Critical Concentration Fluctuations in Polymerizing Solutions

John C. Wheeler
Chemistry Department, University of California, San Diego, La Jolla, California 92093-0340

Pierre M. Pfeuty
Laboratoire Leon Brillouin (Commissariat à l'Energie Atomique-Centre National Recherche Scientifique),
Centre d'Etudes de Saclay, 91191 Gif-sur-Yvette Cedex, France

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Equilibrium polymerization in a solvent exhibits critical concentration fluctuations governed by a nonclassical critical exponent. A dramatic enhancement of the concentration fluctuations above those given by mean field theory (Flory theory) is predicted that persists even far from the transition. The predicted behavior explains recent neutron scattering results on polymerization in living polymer solutions and suggests improvements in experimental conditions. It is also in accord with recent measurements of scattering from solutions of giant polymeric micelles.

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Equilibrium polymerization can lead to critical phenomena which have been described by the $n \to 0$ limit of the n-vector model of magnetism [1,2]. Several examples have been studied, including liquid sulfur [1,3], living organic polymers [4], polymerlike micelles [5], and protein filaments [6]. In many cases solvent is present, and the theory has been extended with the prediction of new phase transition phenomena [7,8]. The possibility of ring formation has been considered with a mapping onto the Ising model [9,10] and new multicritical effects [11].

Equilibrium polymerization in a solvent has been mapped exactly onto the dilute n-vector model in the limit $n \to 0$ and studied in the mean-field approximation [8]. In this approximation, it was shown to be equivalent to Scott's [7] theory of sulfur solutions. At the polymerization transition, the concentration susceptibility [defined in Eq. (1) below] is predicted to exhibit a sudden finite jump, the amplitude of which may diverge at a tricritical point driven by the polymerization. However, from general thermodynamic arguments [12], the concentration susceptibility, χ, should exhibit a weak, specific heatlike singularity as the transition is approached, as discussed briefly recently [13]:

$$\chi \equiv \left(\frac{\partial x_s}{\partial \Delta / k_B T}\right)_T \sim [T - T_c(x_s)]^{-\frac{\alpha}{1-\alpha}}, \qquad (1)$$

where x_s is the number fraction of solvent, Δ is the difference of chemical potentials between solvent and monomer, and α is the specific heat critical exponent for the equilibrium polymerization transition in the neat monomer. The replacement of α by $\alpha/(1-\alpha)$ is due to the *Fisher renormalization* [14] resulting from approaching the transition at fixed concentration, x_s.

In this Letter we first show how the equilibrium polymerization of chains in a solvent can be mapped exactly to the problem of equilibrium polymerization of chains from pure monomer in the special case of zero mixing energy between solvent and monomers. This then permits the study of *nonclassical* critical fluctuations in the presence of solvent in terms of the original, nondilute $n \to 0$ vector model. These critical fluctuations are dramatic even in the absence of any interactions between monomer and solvent. We show explicitly a nonclassical divergence of the concentration susceptibility of the form given by Eq. (1). In addition, the *plateau value* of χ (its limiting value well into the polymerized regime) exhibits a large critical enhancement which itself diverges with a nonclassical critical exponent as $x_s \to 1$. These striking predictions are confirmed experimentally in solutions of poly-α-methylstyrene living polymer solutions [15,16] by neutron scattering and in polymeric micelles [5] by light scattering.

We consider a lattice model in which the volume is divided into C cells on the sites of a regular lattice in $d = 3$ dimensions. Each cell contains either a monomer or an inert solvent molecule. The monomer is inactive or active, and, if active, can be either isolated or bonded to one or two other monomers. This model has been discussed in some detail, both in the absence [2,4] and in the presence [4,8] of a solvent. The crucial observation here is that, in the special case of zero energy of mixing between solvent and monomers, it is possible to sum in closed form over the two possible states ("occupied by inactive monomer" or "occupied by solvent") of every cell not occupied by active monomer. This results in a factor of $1+\zeta$ for each of these $C-N_b-N_p$ cells, where N_b is the number of bonds and N_p the number of polymers, and where (in the notation of [4]) $\zeta = e^{\frac{\mu_0 - \mu_m}{k_B T}} e^{\frac{q(E_{00} - E_{mm})}{2k_B T}}$ is an effective activity of solvent relative to monomer. As a result, the partition function Y of the solution may be written in terms of that in the absence of solvent, Y^0, as

$$Y(K_p, K_1, T, \zeta) = e^{-\frac{qCE_{mm}}{2k_B T}} (1+\zeta)^C Y^0\left(\frac{K_p}{1+\zeta}, \frac{K_1}{1+\zeta}\right), \qquad (2)$$

where q is the number of nearest neighbors of a site on the lattice and K_p and K_1 are statistical weights associated with the bonds and polymer ends, respectively. This provides an exact mapping between the partition function for the solution in the absence of an energy of mixing and that of the neat system. The constants K_p and K_1 are of the Arrhenius form [4] and are assumed to be independent of ζ.

By differentiating the partition function, we obtain

$$x_b = \frac{\langle N_b \rangle}{C} = x_b^0 \left(\frac{K_p}{1+\zeta}, \frac{K_1}{1+\zeta} \right) , \tag{3}$$

$$x_p = \frac{\langle N_p \rangle}{C} = x_p^0 \left(\frac{K_p}{1+\zeta}, \frac{K_1}{1+\zeta} \right) , \tag{4}$$

$$x_s = \frac{\langle N_s \rangle}{C} = \frac{\zeta}{1+\zeta}(1-\phi^0) , \tag{5}$$

where x_b^0 and x_p^0 are the corresponding averages in the absence of solvent and $\phi^0 \equiv x_b^0 + x_p^0$.

The relevant concentration susceptibility is

$$\chi = \left(\frac{\partial x_s}{\partial \ln \zeta} \right)_{K_p, K_1} = \frac{\langle (N_s - \langle N_s \rangle)^2 \rangle}{C} = \frac{x_s}{1+\zeta} + \left(\frac{\zeta}{1+\zeta} \right)^2 \left[\left(\frac{\partial \phi^0}{\partial \ln K_p} \right)_{K_1} + \left(\frac{\partial \phi^0}{\partial \ln K_1} \right)_{K_p} \right] , \tag{6}$$

where the partial derivatives of ϕ^0 are evaluated at $K_p/(1+\zeta)$ and $K_1/(1+\zeta)$.

A mean-field expression for χ can be obtained by using mean-field theory for the $n \to 0$ vector model together with the mapping (2). The result is identical with that obtained [15] from the mean-field approximation to the *dilute* $n \to 0$ vector model with zero mixing energy. At the transition, $K_p^c = (1-x_s)^{-1}$, there is a jump in χ from $x_s(1-x_s)$ when $K_p < K_p^c$ to x_s when $K_p > K_p^c$, with a rounding for nonzero x_p.

Beyond mean-field theory, ϕ^0 exhibits critical behavior in the limit $x_p \to 0$, corresponding to that in the $n \to 0$ vector model:

$$\phi^0(K_p) = A_\pm \left(1 - \frac{K_p^{co}}{K_p} \right)^{1-\alpha} , \tag{7}$$

where $A_+ = 1$ and $A_- = 0$ correspond to K_p greater and less than K_p^{co}, respectively, with α being the specific heat exponent for the $n \to 0$ vector model ($\alpha \simeq 0.236$ from ε expansion [17]). This simple expression has the correct (zero) amplitude below K_p and the correct power law for $K_p > K_p^{co}$. The choice of unit amplitude above K_p gives ϕ^0 the correct behavior ($\phi^0 \to 1$) as $K_p \to \infty$.

From Eqs. (5), (6), and (7), one finds for χ, in the limit $x_p \to 0$ and K_p close to $K_p^c = (1-x_s)^{-1} K_p^{co}$,

$$\chi = x_s(1-x_s) + A_\pm x_s^2 \left[\frac{1-x_s}{x_s} \left(1 - \frac{K_p^c}{K_p} \right) \right]^{-\frac{\alpha}{1-\alpha}} , \tag{8}$$

where $A_\pm$ is the same as in Eq. (7). This corresponds to the behavior predicted from general arguments, given in Eq. (1). The mean-field result is obtained when α is replaced by zero in Eq. (8). The relatively large value of α [it is the largest for the O(n) vector models] results in the critical fluctuations having a strong effect on the concentration susceptibility in the vicinity of the polymerization transition.

Equations (6) and (7) predict another striking effect even far from the transition, well into the polymerized regime. When K_p becomes large, χ approaches a *plateau* value, χ_∞, which is a function of x_s and diverges in the limit of high dilution. In the limit $K_p \to \infty$ and for $1-x_s$ sufficiently small,

$$\chi_\infty \simeq (1-\alpha)(1-x_s)^{-\frac{\alpha}{1-\alpha}} . \tag{9}$$

Equations (7), (8), and (9) apply in the limit $x_p \to 0$, i.e., $K_1 \to 0$. The fact that in real, experimental systems K_1 and x_p are nonzero gives a rounding of the singularity in χ, which exhibits a maximum, χ^*, at K_p^*, shifted from K_p^c. Scaling of the $n \to 0$ vector model equation of state implies the following dependences of K_p^* and χ^* on x_p (and x_s):

$$\frac{K_p^* - K_p^c}{K_p^*} \sim \frac{x_s}{1-x_s} x_p^{-\frac{1-\alpha}{2-\alpha}} , \tag{10}$$

$$\chi^* \sim x_s^2 x_p^{-\frac{\alpha}{2-\alpha}} . \tag{11}$$

Note that the rounding of χ is predicted to become more pronounced with increasing x_s as well as with increasing x_p. Comparison of Eq. (11) with Eq. (9) indicates that for any fixed x_p and large enough x_s, the maximum will disappear into the plateau.

A more detailed study of the shape of χ requires an equation of state of the $n \to 0$ vector model. We use the parametric form already found to give good results for both living polymers and sulfur [3,4]:

$$\begin{aligned} \frac{K_p^{co}}{K_p} - 1 \equiv \tau &= r(1 - b^2\theta^2), \\ x_b &= \frac{1}{2} a m_0 \gamma \, r^{1-\alpha} (\theta^2), \\ x_p &= \frac{1}{2} a m_0 \, r^{2-\alpha} \, \theta^2 (1-\theta^2), \\ K_1 &= \frac{1}{2} a^2 \, r^{2\beta\delta} \, \theta^2 (1-\theta^2)^2, \end{aligned} \tag{12}$$

where $b^2 = \beta(\delta - 3)/\gamma\alpha$, with α, β, γ, and δ being critical exponents of the $n \to 0$ vector model [17], satisfying the scaling laws [18] $\beta(\delta+1) = 2-\alpha$ and $\beta(\delta-1) = \gamma$. The choice of amplitude $(1/2)am_0\gamma = (b^2-1)^{1-\alpha}$ causes this equation of state to reduce to Eq. (7) in the limit $x_p = 0$ or $K_1 = 0$. With $\alpha = 0.236$ and $2\beta\delta = 2.925$ [17], this gives $am_0 = 1.77$, very close to the value (1.74) used in [3,4]. (The two values give essentially identical results.)

The dominant term in the square brackets in (6) is

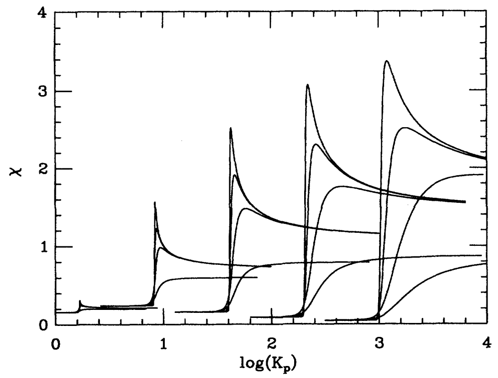

FIG. 1. Concentration susceptibility, χ, as a function of the natural log of K_p for several values of x_p and x_s. From left to right the sets of curves correspond to $x_s = 0.2$, 0.6, 0.8, 0.9, and 0.95. The lowest curve in each set is the mean-field result with $x_p = 10^{-4}$. The remaining curves, in increasing order, correspond to the parametric equation of state with $x_p = 10^{-4}$, 10^{-5}, and 10^{-6}.

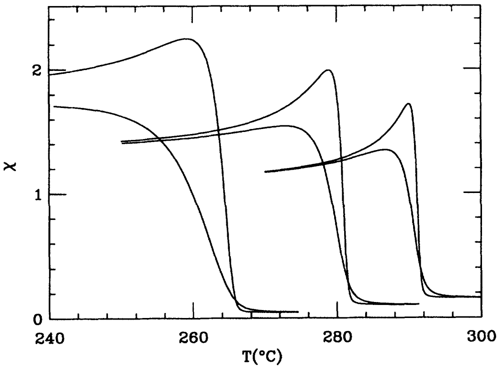

FIG. 2. Concentration susceptibility, χ, as a function of temperature for poly-α-methylstyrene solutions for various x_p and x_s. From left to right the pairs of curves correspond to $x_s = 0.95$, 0.88, and 0.80. The lower curve in each set corresponds to $x_p = 2.5\times10^{-4}$, the upper curve, to $x_p = 2.5\times10^{-5}$.

$(\partial x_b/\partial \ln K_p)_{K_1}$. Using (12) to evaluate this derivative, one obtains the following expression for χ:

$$\chi = \frac{x_s}{1+\zeta} + \left(\frac{\zeta}{1+\zeta}\right)^2 \left(\frac{(1+\zeta)K_p^{co}}{K_p}\right) \times \left(\frac{1}{2}am_0\gamma\right) r^{-\alpha}\theta^2 F(\theta^2), \qquad (13)$$

where $F(\theta^2)$ is a smooth function, decreasing from $\gamma+1 = 2.16$ at $\theta = 0$ to $(1-\alpha)/(b^2-1) = 0.737$ at $\theta = 1$. The remaining terms in the square brackets in (6) scale as higher powers of r and so can be viewed as corrections to scaling near the critical point. In addition, they are proportional to $1-\theta^2$ as well as to θ^2, so they are dominated by other terms in (13) whenever x_p is small. We have included them in our calculations, but the figures are unaffected if they are neglected.

In Fig. 1 we show the behavior of χ for several values of x_p and x_s. The mean-field result at the largest value of x_p is also shown for comparison. Note the dramatic increase in the amplitude of the singularity and the plateau value with increasing x_s. Note also the pronounced increase in rounding as either x_p or x_s increases.

The predicted fluctuation effects can be seen in scattering experiments. Neutron scattering has been measured at low angle in a solution of α-methylstyrene and deuterated tetrahydrofuran placed in a sealed cell with a low concentration, x_i, of initiators [15,16]. This system polymerizes in equilibrium when the temperature is lowered with a fixed concentration of polymers $x_p = \frac{1}{2}x_i$ (two initiators are required to prepare an activated monomer). Because neutrons are sensitive only to the nuclei, the scattering essentially measures the solvent concentration fluctuations (6). A preliminary experiment was done with $x_s = 0.88$ and $x_p = 10^{-4}$ and a small temperature range below the transition [15]. The small q limit of the scattering intensity, which gives the concentration susceptibility, exhibits a slightly rounded jump which was fitted by the mean-field expression for χ with nonzero mixing energy. More recent experiments [16] have been performed with two different samples ($x_{s1} = 0.88$, $x_{p1} = 2.35\times10^{-4}$ and $x_{s2} = 0.95$, $x_{p2} = 2.5\times10^{-4}$) over a wider range of temperature. For the first of these, a maximum in χ is clearly seen, whereas for the second, no maximum is observed, the value of χ rising smoothly to a plateau value with decreasing temperature. This behavior is predicted by the present theory, as shown in Fig. 2, where χ is calculated with the experimental values for x_s and x_p and for the enthalpy and entropy of polymerization ($\Delta H_p = -34.80$ kJ mol^{-1}, $\Delta S_p = -106$ J mol^{-1} K^{-1}). As predicted from Eqs. (8) and (10), the peak gets narrower and less shifted as x_p and x_s get smaller. Limits in the temperature range and sample preparation put limits on practical values of x_s and x_p, but a sample with $x_s = 0.8$ and $x_p = 2.5 \times 10^{-5}$ should be accessible and should show a substantial nonclassical critical effect, as shown in Fig. 2.

The theory can easily be extended to calculate the correlation length, ξ, which has been measured from neutron scattering data. In terms of the parametric model [Eq. (12)], ξ is given by

$$\xi = \xi_0(\theta^2)r^{-\nu}, \qquad (14)$$

where $\xi_0(\theta^2)$ varies smoothly from $\theta = 0$ (unpolymerized region) to $\theta = 1$ (polymerized region) and does not vanish or diverge in either limit. For simplicity, we have chosen it to be a constant, ξ_0. We then find a rounded peak in ξ that diverges as $x_p \rightarrow 0$ and gives results in good agreement with the experiments for the experimental values of x_s and x_p. Results are shown in Fig. 3.

Certain surfactant solutions in aqueous brines seem to form long, cylindrical, polymerlike micelles that grow

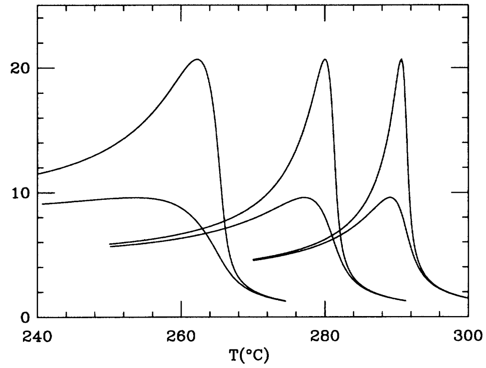

FIG. 3. Correlation length, ξ, for poly-α-methylstyrene solutions for various x_p and x_s. The values of x_p and x_s are as in Fig. 2.

when surfactant is added at constant temperature and salt concentration. This corresponds to a polymerizing solution with K_1 small and K_p large ($K_p \sim 10^4$) so that there is a critical value x_s^c of x_s, and $1 - x_s^c$ is very small ($\sim 10^{-4}$). In these systems K_1 and K_p are fixed and $1 - x_s$ is varied. The osmotic compressibility or concentration susceptibility has been measured by light scattering and is found [5] to increase with x_s according to the power law (K_p large, $1 - x_s$ small, $d = 3$)

$$\chi_\infty \sim (1 - x_s)^{\frac{d\nu - 2}{d\nu - 1}} . \tag{15}$$

This result from semidilute polymer solution theory [19] is identical to our Eq. (9) when one takes into account the hyperscaling relation [20] $d\nu = 2 - \alpha$.

More generally, the connection of the present theory to conventional polymer solution theory [19] can be made by noting that Eqs. (12)–(14) can be combined to give the relation $\chi \sim \phi N$, where $N \sim \xi^{1/\nu}$ is the number of monomers correlated with a given monomer.

The dependence upon x_s of the rounding of the transition due to nonzero x_p revealed by the mapping in Eq. (2) is expected to be much more general than the special case of zero mixing energy for which it is strictly valid. The present theory can be easily extended to polymerizing solutions with polymeric rings [9,10] or branched polymers [21] present by starting from the pure case (without solvent).

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