Brief Reports

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Scaling theory of polydispersity, an infinite chain, and the Flory-Huggins approximation

P. D. Gujrati

*Department of Physics, Department of Polymer Science and Institute of Polymer Science,
University of Akron, Akron, Ohio 44325*
(Received 5 January 1989)

We develop a scaling theory of polydispersity in an equilibrium ensemble of polymers. The theory predicts the existence of an "infinite" chain. The radius of gyration exponent for "finite" chains in the "semidilute" regime is $\frac{43}{76} > 0.5$ in two dimensions. Thus, this exponent cannot be $\frac{1}{2}$ in general. We also show that the Flory-Huggins approximation is qualitatively incorrect.

The Flory-Huggins (FH) approximation[1] has been extremely useful in polymer physics,[2-4] especially in determining the Flory exponent $v = v_F$ defined by $R \sim N^v$, where R is the radius of gyration and N is the average polymerization index in a dilute solution of chains in a good solvent. It has also been argued theoretically using this approximation that the chains must be Gaussian in the amorphous state[2] and the interpretation of some experiments[5] seems to support this. This result has been used to suggest[3] that $R^2 \sim N$ even in a semidilute solution. This is quite remarkable in view of the simplistic nature of the FH approximation.

Oono[4] has argued that $v = \frac{1}{2}$ for a test chain of length N which is much bigger than other chains, whereas others[3,6] have argued for $v = v_F$. But, it is evident that if N is comparable to the volume N_0 of the system, the chain must be compact,[7,8] regardless of whether other chains are present or not. Therefore, neither of the above results[3,4,6] could be valid for $N \sim N_0$: They are valid for "finite" chains ($N/N_0 \to 0$) in the thermodynamic limit ($N_0 \to \infty$). It should be noted that one necessarily has an "infinite" chain ($N/N_0 > 0$ as $N_0 \to \infty$) in the ordered phase[8] of a *single* chain system. This chain is then compact: $v = v_c = 1/d$ where d is the dimension of space. However, when one considers an ensemble of many chains, it is by no means obvious that there must be "infinite" chains in the ordered phase. Indeed, it has been suggested[9] that there are no "infinite" chains in a particular model of equilibrium polymerization (to be discussed below) and, therefore, one would expect the above results[3,4,6] to be applicable.

Our aim in the present Brief Report is to examine this model of equilibrium polymerization. We will construct, for the first time, a scaling theory that will describe polydispersity that exists in our model. We will then compare its predictions with those obtained by the use of the

FH approximation. We will argue that the FH approximation is misleading. In particular, our scaling theory predicts the existence of an infinite chain, which is compact, along with finite chains. This contradicts previous claims.[9] The existence of such a chain, which appears when $N > N^*$ is *not* predicted by the FH approximation. When $N < N^*$, the chains are far apart and remain swollen.[7] However, we will present evidence that when $N > N^*$, the chains, even though they overlap tremendously, are no longer as swollen. Here, N^* is some critical length that will be determined below. It is the regime $N > N^*$ that is of interest to us here, because of its novel behavior. In this instance, finite chains have a radius $R \sim N^{\tilde{v}}$ with $\tilde{v}$, in general, different from v. Furthermore, they form a "semidilute" solution. We show that in two dimensions, $\tilde{v} = \frac{43}{76} \approx 0.566 > 0.5$. This suggests that $\tilde{v}$ is probably not 0.5 in $d = 3$ as is customarily believed. This is a new and remarkable result, and should have profound impact on our conceptual thinking about the nature of polymer melt, rubber, glassy polymers, etc. We also confirm a recent prediction by Saleur[10] in $d = 2$. An expanded version of the work will be reported elsewhere. However, all the necessary details have been given here.

We wish to study the following model of the polymer system which is defined by the partition function on a lattice

$$\hat{Z} = \sum_{p,l} \kappa^l \eta^{2p} U_{p,l},\qquad(1)$$

where η is the activity for creating a chain end, κ is the activity for creating a chain bond or link, and $U_{p,l}$ is the number of distinct configurations of p different chains of total length l on the lattice of coordination number q and total number of sites N_0.[11] We only allow chains having at least one link (two monomers) in Eq. (1). The model is closely related to the $n = 0$ limit of the n-component mag-

netic system. This model is particularly suited for our purpose as it has been studied extensively not only using FH approximation,[12] but also either directly or using the $n = 0$ limit.[7,9,10,13,14] Here we will go one step further and develop a scaling theory for the distribution of chains of various lengths. We consider this to be the most fundamental quantity to be investigated. Therefore, we can check the validity of the FH approximation by comparing its predictions with those obtained from our scaling theory.

Let ϕ_p, ϕ_l, and $\phi_m = \phi_l + \phi_p$ denote the densities of polymer chains, polymer links, and polymer monomers, respectively. The following results for Eq. (1) are well known:[13] The polymer density $\phi_p \rightarrow 0$ as $\eta \rightarrow 0$ for all values of ϕ_l. For $\eta = 0$, the system undergoes a phase transition at $\kappa = \kappa_c$, with ϕ_l zero below κ_c and nonzero above κ_c. For $\eta > 0$, $\phi_p > 0$. The average polymerization index N is given by ϕ_l/ϕ_p.

From the $n = 0$ analogy, we had argued for a phase transition in the model described by Eq. (1) across a certain curve AC in the κ-η plane (see Fig. 1 in Ref. 14). As a matter of fact, it has been shown[15] that a phase transition does exist at finite fields at low temperatures in the discrete n-vector model for $n < 1$. Since the magnetic system ($n = 0$) is identical to our model (1) above AC, a phase transition must also occur in this model (1) across AC. Such a transition from a swollen phase ($\nu = \nu_F$) above to a collapsed phase below AC was conjectured in a recent study,[7] by using scaling arguments. The study of the polydispersity in the present work will clarify the nature and the physical significance of this phase transition in the polymer context.

According to the FH approximation,[1,2,12] the number $U_p(\{N_s\})$ of distinct configurations of p chains, with N_s chains of length $s = 1, 2, 3, \ldots$, is given by

$$U_p(\{N_s\}) = \left[\frac{q}{2(q-1)}\right]^p \left[\frac{q-1}{N_0}\right]^l \frac{N_0!}{(N_0-m)!} \left[\prod_s N_s!\right]^{-1},$$

(2)

where $p = \sum N_s$, $l = \sum sN_s$, and $m = l + p$. Inserting (2) into (1), we find that the most probable distribution of the density $n_s = N_s/N_0$ ($N_0 \rightarrow \infty$) is given by

$$n_s = (\eta^2/2)\phi_0(\kappa\phi_0)^s \equiv (\eta^2/2)\exp[-s\sigma(\kappa,\eta)],$$

(3)

where $\phi_0 = 1 - \phi_m$ is the density of sites uncovered by polymers, and where we have redefined $\eta^2 q/(q-1)$ and $\kappa(q-1)$ by η^2 and κ, respectively. The definition of σ is evident from Eq. (3). Furthermore, $\phi = \kappa\phi_0 \leq 1$ in order that n_s is bounded. Using $\phi_0 = 1 - \sum n_s - \sum sn_s$, we find that ϕ is determined by

$$\kappa = \phi + (\eta^2/2)(2-\phi)\phi^2/(1-\phi)^2.$$

(4)

It is easily seen that as $\eta \rightarrow 0$, $\phi = \kappa$ for $\kappa < 1$ and $\phi = 1$ for $\kappa > 1$; $\kappa = \kappa_c = 1$ and $\eta = 0$ is the critical point as discussed above.

For $\kappa \lesssim \kappa_c$ and $\eta \rightarrow 0$, $\phi \sim \kappa \equiv e^{-\tau}$, $\tau = \kappa_c - \kappa$, and σ introduced in Eq. (3) is given by $\sigma = \tau$. Therefore, for any $\eta \neq 0$, the polymer phase below κ_c is highly *polydisperse*. However, as $\eta \rightarrow 0$, $\phi_l \rightarrow 0$ and there are no polymers left in the system. For $\kappa > \kappa_c$ and $\eta \rightarrow 0$, $\phi \sim 1$. From Eq.

(4), we find that $\phi \sim 1 - \eta/(2|\tau|)^{1/2}$. Therefore, $\sigma = \eta/(2|\tau|)^{1/2}$, and $\phi_p \sim (\eta/2\kappa)(2|\tau|)^{1/2}$ and $\phi_l \sim |\tau|/\kappa$. As $\eta \rightarrow 0$, n_s and ϕ_p both vanish, yet $\phi_l \neq 0$. Therefore, there are polymers left in the system ($\eta \rightarrow 0$) provided $\kappa > \kappa_c$. This phase is again polydisperse. At $\kappa = \kappa_c$, $\phi \sim 1 - (\eta^2/2)^{1/3}$ and $\sigma = (\eta^2/2)^{1/3}$.

The prediction of a polydisperse phase above κ_c as $\eta \rightarrow 0$ in the FH approximation is in disagreement with the prediction of a collapsed phase[14] using the $n = 0$ magnetic analogy and other calculations based on finite-size scaling ideas.[7,16] We will now show that the above polydispersity in the FH approximation above κ_c is qualitatively *incorrect*. To this end, we develop a scaling theory of polydispersity that exists in our model. This is a first attempt of its kind for the polymer system. Our analysis will depend heavily on the results already known in the context of percolation clusters.[17]

Our proposed scaling form of polydispersity in Eq. (1) is an extension of n_s given in Eq. (3) and is based on the Fisher droplet model:[18]

$$n_s = (\eta^2/2)s^{\gamma-1}\exp[-s\eta^{1/\Delta}\lambda(\tau/\eta^{1/\Delta})].$$

(5)

This form is dictated by the well-established result $W_s = \mu^s s^{\gamma-1}$ for the number of self-avoiding walks of length s; here μ is the effective coordination number of the lattice and γ is the "magnetic-susceptibility" exponent. In the dilute limit ($\kappa < \kappa_c$), the chains are far apart and the above form of W_s is valid. Therefore, with the weights in Eq. (1), n_s is given by

$$n_s = (\eta^2/2)\kappa^s W_s \sim (\eta^2/2)s^{\gamma-1}\exp(-s\tau)$$

(with the replacement $\kappa\mu \rightarrow \kappa$) near the critical point $\kappa_c = 1$. In the mean-field calculation of the FH type, $\gamma = 1$ and the enhancement factor $s^{\gamma-1}$ is missing in Eq. (3). Of course, as usual, we expect logarithmic corrections in $d = 4$.

Let us now consider various possible values of the scaling functions $\lambda(z)$, $z = \tau/\eta^{1/\Delta}$. As $z \rightarrow \infty$ ($\kappa < \kappa_c$, $\eta \rightarrow 0$), we expect the η dependence in the dilute limit to disappear in the exponential: $\lambda \sim z$. This is consistent with $\sigma = \tau$ in the FH approximation. For $z \rightarrow 0$ ($\kappa = \kappa_c, \eta \neq 0$), n_s must become independent of τ. Therefore, $\lambda = $const, which we take to be unity: $\lambda(0) = 1$. This is consistent with $\sigma \sim \eta^{2/3}$ in the FH approximation. For $z \rightarrow -\infty$ ($\kappa > \kappa_c$, $\eta \rightarrow 0$), λ must behave in such a way so that $\phi_p \sim \eta|\tau|^\beta$ as expected from the magnetic analogy if the analogy is to work all the way down to $\eta = 0$, $\kappa > \kappa_c$. This implies that $\lambda \sim |z|^{-\beta/\gamma}$ and

$$n_s \sim (\eta^2/2)s^{\gamma-1}\exp[-s(\eta/|\tau|^\beta)^{1/\gamma}].$$

Therefore,

$$\phi_l^{(f)} = \sum sn_s \sim \eta^{1-1/\gamma}|\tau|^{\beta(1+1/\gamma)},$$

(6)

whereas $\phi_p = \eta|\tau|^\beta$, as required. The superscript f on $\phi_l^{(f)}$ has been added to remind us that the sum in Eq. (6) gives the contribution to ϕ_l due to all finite chains of length $s = 1, 2, 3, \ldots$. In the mean field, $\beta = \frac{1}{2}$, $\gamma = 1$, and $\phi_l^{(f)} \sim |\tau|$ as we saw earlier in the FH approximation.

We consider Eq. (6) to be our most important result which has very significant consequences as we will see

below. First of all, since $\gamma > 1$ in $d = 3$, we observe from Eq. (6) that the contribution $\phi_l^{(f)}$ from all finite chains vanishes as $\eta \to 0$. (This is not the case in the FH approximation, because $\phi_l^{(f)}$ is independent of η as $\gamma = 1$.) On the other hand, ϕ_l is nonzero above κ_c even as $\eta \to 0$. Therefore, there must exist an infinite chain which must give rise to the entire density ϕ_{lo} at $\eta = 0$. The existence of this infinite chain is not predicted by the FH approximation, as the approximation is qualitatively incorrect and misleading.

As η is decreased, $\phi_l^{(f)}$ begins to decrease. Let $\eta = \eta^*$ be the value at which $\phi_l^{(f)} = \phi_{lo} \sim |\tau|^{dv-1}$. This means that $\eta^* = |\tau|^\Delta$. At $\eta = \eta^*$, $N = N^* = 1/|\tau|$. For $\eta > \eta^*$, $\phi_l^{(f)} > \phi_{lo}$ and there is no infinite chain in the system. Here $N < N^*$. However, an infinite chain appears at $\eta = \eta^*$, but contributes nothing to ϕ_l. For $\eta < \eta^*$, this infinite chain makes a finite contribution to ϕ_l to make up for the concentration difference $\phi_{lo} - \phi_l^{(f)}$ which is nonzero below η^*. Here, $N > N^*$. The phase transition that has been observed in the $n = 0$ magnetic system now has the following analog for the polymer system: The phase transition in the polymer system corresponds to the emergence of an infinite chain in the system at $\eta = \eta^* = |\tau|^\Delta$. The monomer concentration, due to this infinite chain, is given by $\phi_l^{(\infty)} = |\tau|^{dv-1}[1 - (\eta/\eta^*)^{1-1/\gamma}]$. However, the chain density $\phi_p^{(\infty)}$ due to this infinite chain must be zero as ϕ_p is completely made up by all finite chains, $\phi_p = \Sigma n_s$. This infinite chain disappears for $\eta > \eta^*$. The distribution n_s does not undergo any singular change as the system undergoes the phase transition. The form of n_s remains smooth across $\eta = \eta^*$. This is precisely what happens in percolation.[17] The only signature of the phase transition is the existence or the nonexistence of the infinite chain. We expect this infinite chain to exist below η^* even in high enough dimensions ($d \geq 4$) where $\gamma = 1$, i.e., we believe that $\phi_l^{(f)}$ is not the total contribution to ϕ_l—there must be an additional contribution $\phi_l^{(\infty)} \sim |\tau|$ to ϕ_l.

The infinite chain, which exists below η^*, is distinct from other finite chains even as $s \to \infty$, in that it is compact. Since $\phi_p^{(\infty)}$ is zero, it is clear that the ends of this chain do not couple with η, even though η may be nonzero. This again distinguishes this chain from finite chains. Therefore, we can safely assume that we have a single compact chain below η^*.

Let us make some important observations about our scaling form (5). In terms of $N = \phi_l/\phi_p \sim (\eta^{1/\Delta}\lambda)^{-1}$, we can rewrite n_s as

$$n_s = (\eta^2/2)s^{\gamma-1}\exp(-s/N) \tag{7}$$

in a more elegant and customary scale-invariant form.[17,18] We note that n_s/n_N can be written entirely as a function of the scaling variable s/N. Our original form (5) is justified because it is equivalent to Eq. (7). Moreover, the normalized distribution

$$P(s) = n_s/\phi_p = (1/N)(s/N)^{\gamma-1}\exp(-s/N)$$

is the usual Schultz distribution.[19] This further adds to the validity of Eq. (5).

Let us now consider chains of a fixed length s below η^*.

The link density $\phi_l(s)$ due to these chains is given by $sn_s = (\eta^2/2)s^\gamma\exp(-s/N)$, whereas the chain density is n_s. The link density contribution due to a single chain of length s is $\phi_l^{(1)}(s) = s^{1-d\tilde{v}}$, where we are assuming that the chain occupies a volume $s^{\tilde{v}d}$. The necessity of a different $\tilde{v}$ will become apparent below. Therefore, we need to put $n_{ov}(s)$ different overlapping chains, each of length s, in a given region to make up the link density $\phi_l(s)$:

$$n_{ov}(s) = \phi_l(s)/\phi_l^{(1)}(s)$$
$$= (\eta^2/2)s^{\gamma+d\tilde{v}-1}\exp(-s/N),$$

which is nothing but $s^{\tilde{v}d}n_s$. If $n_{ov}(s) > 1$, these chains overlap, otherwise they do not overlap. It is easily seen from this that the maximum overlap occurs when $s \sim N$. Therefore, in the following we will replace our polydisperse system by typical chains of lengths $\sim N$ and the width $\Delta N = Ne$ such that $n_N \Delta N = \phi_p$ and $n_N N \Delta N = \phi_l^{(f)}$. The total overlap now is given by $n_{ov} = n_{ov}(N)\Delta N$:

$$n_{ov} = (\eta^2/2)N^{d\tilde{v}+\gamma} = \frac{1}{2}\eta^{1-d\tilde{v}/\gamma}|\tau|^{\beta(1+d\tilde{v}/\gamma)}.$$

Obviously, $n_{ov} = N^{d\tilde{v}}\phi_p$, as should be expected. We need some extra information to determine the value of $\tilde{v}$. If we choose $\tilde{v} = v$, we find that $n_{ov} \sim (|\tau|^\Delta/\eta)^{2\beta/\gamma} \to \infty$ as $\eta \to 0$ in all dimensions, provided $\beta/\gamma > 0$. In $d = 1$, $\beta = 0$ and there is no overlap, as is evident. Therefore, for all $d > 1$, there is tremendous overlap among finite chains and the overlap becomes unbounded as $\eta \to 0$. In this regard, finite chains form a "semidilute" solution with the exception of the infinite chain. As $\eta \to 0$, the finite chains also disappear and, therefore, the overlap among finite chains is presumably of no physical consequence. The physics of the model is solely determined by the infinite chain. However, it is clear that the predicted overlap in $d = 2$ cannot be correct.

Another alternative choice for $\tilde{v}$ is $\tilde{v} = \frac{1}{2}$.[3] This choice is obviously restricted to $d \geq 2$. Again, there is overlap among finite chains provided $d > 2\gamma$. However, for $d = 2$, this inequality is violated and there is no overlap. Therefore, it appears that the choice $\tilde{v} = \frac{1}{2}$ is more appealing than $\tilde{v} = v$.

However, we will now argue that $\tilde{v} \neq \frac{1}{2}$ in $d = 2$. There is strong evidence[10] that ϕ_p in $d = 2$ behaves as $\phi_p \sim \eta^{1-a}|\tau|^{\beta'}$, $a = \frac{3}{35}$, $\beta' = \beta + \Delta a > 0$. This implies that $N \sim (|\tau|^{\beta'}/\eta^{1+a})^{1/\gamma} = \eta^{-57/70}|\tau|^{\beta'/\gamma}$, where we have used $v = \frac{3}{4}$ and $\gamma = \frac{4}{3}$. Moreover, $\phi_l^{(f)} \sim \eta^{1/10}|\tau|^{\beta'(\gamma+1)/\gamma} \to 0$ as $\eta \to 0$ and we must still have an infinite chain for $\eta < \eta^* \sim |\tau|^\Delta$ and $\kappa > \kappa_c$. Therefore, our picture of the emergence of an infinite chain is still valid, even though $a \neq 0$.

The number of overlapping chains is now given by

$$n_{ov} = N^{d\tilde{v}}\phi_p \sim \eta^{1-a-d\tilde{v}(1+a)/\gamma}|\tau|^{\beta'(1+d\tilde{v}/\gamma)}.$$

Because of the topological constraint in $d = 2$ which forbids chains to overlap, the exponent of η must vanish. This determines $\tilde{v}$ for us ($\gamma = \frac{43}{32}$):

$$\tilde{v} = [\gamma(1-a)]/[d(1+a)] = \frac{43}{76}. \tag{8}$$

Therefore, $\tilde{v}$ is uniquely determined. The correlation

length $\xi \sim N^{\tilde{\nu}}$ is now given by $\xi \sim \eta^{(1-a)/2} = \eta^{-16/35}$, which is what is predicted by Saleur[10] in $d=2$. It is easy to see that the monomer concentration due to this chain is $N/\xi^2 \sim \eta^{1/10} \sim \phi_l^{(f)}$ and no overlap is needed. It is indeed gratifying to see that our scaling theory confirms the prediction of Saleur who used a very different approach. We further observe that $\tilde{\nu} = \gamma/2 \neq \frac{1}{2}$ even if $a=0$.

It is very likely that a is nonzero and positive for $d<4$. From the finiteness of $\phi_l^{(f)}$, it is easily deduced that $(1+\gamma)(1+a) \leq 2\gamma$. This implies that $a \to 0$ as $d \to 4$ ($\gamma=1$). Our experience with $d=2$ suggests that $\phi_l^{(f)} \to 0$ as $\eta \to 0$ provided $\gamma \neq 1$. Therefore, it is safe to assume the existence of the infinite compact chain at $\eta=0, \kappa > \kappa_c$ even if $a \neq 0$. In that case, all our conclusions remain unchanged.

We can now appreciate the physical significance of $\tilde{\nu}$ in $d=2$. Due to the presence of the infinite chain, finite chains do not have to make up for the total link density by themselves.[3] This then allows for $\tilde{\nu} > \frac{1}{2}$; the chains are somewhat swollen compared to Gaussian chains ($\tilde{\nu} = \frac{1}{2}$). Since the conformations of finite chains are affected by the infinite chain in $d=2$, it is not inconceivable that the same happens in higher dimensions.

A recent Monte Carlo simulation in $d=3$ (Ref. 20) has confirmed our basic assumption that n_s remains smooth across η^*, with an infinite chain appearing below η^*. Our results in $d=2$ also confirm its validity. However, we believe that there is an essential singularity at η^* due to the emergence of the infinite chain and that most approximate calculations are incapable of detecting such a weak singularity.

We have clearly established that $\tilde{\nu} = \frac{1}{2}$ cannot be true in general. What happens in $d=3$? It is clear that $\tilde{\nu}=1$ in $d=1$. Furthermore, it is not counterintuitive to assume that $\tilde{\nu} = \frac{1}{2}$ in $d \geq 4$. If one further assumes $\tilde{\nu}$ to be a monotonic and smooth function of d, then it is obvious that $\tilde{\nu}$ cannot be $\frac{1}{2}$ in $d=3$. It probably is closer to $\frac{1}{2}$ but not exactly equal to it. Our present analysis is incapable of determining $\tilde{\nu}$ uniquely. It would, indeed, be very interesting to evaluate $\tilde{\nu}$ in $d=3$, as it is a first step towards an understanding of a more concentrated solution of chains. It is also possible that $d=2$ is special because of the topological constraint that uniquely determines $\tilde{\nu}$. Since such a constraint is not present in $d>2$, there may be no unique value of $\tilde{\nu}$. It is also possible that $\tilde{\nu} = \frac{1}{2}$ for all $d>2$. However, we have clearly demonstrated that the existence of the infinite chain has a profound effect on the conformational properties of finite chains, at least in $d=2$. We hope that our scaling analysis is a first step towards a complete understanding of the effects of the infinite chain in $d=3$.

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