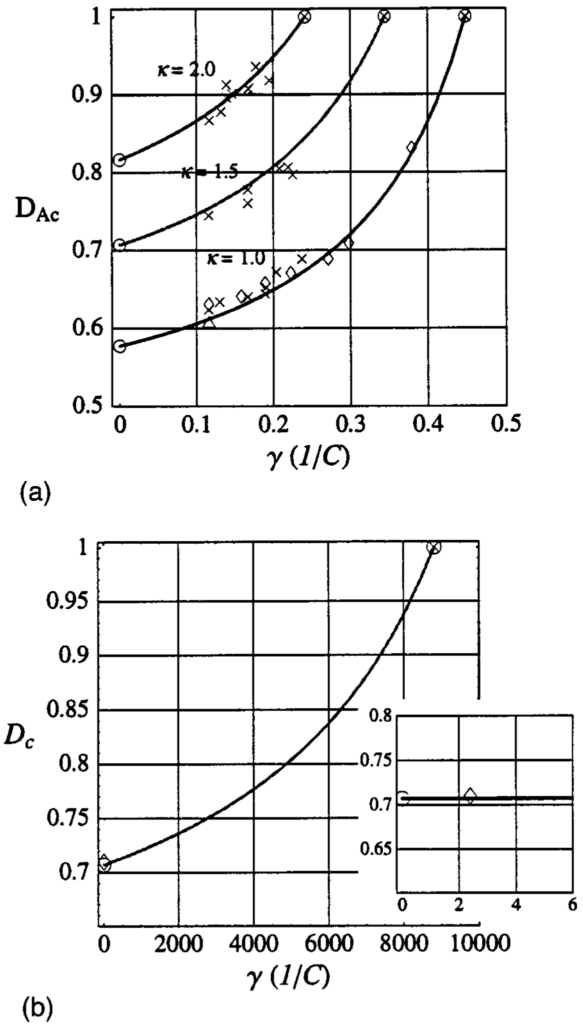

FIG. 1. D_c vs γ (l/mol) curve. (a) Comparison of Eq. (8) (solid line) and the experimental gel points of Flory (△, $\kappa=1$), Wire (◇, $\kappa=1$), and Gordon and Scantlebury (×, $\kappa=1$, 1.5, and 2.0). D_{Ac} is the extent of reaction of the A-type functional unit (OH). (○), classical gel points; (⊗), critical dilutions. (b) Comparison of Eq. (8) (solid line) and the experimental gel point of Muller *et al.* [3] (◇). The inset is a magnification of the same figure. ○, classical gel points; ⊗, critical dilutions.

cal characterization of polymer solutions has enabled experimentalists to identify the gel point. This new field was originated by Tung and Dynes [21], and later developed by Chambon and Winter [22]. The essence of this work is neatly disclosed in the short paper by Tung and Dynes. They showed that a crossover of the loss (G'') and storage (G') moduli occurs near the gel point. Muller *et al.* [3,23] applied this finding to the gelation of a mixture of polyethylene oxide ($g=2$, $\overline{M}_n\cong 1000$) and Desmodur RF ($f-g=3$, $M_n=465$) diluted by dioxane, and they observed $D_c=0.71$.

We now estimate the theoretical gel point in this system. The mean molecular mass of the mixture of interest is calculated to be $\frac{3}{5}\times 1000+\frac{2}{5}\times 465=786$ g/mol for the equimolar case ($\kappa=1$). Considering the dilution effect (33 wt %) by dioxane, it follows that $\gamma\approx 2.4$ l/mol. The polyethylene oxide molecule in question is composed of ≈ 70 skeletal bonds on average. With the Flory characteristic constant [24] $C_n=\langle r_n^2\rangle/n\ell^2\cong 4$ for polyethylene oxide in the Θ regime, one has $\Sigma_{j=1}^{\infty}\varphi_j/2j\cong 1.5\times 10^{-5}$ and $\Sigma_{j=1}^{\infty}\varphi_j\cong 6.0\times 10^{-5}$. As this extremely small relative cyclization frequency φ_j indicates, the production of rings is nearly negligible in the system under consideration. So, without any further calculation, one gets the classical value $D_c=0.707$, in agreement with the observation of Muller *et al.*, $D_c=0.71$. For comparison, in Fig. 1(b) is plotted the theoretical line (solid line) based on Eq. (8) as a function of γ together with the experimental point (◇) of Muller *et al.*

As we saw in Fig. 1, for every example examined, agreement between the theory and the experiments is very satisfactory, in support of the mathematical soundness of the present theory. Equations (8) and (8′) make one prediction, the existence of the critical dilution

$$\gamma_c=\frac{1-D_{Aco}}{(f-g+g\kappa)/[g(f-g)]\sum_{j=1}^{\infty}(1/D_{Aco}-1+1/2j)\varphi_j} \tag{9}$$

beyond which gelation cannot occur. According to Eq. (9), the larger κ, the more γ_c should shift downward, consistent with the observations [Fig. 1(a)]. For the ideal tree model, one has $\varphi_j\rightarrow 0$, so that $\gamma_c\rightarrow\infty$, and the critical dilution vanishes. In real gelation such vanishing of γ_c never occurs because of the presence of a finite cyclization probability. The critical dilution is a general theorem for real branching reactions [25].

D. Percolation model

To apply the present theory to the percolation model, it is essential to take into consideration the specifics of the percolation model [13(c),14]. Let p_s be the fraction of sites to be occupied by monomer units. The total possible bond number is given by $\frac{1}{2}fM_0p_s^2$. The fundamental equality is then modified as follows:

$$D_c=(1-p_R)\left\{\frac{1}{\langle f\rangle-1}\right\}+\frac{2[\Gamma]}{fCp_s^2}, \tag{10}$$

where C is the site concentration. The mean functionality $\langle\cdots\rangle$ is an unknown quantity, but, if a random distribution of cyclic bonds is assumed, it simplifies again to the weight-averaged quantity

$$\langle f\rangle=\frac{\overline{f_i^2}}{\overline{f_i}}=(f-1)p_s(1-p_R)+1,$$

and one has

$$D_c=\frac{1}{(f-1)p_s}+\frac{2[\Gamma]}{fCp_s^2}. \tag{11}$$

Now the only task we should do is to derive a ring distribution function on lattices. Recall that, whereas real systems converge on the tree diagram with no rings as $C\rightarrow\infty$, it is as $d\rightarrow\infty$ that the percolation model converges on the same diagram (Bethe lattice). Phenomenologically [26], high dimensions in the percolation model correspond to high concentra-

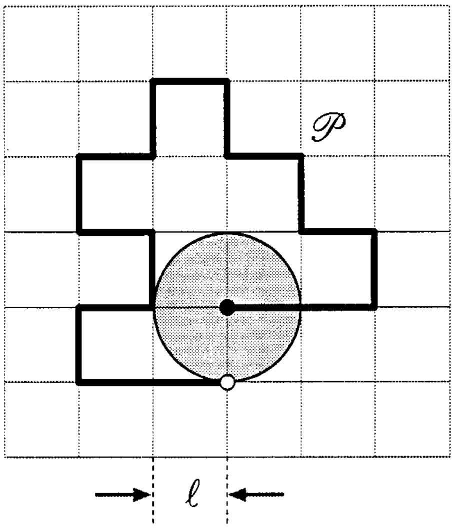

FIG. 2. Schematic representation of cyclization probability $\mathcal{P}$.

tions in real systems. We make full use of this property to derive ring distribution functions on lattices. Relegating the lengthy derivation to Appendix B, we show the result only:

$$[\Gamma]_{d\to\infty}\cong C p_s\sum_{j}^{\infty}\mathcal{P}[(f-1)p_s D]^j/2j \quad (\text{site-bond model}) \tag{12}$$

for the limiting case of $d\to\infty$, where $\mathcal{P}$ is the cyclization probability that one end of a chain enters into the small volume v within the radius of a bond length ℓ around the other end (see Fig. 2). Our previous work is the special case of $p_s=1$.

The corresponding expression for $C\to\infty$ for the same R-A_f model of real systems is of the form

$$[\Gamma]_{C\to\infty}=\sum_{j=1}^{\infty}\varphi_j[(f-1)D]^j/2j$$

$$(C\to\infty \ \text{ for real systems}). \tag{6'}$$

Comparing Eqs. (12) and (6′), it turns out that there are substantial differences in cyclic production between the percolation model and real systems. All these arise from the fact that the percolation clusters are fixed on lattices (see Appendix B and Ref. [13(c)]) so that the intermolecular reaction rate (B1) follows the first order of C and has no dimension-dependent term.

Percolation threshold

As the critical point is approached, the total chances of cyclization $\Sigma_j\phi_j$ should diverge (see Appendix B), so that the site-bond threshold is given by

$$D_{co}=\frac{1}{(f-1)p_s} \quad \text{for } d\to\infty (\text{site-bond problem}). \tag{13}$$

Now we derive a more general formula for the percolation threshold. Simulation experiments tell us that the site-bond percolation line is a continuous function of D_c (or d). By analogy with the discussion in real systems, we now confine ourselves to high dimensions so that Eq. (12) is a good approximation of $[\Gamma]$. Then we regard Eq. (12) as a function of D_c and expand with respect to $D_c=D_{co}$ $(1/d=0)$. With the help of Eq. (13), and collecting the leading two terms, one gets

$$[\Gamma]\cong C p_s\left(\sum_{j}^{\infty}\mathcal{P}/2j+(f-1)p_s\sum_{j}^{\infty}\mathcal{P}/2(D_c-D_{co})\right).$$

Substituting this series into Eq. (11), and with some rearrangement, one obtains a general formula for the bond percolation threshold:[2]

$$D_c=\frac{1}{(f-1)p_s}\left\{\frac{1-[(f-1)/f]\sum_{j}^{\infty}(1-1/j)\mathcal{P}}{1-[(f-1)/f]\sum_{j}^{\infty}\mathcal{P}}\right\}$$

$$(\text{site-bond problem}) \tag{14}$$

for $d\geqslant 3$ (see Appendix A).

It is clear that $\mathcal{P}\to 0$ as $d\to\infty$, and one recovers Eq. (13) in the asymptotic limit. By virtue of the $1/d=0$ expansion of $[\Gamma]$, Eq. (14) is exact in high dimensions. Equation (14) suggests a simple relation between D_c and p_s,

$$D_c\propto p_s^{-1},$$

showing that the bond percolation threshold changes linearly with the reciprocal of the fraction of sites, in accordance with the observations by Agrawal *et al.* [16] and by Stauffer [15].

Now the present result is subjected to test by simulation experiments using the percolation theory. For this purpose, Eq. (14) is computed assuming Gaussian behavior of $\mathcal{P}$,

$$\mathcal{P}=\int_0^l S_d P(r)dr,$$

together with the average end-to-end distance of j chains without excluded volume effects,

$$\langle r_j^2\rangle=\frac{f}{f-2}n_j\ell^2-\frac{2(f-1)}{(f-2)^2}\ell^2 \quad (\text{hypercubic lattices}),$$

where S_d is the surface area of a d-dimensional sphere, $P(r)$ the end-to-end distance distribution, ℓ the size of a unit cell (bond length), and n_j the number of bonds constituting a j chain. Let the j chain be comprised of j sites; then one has $n_j=j-1$. Only even-numbered rings can occur for hypercubic lattices. One has therefore $n_j=3,5,7,\ldots,2k+1,\ldots,$ for

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[2] One may wish to use the exact equation (B3) in place of Eq. (B3′), expressing the threshold equation as

$$D_c=\frac{1}{(f-1)p_s}\left\{\frac{1-\Sigma_j^{\infty}(1-1/j)\mathcal{P}}{1-\Sigma_j^{\infty}\mathcal{P}}\right\}. \tag{14'}$$

Equation (14′) slightly improves agreement with the simulation values [10] compared with Eq. (14).

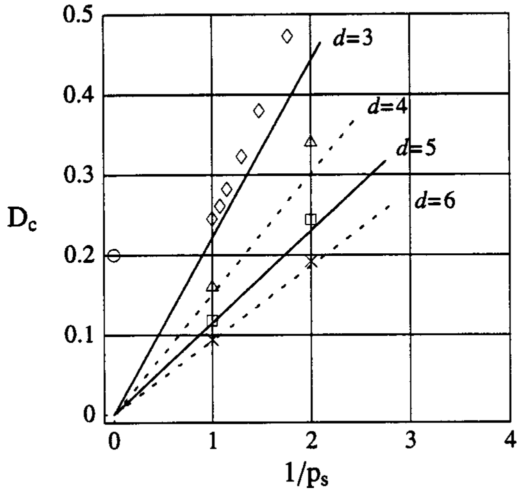

FIG. 3. Comparison of Eq. (14) (solid lines for $d=3$ and 5; broken lines for $d=4$ and 6) and simulation points (◇, $d=3$; △, $d=4$; □, $d=5$; ×, $d=6$) by Stauffer [15]. The open circle (○) is the corresponding classical threshold $1/(2d-1)$; i.e., 1/5 for $d=3$.

$j=4,6,8,\ldots$, respectively. With the substitution $\langle r_j^2\rangle \doteq \nu\ell^2$ along with $\nu=[f/(f-2)]n_j-2(f-1)/(f-2)^2$, $\mathcal{P}$ reduces to

$$\mathcal{P}=1-\frac{\Gamma(d/2,d/2\nu)}{\Gamma(d/2)},$$

where $\Gamma(d/2,d/2\nu)$ is an incomplete gamma function defined by $\Gamma(a,z)=\int_z^\infty t^{a-1}e^{-t}dt$.

Examples for $d=3-6$ computed according to the above equations are shown in Fig. 3 against the reciprocal of p_s, together with simulation results by Stauffer (◇, $d=3$; △, $d=4$; □, $d=5$;×,$d=6$) [15]. The theoretical lines (solid lines for $d=3$ and 5; broken lines for $d=4$ and 6) are in good conformity with the observed points by Stauffer. To date, within our knowledge, the corresponding site-bond diagrams in higher dimensions have not been investigated, so we cannot test Eq. (14) in these regimes at present. However, there is a reason to believe that better agreement between the theory and simulation experiments will be observed for $d\geqslant 8$. We show below the grounds for this conjecture through comparison with pure bond percolation simulations ($p_s=1$) and in light of the Lubensky-Isaacson excluded volume theory.

Comparison with pure bond percolation simulations ($p_s=1$)

Although the outline of the examination has been reported in our previous paper, here we scrutinize the result in more detail. In Fig. 4(a) the theoretical line (heavy line) was computed again assuming Gaussian behavior of $\mathcal{P}$, and agrees remarkably well with the simulation points (◇) in higher dimensions, but fails in lower dimensions. The discrepancy amounts to ≅ 10% in three dimensions, 6% in four dimensions, 3% in five dimensions, and so forth, rapidly decreasing with increasing dimension. To show up the discrepancy, the same data are replotted in Fig. 4(b) in terms of scaled critical points $(D_c-D_{co})/D_{co}$. Upon inspecting the magnified curves in Fig. 4(b), we meet with the prominent feature of modern statistical physics, the marginal dimensionality, where the theoretical line abruptly merges with the simulation line exactly at $d=8$, testifying that the shift from an excluded volume to an ideal cluster is really a phase transition and not an asymptotic phenomenon, consistent with the Lubensky-Isaacson prediction [17].

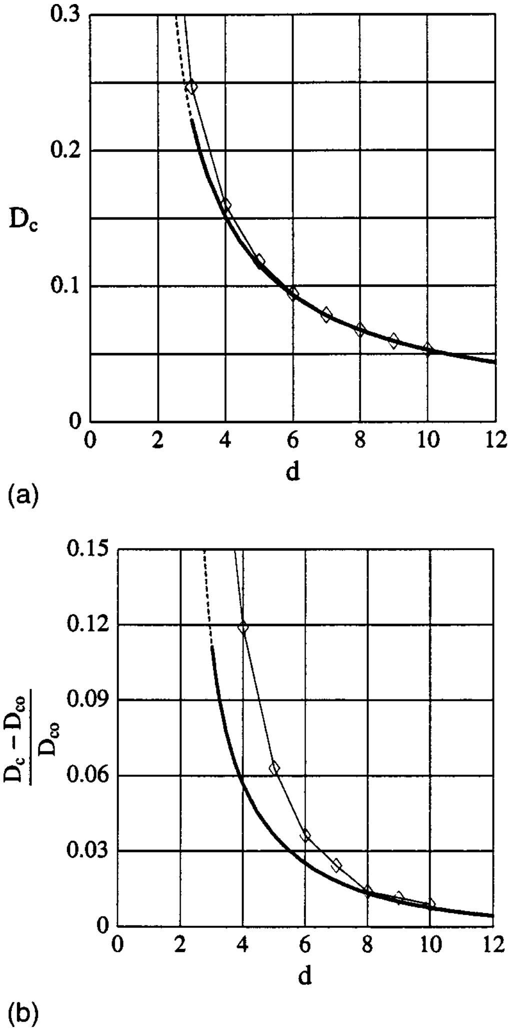

FIG. 4. Comparison of Eq. (14) (heavy line, $p_s=1$) and the bond percolation thresholds (a) ◇ and (b) ◇ [10].

III. *d* DEPENDENCE OF CYCLIZATION

In our previous papers [13] an unexpected feature of dimensionality was disclosed for real branching reactions. Here we shall present a more general proof.

Suppose chemical reactions in real systems, and consider a transition per unit bond formation from $i-1$ bonds to i bonds. The transition must be either an intermolecular reaction or cyclization. Let ν_{R_j} be the rate of cyclization of j chains and ν_L the rate of intermolecular reaction. The cyclization probability of j chains during this small interval $\delta i(=1)$ can be written as $p\{\text{ring}\,j\}=(\nu_{R_j}/\nu_L)/(1+\Sigma_j\nu_{R_j}/\nu_L)$, and the total probability is

$$p\{\text{ring}\}=\sum_{j=1}^{\infty} p\{\text{ring}\ \ j\}=\frac{\displaystyle\sum_j \nu_{R_j}/\nu_L}{1+\displaystyle\sum_j \nu_{R_j}/\nu_L}. \tag{15}$$

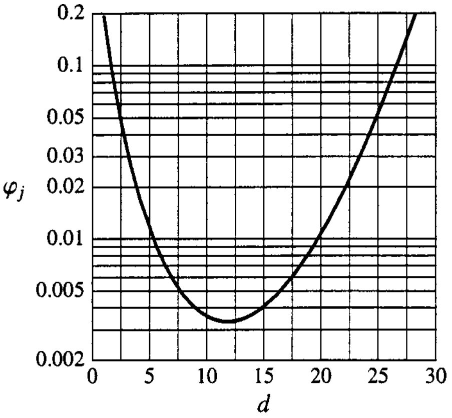

FIG. 5. Dimensionality dependence of the relative cyclization frequency φ_j [molecules/length^d]. Calculated for a Gaussian chain.

Experiments have shown that the intermolecular reaction rate follows the second order of the monomer concentration and cyclization the first order. We can thus formulate

$$p\{\text{ring}\}=\frac{\sum_j \mathcal{B}_j\varphi_j/C}{1+\sum_j \mathcal{B}_j\varphi_j/C}\quad \text{for real systems} \tag{16}$$

with $\mathcal{B}_j$ being a function of D, but independent of the dimension d, and φ_j the relative cyclization frequency as defined earlier. Now suppose a hypothetical dense solution where the Gaussian behavior applies to branched molecules. According to the definition, φ_j can be written as

$$\varphi_j=\frac{d}{l^d}\int_0^l r^{d-1}\left(\frac{d}{2\pi\langle r_j^2\rangle}\right)^{d/2}\exp\left(-\frac{d}{2\langle r_j^2\rangle}r^2\right)dr,$$

which reduces to

$$\varphi_j=\frac{d}{2\pi^{d/2}l^d}\left[\Gamma\left(\frac{d}{2}\right)-\Gamma\left(\frac{d}{2},\frac{d}{2\nu}\right)\right].$$

It is easy to show that φ_j first decreases with increasing d to attain a minimum point, then increases indefinitely as $d\to\infty$ (Fig. 5). Broadly speaking, φ_j varies as $\sim d^{d/2}$, but C as $\sim\text{const}^d$, which leads Eq. (16) to $p\{\text{ring}\}\to 1$ and $p\{\text{inter}\}=1-p\{\text{ring}\}\to 0$, as $d\to\infty$. Hence, at sufficiently high dimensions all the products should become cyclic in origin for branching reactions in real systems.

An important feature is that the dimensionality is closely connected with cyclization. This feature does not appear to have been fully recognized up to the present. The reason simply comes from the fact that the occurrence of rings, together with excluded volume effects, has often been ignored for the sake of mathematical simplicity in the theory of gelation. It is therefore not surprising that the unexpected dimension dependence of real systems has not been realized so far.

IV. DISCUSSION

The examinations in Sec. II support the mathematical soundness of the present theory, which in turn means that the shift of D_c is caused by the waste of FU's due to cyclization throughout sol reactions up to the gel point, in accordance with the conjecture of most polymer chemists [1,27–29]. In consequence, we expect that, given the general solution for $[\Gamma]$, we would be able to estimate more accurately the critical point over all concentrations. Unfortunately, however, there does not seem to be a hope of a general solution. To date, only the following mathematical representation written in terms of the transition probability is known:

$$[\Gamma]=\frac{1}{2}fC\sum_{j=1}^{\infty}\int_D p\{\text{ring } j\}dD. \quad (R-A_f) \tag{17}$$

$p\{\text{ring}\, j\}$ is given explicitly in Eq. (15) as the ratio of cyclization rate to total reaction rate. However, so far a full description of the rate equations has not been found. Even worse is that the above integral does not appear soluble even for the most elementary rate equations. Equation (17) has been solved exactly only for the limiting cases of $C\to\infty$ in real systems and $d\to\infty$ in the percolation model, to yield Eqs. (6) and (12), respectively [13]. These circumstances led us to the technique of the perturbation expansions mentioned in Sec. II. As a result, whereas simple analytic formulas of the critical points were gained, their validity was in return restricted to the neighborhood of the asymptotic regimes. With this background in mind, we review the foregoing results.

The only unknown quantity in the present theory is the relative cyclization frequency φ_j, which is correlated with the equilibrium constant by the relation $\varphi_j/2j=K_j$. For shorter chains, K_j is known to vary widely according to polymer species. Calculating φ_j from first principles is therefore not yet on a firm foundation. For this reason, whereas we have assumed the known power law $\varphi_j\propto j^{-3/2}$ for long chains, we have made use of the experimental values for the corresponding linear molecules for shorter chains. This is the ideal chain approximation. It is noteworthy that Eq. (8) then reproduces remarkably well the observed gel points in entire regions (Fig. 1). The discrepancy is less than a few percent, comparable to the experimental errors mentioned in Sec. I. This suggests that the high concentration expansion in Sec. II has a sound mathematical basis and that a three-dimensional branched molecule in the concentrated sol phase is not far from a Gaussian molecule realizable in the limit of $C\to\infty$ or above the critical dimension.

In contrast to the situation in real systems, a distinct, large deviation ($\approx$10%) was found in comparison with the three-dimensional percolation model. The discrepancy decreases with increasing dimension, and disappears suddenly in eight dimensions (Fig. 4). Equation (14) is thus exact for $d\geqslant 8$, much larger than the case in real systems.

The difference between real systems and the percolation model is comprehensible in light of the excluded volume theory [17]: According to the Lubensky-Isaacson theory, a branched molecule in a monodispersed melt should have the critical dimension $d_c=4$, above which Gaussian behavior applies, whereas a branched molecule in the dilution limit has $d_c=8$. The latter critical dimension ($d_c=8$) is exactly equal to the value predicted for a percolation cluster in the sol phase [15,30]. For the present case, the critical dimension of $d_c=8$ applies, since D_c depends on the frequency of cyclization in the sol phase up to the gel point. In the percolation model, our world ($d=3$) is farther away from the critical dimension ($d_c=8$) than is the case ($d_c<8$) of real branching reactions. This is the reason for the remarkable agreement between the theory and experiments in real gelations ([13(a)]; Fig. 1) and the large deviation in the percolation model in low dimensions (Figs. 3 and 4).

Finally, we would like to mention that the present theory is in harmony with recent work based on physical approaches [10–12,31]. Now we restrict our arguments to the critical dimension ($d_c = 8$) or higher. Then the threshold, Eq. (14), is determinable by two parameters, f (q in the notation of [10]) and d, in accordance with the Galam and Mauger work (note that n_j in $\mathcal{P}$ disappears by summation). We see, on the other hand, that Eq. (14) includes a hidden variable, the cyclization probability $\mathcal{P} = 1 - \Gamma(d/2, d/2\nu)/\Gamma(d/2)$ that varies widely depending on lattice type, in accordance with the van der Marck conjecture [11].

V. CONCLUDING REMARKS

(1) The analytic expression (8) for the gel point was reexamined with gelation experiments on nonstoichiometric systems by Gordon and Scantlebury [5], showing excellent agreement between theory and experiment in every region examined, which has again confirmed the mathematical soundness of the present theory.

(2) We have presented Eq. (14) which predicts the bond percolation threshold. The theory is exact above eight dimensions, suggesting the critical dimension $d_c = 8$ for sol clusters on lattices, consistent with the Lubensky-Isaacson excluded volume theory.

APPENDIX A: EXPANSION METHOD

Differentiate Eq. (7) with respect to $D_c = D_{co}$ to yield

$$Z^{(n)}|_{D_c = D_{co}} = \frac{1}{D_{co}^n} \sum_j^{\infty} \varphi_j \frac{(2j-1)!}{(2j-n)!}. \tag{A1}$$

Now suppose a special situation where a branched molecule is Gaussian so that $\varphi_j \propto j^{-d/2}$. Then it is obvious that the right hand side of Eq. (A1) diverges for $n \geqslant 1$, if $d \leqslant 2$. Thus, the expansion method [and therefore Eqs. (8) and (14) in the text] applies for $d \geqslant 3$.

APPENDIX B: CYCLIC DISTRIBUTION IN SITE-BOND PERCOLATION

Consider a lattice of sufficiently large size and high dimension $\mathcal{L}^d$($\mathcal{L}$ and $d \to \infty$) so that clusters can be ideal. Let the probability of a given site being a monomer molecule be p_s. The intermolecular reaction rate ν_L can be equated to the product of the probability of a given functional unit on a cluster entering into a small volume v with the radius of a bond length ℓ around a FU on the other cluster, and the total number of all pairs (we put ℓ as the size of the unit cell). For the present case, molecules are fixed on lattices, and each FU has a single chance to react, so that it can react with the nearest neighbor alone, which is always unreacted because of the lattice specificity. Thus, the intermolecular reaction rate is simply

$$\nu_L = \tfrac{1}{2} I' f M_0 p_s^2 (1-D) \times 1, \tag{B1}$$

where I' is a coefficient.

Then we proceed to calculation of the cyclization rate. The cyclization rate ν_{R_j} of j chains is in proportion to the cyclization probability $\mathcal{P}$ multiplied by the total number ϕ_j of chances of cyclization:

$$\nu_{R_j} \propto \mathcal{P} \times \phi_j .$$

$\mathcal{P}$ is the quantity defined in the text (Sec. II D).

The total number ϕ_j of chances of cyclization for j chains can be estimated as follows. Suppose an m tree that has l reacted FU's, m unreacted FU's, and n dead ends in the first generation. Then, $l + m + n = f$, which follows the trinomial distribution [32]:

$$\begin{aligned}&[p_s D + p_s(1-D) + 1 - p_s]^f \\ &\quad = \sum_{l=0}^{f} \sum_{m=0}^{f-l} \frac{f!}{l!\,m!\,n!} (p_s D)^l [p_s(1-D)]^m (1-p_s)^n.\end{aligned}$$

Let $N(A)_j$ be the number of FU's in the jth generation. It is clear that

$$N(A)_1 = l.$$

Each individual FU creates $(f-1)p_s$ new FU's on average. So the number of FU's in the second generation is

$$N(A)_2 = l(f-1)p_s$$

and

$$\begin{aligned}N(A)_j &= (f-1)p_s D N(A)_{j-1} \\ &= [(f-1)p_s D]^{j-2} N(A)_2 .\end{aligned}$$

The total number of chances of cyclization for j chains is calculated via

$$\begin{aligned}\phi_j = {}& \frac{1}{2} M_0 p_s \sum_{l=0}^{f} \sum_{m=0}^{f-1} m \frac{f!}{l!\,m!\,n!} \\ & \times (p_s D)^l [p_s(1-D)]^m (1-p_s)^n N(A)_j (1-D),\end{aligned}$$

which results in

$$\phi_j = \tfrac{1}{2} M_0 p_s^3 f(f-1)(1-D)^2 [(f-1)p_s D]^{j-1}.$$

Then we turn attention to the self-avoiding walk for a lattice chain. After j steps, let one end enter into the volume v around the other end; more exactly, on any one of the neighboring f sites. Because of excluded volume effects, immediate reversals are forbidden for the end; so there exist $(f-1)p_s$ possible paths (FU's) for another step. The probability of these paths being vacant (unreacted) is $1-D$. The total number of paths available for the end is therefore $(f-1)p_s(1-D)$. Of these only one path can lead to the other end. Thus the probability of the two ends closing in a ring can be written

$$P_{\text{cy}} = \frac{\mathcal{P}}{(f-1)p_s(1-D)},$$

whence the cyclization rate can be formulated as

$$\nu_{R_j}=I'\left(\frac{\mathcal{P}}{(f-1)p_s(1-D)}\right)\{\tfrac{1}{2}M_0p_s^3f(f-1)\times(1-D)^2[(f-1)p_sD]^{j-1}\}. \tag{B2}$$

The relative rate therefore becomes

$$\frac{\nu_{R_j}}{\nu_L}=\mathcal{P}[(f-1)p_sD]^{j-1}.$$

Recall that $\mathcal{P}$ is a monotonically decreasing function of d, so that the transition probability, Eq. (15), reduces to

$$p\{\text{ring } j\}\to\nu_{R_j}/\nu_L \quad \text{for } d\to\infty.$$

The transition probability is equivalent to the number fraction of rings, and one has via $\delta i=\frac{1}{2}fM_0p_s^2\delta D$

$$\delta[\Gamma]_{d\to\infty}=\delta\sum_j^\infty N_{R_j}/V=\frac{fp_s}{2(f-1)}\times C\sum_j^\infty \mathcal{P}[(f-1)p_s]^jD^{j-1}\delta D.$$

Now integrate the above differential with respect to D, and one arrives at the asymptotic solution of the ring distribution function for the site-bond problem:

$$[\Gamma]_{d\to\infty}=\frac{f}{(f-1)}Cp_s\sum_j^\infty \mathcal{P}[(f-1)p_sD]^j/2j. \tag{B3}$$

Since f is an increasing function of d, the prefactor may be approximated as

$$\frac{f}{(f-1)}\cong 1 \quad \text{for large } f.$$

Then Eq. (B3) reduces to

$$[\Gamma]_{d\to\infty}\cong Cp_s\sum_j^\infty \mathcal{P}[(f-1)p_sD]^j/2j. \tag{B3$'$}$$

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