Competition of mesoscales and crossover to tricriticality in polymer solutions

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We show that the approach to asymptotic fluctuation-induced critical behavior in polymer solutions is governed by a competition between a correlation length diverging at the critical point and an additional mesoscopic length-scale, the radius of gyration. Accurate light scattering experiments on polystyrene solutions in cyclohexane with polymer molecular weights ranging from 200 000 up to 11.4×10^6 clearly demonstrate a crossover between two universal regimes: a regime with Ising asymptotic critical behavior, where the correlation length prevails, and a regime with tricritical Θ-point behavior determined by a mesoscopic polymer-chain length.

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Close enough to the critical point, the correlation length ξ of the fluctuations of the order parameter has grown so large that the microscopic and even the mesoscopic structure of fluids become unimportant: complex fluids become "simple." This feature is known as critical-point universality [1]. Within a universality class, determined by the nature of the order parameter, properly chosen physical properties of different systems exhibit the same near-critical behavior. All critical phase-separation transitions in fluids belong to the three-dimensional Ising-model universality class, as the order parameter (associated with density or/and concentration) is a scalar. However, in practice, the pure asymptotic regime is often hardly accessible. Even in simple fluids, such as xenon and helium, the physical properties in the critical region show a tendency to crossover from Ising asymptotic behavior to mean-field behavior [2,3]. This crossover depends on the microscopic structure of the system, namely, on the range of interaction and on a molecular-size "cutoff." In simple fluids, crossover to mean-field critical behavior is never completed within the critical domain (which can be defined roughly as within 10% of the critical temperature): the "cutoff" length and the range of interactions are too short. In complex fluids, regardless of the range of interaction, the role of the cutoff is played by a mesoscopic characteristic length scale ξ_D that is associated with a particular mesoscopic structure [4]. If the cutoff length is mesoscopic, it can compete with the correlation length ξ within the critical domain. The temperature at which the correlation length becomes equal to the structural length can be naturally defined as a crossover temperature between two regimes, namely, an Ising asymptotic critical regime and a regime determined by the nature of the mesoscopic structure of the complex fluid. In some complex fluids, like polymer solutions, it is possible to tune the structural length scale and make it very large. If both lengths, the correlation length of the critical fluctuations associated with the fluid-fluid separation and the structural correlation length, diverge at the same point, this point will be a multicritical point. A perfect example of such a multicritical phenomenon appears in a polymer solution near the Θ point. The Θ point is the point of limiting (infinite molecular weight of polymer) of phase separation in an infinitely dilute solution [5]. It is well known that the Θ point is a "symmetrical tricritical point" [6]. Both the radius of gyration R_g (assumed to be proportional to ξ_D) of the polymer molecule and the correlation length of the concentration fluctuations diverge at the Θ point, leading to tricriticality. Phenomenologically, a tricritical point emerges because of a coupling between two order parameters, one scalar and one vectorlike, which results in a change in the order of the phase transition: a second-order transition associated with the structural order parameter becomes of first order and thus is accompanied by a phase separation [7]. At a tricritical point, two universality classes meet each other, making tricritical behavior (in three dimensions) almost mean-field-like. Thus, the radius of gyration serves as a "screening length" for the critical fluctuations of concentration. By tuning the radius of gyration (probing different molecular weights) and the correlation length of critical fluctuations (changing the temperature distance from the liquid-liquid critical point), one can probe the crossover from the Ising asymptotic behavior to the mean-field-like tricritical Θ-point behavior. Such a crossover was first detected from analyses of the osmotic susceptibility obtained in a neutron scattering experiment [8] and of the shape of polymer solution coexistence curves [9]. Unfortunately, experimental data analyzed so far were not close enough to the Θ point to unambiguously separate crossover to tricriticality from non-asymptotic regular effects [10].

To observe the competition of two mesoscales in polymer solutions and convincingly prove crossover to Θ-point tricriticality, one needs to tune both the radius of gyration and the correlation length of the critical fluctuations over a large range, that is, to probe as high molecular weights as possible, and to measure both the critical susceptibility and the correlation length with an accuracy of the order of 1%. It is a challenging experimental task, and even most recent light-scattering experiments in polymer solutions [11,12] did not resolve the crossover to mean-field Θ-point behavior.

In this communication we report accurate light-scattering experiments performed for polystyrene solutions in cyclohexane with the polymer molecular weight M_w ranging from 200 000 to 11.4×10^6. The data clearly and unambiguously confirm the physical nature of the crossover to Θ-point tricriticality as described above. Moreover, the crossover behav-

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ior of the susceptibility and correlation length is in excellent agreement with the theory of the crossover critical phenomena, also developed at the University of Maryland (see [13,14] and bibliography there). We have also attempted to solve one of the most subtle problems of tricriticality, namely, experimental detection of so-called logarithmic corrections to mean-field tricritical behavior [15,16]. Such corrections have a universal nature as they are predicted theoretically to exist near all kinds of tricritical points [17].

Experimental technique, sample preparation, and experimental procedure have been described in detail elsewhere [18]. Five polystyrene samples (obtained from Polymer Laboratories Inc.) with a polydispersity index 1.02 ($M_w = 1.96\times10^5$), 1.06 ($M_w = 1.12\times10^6$), 1.04 ($M_w = 1.95\times10^6$), 1.05 ($M_w = 3.95\times10^6$), and 1.09 ($M_w = 11.4\times10^7$) have been investigated. Two identical He:Ne lasers and a receiving photomultiplier system have been aligned at two fixed scattering angles, 30° and 150°. Small parts of the incident-beam intensity of both lasers, directed by means of beam splitters and optical guides to the photomultiplier, served as calibration intensities. Our measurement procedure allows elimination of the influence of any laser power drift, as well as of slow fluctuations in the sensitivity of the photomultiplier. A square optical cell with an optical path of 2 mm is placed in a two-stage thermostat. This system allows stabilization of the temperature to within 0.5 mK over a few days. We determined the critical temperature T_c (more precisely, the temperature of phase separation) by monitoring the intensity of the transmitted beam and the scattering intensity while the sample is cooled from above the critical temperature in steps of 2–3 mK. The critical composition ϕ_c was checked by equality of volumes of the coexisting phases and established with an accuracy of at least 3–5%. Turbidity measurements were made, enabling us to apply the corrections due to turbidity loss and multiple scattering evaluated by a Monte Carlo simulation [19,11]. The overall accuracy of the intensity measurements in the range of $\tau = (T - T_c)/T_c$ varying from 10^{-6} to 10^{-1} is estimated to be about 1–2%. Data at $\tau < 10^{-5}$ and $\tau > 6\times10^{-2}$ were not included in the analysis as they became strongly affected by uncertainty in the critical composition and by polydispersity (close to T_c), and by background scattering (far away from T_c).

The corrected scattering intensity I was fitted to the following expression:

$$I = I_0 \chi G(q\xi) + I_b. \tag{1}$$

Here χ is the osmotic susceptibility, I_b is a background intensity, I_0 is an instrumental constant, $q = 4\pi n \lambda_0^{-1}\sin(\theta/2)$ is the scattering wave number (n is the refractive index, λ_0 is the wavelength of the incident light, θ is the scattering angle), and $G(q\xi)$ is the spatial correlation function taken in the Fisher-Burford approximation [20],

$$G(q\xi) = \frac{[1 + 0.084^2 (q\xi)^2]^{\eta/2}}{1 + (q\xi)^2 \left(1 + \frac{\eta}{2} 0.084^2\right)}, \tag{2}$$

with $\eta = 0.033$, a universal critical exponent.

The osmotic susceptibility and the correlation length were represented by the following crossover expressions [8] taken for the particular case of the normalized coupling constant $\bar{u} = 1$:

$$\chi^{-1} = a_0 \tau Y^{(\gamma-1)/\Delta_S} \left[1 + \frac{u^* \nu z^2}{2(z^2 + 2\nu)}\right], \tag{3}$$

$$\xi = \bar{\xi}_0 \tau^{-1/2} Y^{(1-2\nu)/2\Delta_S}, \tag{4}$$

where Y is a crossover function of a single argument, $z = \xi/\xi_D$, defined as

$$Y = (1 + z^2)^{-\Delta_S/2\nu}. \tag{5}$$

In Eqs. (3)–(5), $\gamma = 1.239$, $\nu = 0.630$, and $\Delta_S \cong 0.50$ (we adopted $\Delta_S = 0.51$ [13]) are universal critical exponents and $u^* = 0.472$ for the three-dimensional Ising universality class [1,13]; a_0 and $\bar{\xi}_0$ are mean-field amplitudes of the inverse susceptibility and of the correlation length. In principle, the crossover function depends on two crossover parameters, z, and a normalized coupling constant $\bar{u}$. However, the analysis of the experimental data has shown that $\bar{u}$ is almost independent of M_w and always close to unity. Since a theoretical analysis [10] confirms that this parameter is irrelevant for crossover to the Θ-point tricriticality, we have adopted $\bar{u} = 1$.

In the limit $z \to 0$, the crossover function $Y \to 1$, the susceptibility and correlation lengths follow mean-field behavior $\chi^{-1} = a_0 \tau$ and $\xi = \bar{\xi}_0 \tau^{-1/2}$. In the limit $z \to \infty$, $Y \to (\tau \xi_D / \bar{\xi}_0)^{\Delta_S} \to 0$, the susceptibility and the correlation length exhibit Ising asymptotic critical behavior: $\chi = \Gamma_0 \tau^{-\gamma}$ and $\xi = \xi_0 \tau^{-\nu}$ with amplitudes $\Gamma_0 = 0.871 a_0^{-1} (\bar{\xi}_0 / \xi_D)^{2(\gamma-1)}$

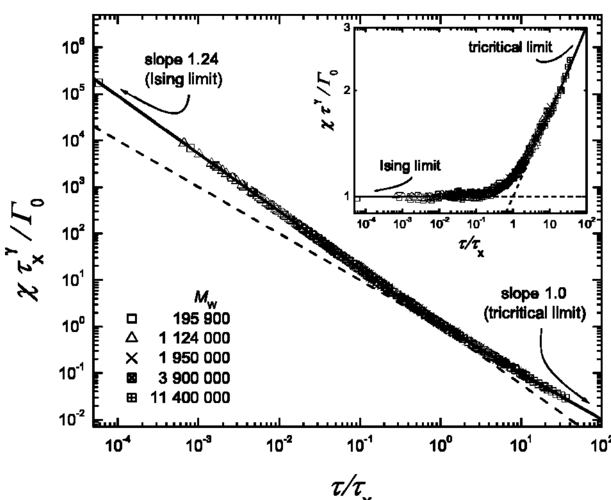

FIG. 1. Scaled osmotic susceptibility and deviation of the susceptibility from Ising critical behavior (shown as inset) for solutions of polystyrene in cyclohexane as a function of the scaled distance τ/τ_x to the critical temperature. The symbols represent experimental data, the dashed lines represent two limiting behaviors: Ising asymptotic behavior and mean-field behavior, while the solid curves represent the crossover theory.

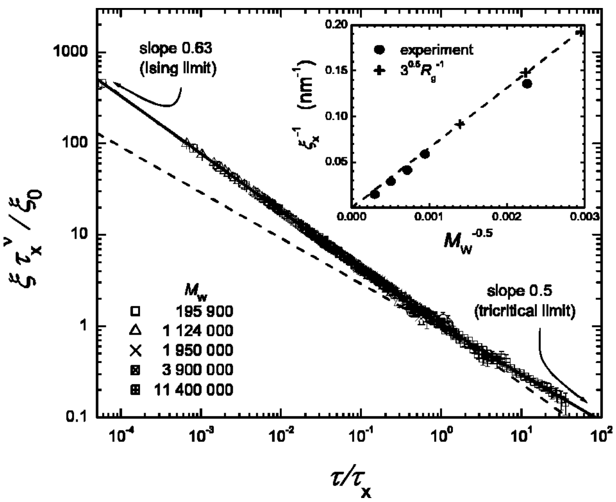

FIG. 2. Scaled correlation length for solutions of polystyrene in cyclohexane as a function of the scaled distance $\tau/\tau_\times$ to the critical temperature. The symbols represent experimental data, the dashed lines represent Ising asymptotic behavior and mean-field behavior, while the solid curve represents the crossover theory. In the inset: molecular-weight dependence of the inverse correlation length at the crossover temperature (closed circles); crosses are the normalized radius of gyration $R_g/\sqrt{3}$ scaled as squared root of the molecular weight of the polymer [8]. For $M_w \geqslant 10^6$, the values of R_g have been extrapolated (dashed line).

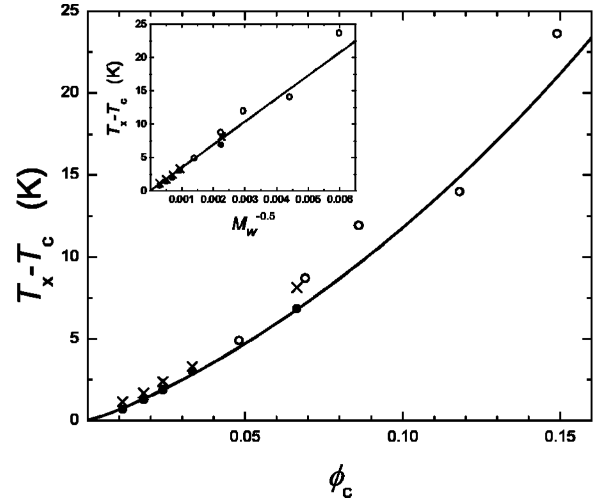

FIG. 3. Difference between the crossover temperature $T_\times$ and the critical temperature T_c of polystyrene-cyclohexane solutions as a function of the critical volume fraction ϕ_c and of $M_w^{-1/2}$ (inset). Solid circles correspond to the inflection points of $\gamma_{\mathrm{eff}}(\tau)$. Crosses correspond to the temperatures at which $\xi = R_g/\sqrt{3}$. Open circles are the temperatures at which $\xi = R_g/\sqrt{3}$ for the system of polystyrene-deuterocyclohexane [8]. For $\phi_c \leqslant 0.05$, the values of R_g have been extrapolated. The solid curve is an approximation based on $(T_\times - T_c) \propto N^{-1/2}$, with $N(\phi_c)$ defined parametrically by Eq. (6).

and $\xi_0 = \overline{\xi_0}(\overline{\xi_0}/\xi_D)^{1-2\nu}$ [14]. Actually, the Ornstein-Zernike approximation for the correlation function should replace the Fisher-Burford approximation in the mean-field limit. However, the difference between these two approximations is negligible when the correlation length is small as it is in the mean-field regime.

To represent the experimental data for each molecular weight, four parameters were used as adjustable: I_0, I_b, $\overline{\xi_0}$, and ξ_D. Although the amplitude a_0 is absorbed in I_0, to calculate Γ_0, we fixed $a_0 = 1$, as predicted by the Flory model in the Θ-point limit [10]. The parameter I_b becomes important farther away from the critical temperature, where I_b and ξ_D are strongly statistically correlated. To make sure that we found accurate values for the parameters I_b and ξ_D we checked the results obtained for different fitting intervals of τ.

A sensitive test of the shape of the crossover behavior can be obtained from an analysis of the effective exponent of the susceptibility, defined as $\gamma_{\mathrm{eff}} = -\partial \ln \chi / \ln \tau$. The exponent γ_{eff} exhibits crossover from its classical value $\gamma = 1.00$ to its Ising value $\gamma = 1.24$. The reduced crossover temperature $\tau_\times = (T_\times - T_c)/T_c$ can be defined as the inflection point of γ_{eff}. It turns out that $\tau_\times \cong (\overline{\xi_0}/\xi_D)^2$.

It follows from Eqs. (3) and (4) that the susceptibilities and the correlation lengths obtained for different molecular weights (different ξ_D) when reduced as $\chi\tau_\times^{\gamma}/\Gamma_0$ and $\xi\tau_\times^{\nu}/\xi_0$, respectively, should collapse into master curves as functions of the scaled temperature $\tau/\tau_\times$. The master curve for the susceptibility shown in Fig. 1 clearly demonstrates a crossover between two limits, Ising and mean field, over seven orders of $\tau/\tau_\times$. In Fig. 2, the same crossover is manifested by the correlation length. It is remarkable that the correlation length taken at the crossover temperature follows almost perfectly the normalized radius of gyration $R_g/\sqrt{3}$, independently measured by neutron scattering [21]. It also follows from our analysis that the dependence of the critical amplitudes on the molecular weight can be described within experimental accuracy by de Gennes's scaling [6,22]. In Fig. 3, the difference between the crossover temperature $T_\times$ [determined as the inflection point of $\gamma_{\mathrm{eff}}(\tau)$ and as the tempera-

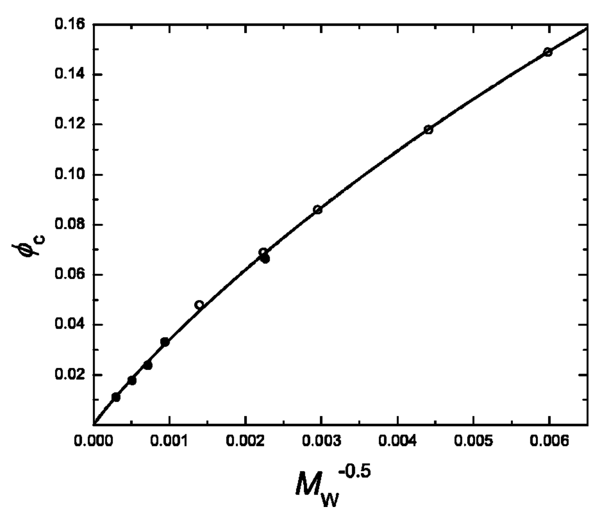

FIG. 4. Critical volume fraction ϕ_c of solutions of polystyrene in cyclohexane, scaled as a function of the squared root of the inverse molecular weight (closed circles). Open circles are the data for the system of polystyrene-deuterocyclohexane [8]. The solid curve represents Eq. (6) with $\upsilon = 1.26$.

ture where $\xi = R_g/\sqrt{3}$] and the critical temperature is plotted as a function of the critical volume fraction and of the molecular weight. The difference vanishes at the Θ-point limit and scales approximately as $M_w^{-1/2}$, as predicted by the crossover theory. In the Flory model, the critical volume fraction $\phi_c = 1/(1+\sqrt{N})$, where $N = M_w/M_0$ is the degree of polymerization (M_0 is the molecular weight of a polymer-chain unit). According to de Gennes's scaling, ϕ_c also scales as $M_w^{-1/2}$. However, the dependence of $T_\times - T_c$ on ϕ_c and, correspondingly, the dependence of ϕ_c on $M_w^{-1/2}$ exhibit a pronounced nonlinearity (Figs. 3 and 4). The violation of the Flory prediction for the critical volume fraction is a well-known fact: it has been attributed to partial collapsing of the polymer coils and described by a power law with an additional critical exponent [23,24]. Our analysis, which includes old data of Melnichenko *et al.* [8] and our new data very close to the Θ point, show that such an exponent is not needed and that all data are well described by the Flory-model formula corrected by a renormalization-group-theory logarithmic term associated with tricritical fluctuations,

$$\phi_c = \frac{1}{1+\sqrt{N}(1+\upsilon \ln N)^{-1/2}}. \tag{6}$$

Equation (6) contains only one system-dependent parameter, $\upsilon = 1.26 \pm 0.02$, and, in contrast to the mean-field prediction, shows zero slope at the Θ point. Computer simulations reported recently also indicate the existence of logarithmic corrections [25–28]. We suggest that the logarithmic correction is indeed responsible for the observed behavior of ϕ_c as the data used here are much closer to the Θ point and less affected by nonasymptotic contributions.

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