Sharp Crossover of the Susceptibility in Polymer Solutions near the Critical Demixing Point

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We have observed a sharp and nonmonotonic crossover of the susceptibility (osmotic compressibility) from mean-field to Ising critical behavior in semidilute solutions of polystyrene in deuterocyclohexane as the temperature decreases from the Θ region down to the critical temperature of the phase separation. We describe this crossover in terms of a competition between the long-range but finite intramolecular correlations of monomers in the polymer chain and the diverging correlation length of concentration fluctuations. [S0031-9007(97)04881-3]

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A recent analysis of the susceptibility χ of fluids and fluid mixtures has shown that the character of the crossover from mean-field to Ising critical behavior can depend on a nano/mesoscopic structure [1]. In simple fluids and fluid mixtures the crossover is gradual and is characterized by a single crossover temperature scale, the Ginzburg number N_{Gi}. Specifically, the effective susceptibility exponent γ_{eff}, defined as $\gamma_{\mathrm{eff}} = -\tau d \ln \chi / d\tau$, is then a monotonic function of $\tau = 1 - T_c/T$ (where T is the temperature, T_c the critical temperature) smoothly decreasing from the asymptotic Ising value $\gamma = 1.24$ at $\tau \ll N_{\mathrm{Gi}}$ towards the mean-field value $\gamma = 1$ at $\tau \gg N_{\mathrm{Gi}}$. In simple fluids with short-range interactions, however, the crossover to the mean-field regime is never completed in the neighborhood of the critical point as $N_{\mathrm{Gi}} \gtrsim 10^{-2}$. In complex fluids such as nonaqueous ionic solutions [2] or metal-ammonia solutions [3] the susceptibility exhibits a clear crossover between Ising and mean-field regimes, and γ_{eff} is a sharp and sometimes even nonmonotonic function of the temperature distance from the critical point. It was suggested in Ref. [1] that the sharp crossover might be related to an additional characteristic length scale which competes with the correlation length ξ of the critical fluctuations. Polymer solutions in low molecular-weight solvents seem to be a good choice for studying such type of crossover behavior as the additional length scale is clearly related to the molecular weight M_{W} of the polymer and thus might be easy to control and interpret.

Investigations of polymer solutions have shown that, like simple fluids, they belong to the universality class of the three-dimensional Ising model near the critical demixing point (see, e.g., [4] and references therein). However, the manner in which polymer solutions cross over to asymptotic Ising criticality has not been studied thus far. The purpose of this Letter is to report results for measurements of the susceptibility and the correlation length for solutions of polystyrene in deuterocyclohexane from small-angle neutron scattering (SANS). Semidilute polymer solutions, i.e., solutions of moderately overlapping polymer coils, are characterized by two distinct types of monomer-monomer correlations with different length scales [5]. *Intramolecular* correlations between monomers which belong to the same chain are closely related to the conformation of the macromolecules in the solution and occur on length scales of the radius of gyration R_{G} of polymer coils. *Intermolecular* correlations are defined by fluctuations of the total concentration with a correlation length ξ. While, in the Θ region the ratio $\xi/R_{\mathrm{G}} < 1$, in the vicinity of the critical temperature of the phase demixing the correlation length increases dramatically. Thus, ultimately, the correlation length exceeds the radius of gyration and becomes a dominant length scale in the system. Hence, Ising behavior is expected when $\xi \gg R_{\mathrm{G}}$.

Polystyrene (PS) standards with a polydispersity index $1.03 < M_{\mathrm{W}}/M_{\mathrm{N}} < 1.07$ were purchased from Polymer Laboratories. Solutions of PS at the critical volume fraction φ_c were prepared in deuterocyclohexane (99.5% deuterium) from Sigma. Characteristic properties of the polymer constituents and solutions are given in Table I. Values of (z averaged) R_{G} were determined by a high-concentration labeling method [6]; they do not depend on the proximity to the critical point. Each solution was contained in a 5 mm thick quartz cell and the temperature was controlled to better than ±0.1 K. The appearance of the meniscus (phase demixing) was detected visually. The critical composition (volume fraction) φ_c was assigned in accordance with the empirical power law $\varphi_c = 7.69 M_{\mathrm{W}}^{-0.385}$ [7]. The measurements were performed with the 30-m SANS spectrometer at the Oak Ridge National Laboratory. The neutron wavelength was $\lambda = 4.75$ Å ($\Delta\lambda/\lambda = 0.05$). The range of the scattering vectors $Q = 4\pi\lambda^{-1}\sin(\theta/2)$, where θ is the scattering angle, was $0.003 < Q < 0.05$ Å^{-1}. The data were collected and put onto an absolute scale with a procedure described elsewhere [8]. The scattering intensity I (in units of cm^{-1}) obtained at each θ was radially averaged to obtain the intensity I as a function of Q. $I(Q = 0)$ and

TABLE I. Characteristics ($M_{\mathrm{W}}, \varphi_{\mathrm{c}}, T_{\mathrm{c}}, R_{\mathrm{G}}, v_0$) of polymer solutions and parameters ($c_t, c_\rho, \bar{u}$, and Λ) of the crossover model [Eqs. (1)–(3)]. Expressions to calculate ξ_0, ξ_{D}, and $\bar{\xi}_0$ are given in the text.

	PS1	PS2	PS3	PS4	PS5
$M_{\mathrm{W}} \times 10^3$ g mol^{-1}	28	51.5	115	200	515
φ_{c}	0.149	0.118	0.086	0.069	0.048
T_c, K	285.06	291.39	298.37	301.20	306.9
$v_0^{1/3}$, Å	5.96	5.89	5.82	5.79	5.74
R_{G}, Å	43	62	90	117	189
c_t	0.89	0.69	0.39	0.32	0.16
c_ρ	0.85	0.89	1.1	1.2	1.6/1.7[a]
$\bar{u}$	1.9	2.1	2.3	2.5	3.1
Λ	0.17	0.13	0.092	0.075	0.039
ξ_0, Å	4.8	5.2	7.1	7.7	10.1
$\bar{\xi}_0$, Å	6.3	7.1	9.4	10.2	14.6
ξ_{D}, Å	35	47	63	77	147
T_{x}, K	292.3	296.4	304.8	305.8	310.0

[a] Above the crossover temperature T_{x}.

ξ were deduced from $I(Q,T)$ at each temperature by fitting the small-Q region to the Ornstein-Zernike formula $I(Q,T) = I(0)/(1 + Q^2\xi^2)$. The magnitude of $I(0)$ in absolute units is directly related to the susceptibility, which in our case is the isothermal osmotic compressibility, as $I(0) = b_{\mathrm{v}}^2 \chi \varphi / n$ with $\chi = n k_B T (\partial \varphi / \partial \Pi)$, where Π is the osmotoic pressure, φ the volume fraction of the polymer, k_B Boltzmann's constant, n the number of monomers per volume, and b_{v} the contrast factor between the monomer and the solvent molecule.

We fitted $\chi(\tau)$ and $\xi(\tau)$ simultaneously using the same crossover model for the free energy that was previously used to describe the crossover behavior of χ in simple and ionic fluids [1]. The model is based on renormalization-group (RG) matching [9,10] and the equations for the inverse susceptibility and correlation length read

$$\chi^{-1} = c_\rho^2 c_t \tau Y^{(\gamma-1)/\Delta_{\mathrm{s}}} \left(1 + \frac{u^* \nu}{2\Delta_{\mathrm{s}}} \left\{ 2\left(\frac{\kappa}{\Lambda}\right)^2 \left[1 + \left(\frac{\Lambda}{\kappa}\right)^2\right] \left[\frac{\nu}{\Delta_{\mathrm{s}}} + \frac{(1-\bar{u})Y}{1-(1-\bar{u})Y}\right] - \frac{2\nu - 1}{\Delta_{\mathrm{s}}} \right\}^{-1}\right), \qquad (1)$$

$$\xi = v_0^{1/3} \kappa^{-1} = v_0^{1/3} [c_t \tau Y^{(2\nu-1)/\Delta_{\mathrm{s}}}]^{-1/2}, \qquad (2)$$

with the crossover function Y defined by

$$1 - [1 - \bar{u}]Y = \bar{u}\left[1 + \left(\frac{\Lambda}{\kappa}\right)^2\right]^{1/2} Y^{\nu/\Delta_{\mathrm{s}}}. \qquad (3)$$

Here the normalized coupling constant $\bar{u}$ and "cutoff" Λ ($\Lambda^{-1} = \xi_{\mathrm{D}} v_0^{-1/3}$ with ξ_{D} the characteristic length reflecting a discrete structure of the fluid) are crossover parameters, with u^* being a RG fixed-point coupling constant. For three-dimensional Ising-like systems $\gamma = 1.239 \pm 0.002$, $\nu = 0.630 \pm 0.001$ [11]; Wegner's correction exponent $\Delta_{\mathrm{s}} = 0.54 \pm 0.03$ [12] (we actually used $\Delta_{\mathrm{s}} = 0.51$) are universal critical exponents and $u^* = 0.472$ [11]; c_ρ and c_t are system-dependent amplitudes; v_0 is the average volume per molecule in the solution.

The crossover parameters $\bar{u}$ and Λ and the amplitudes c_t and c_ρ are related to the coefficients of the local density of the Landau-Ginzburg free-energy F

$$f = \frac{v_0}{k_B T}\frac{dF}{dV} = \frac{1}{2} a_0 \tau \phi^2 + \frac{1}{4!} u_0 \phi^4 + \frac{1}{2} c_0 (\nabla\phi)^2, \qquad (4)$$

with $\phi = \varphi - \varphi_{\mathrm{c}}$, $a_0 = c_\rho^2 c_t$, $u_0 = u^* \bar{u} \Lambda c_\rho^4$, and $c_0 = c_\rho^2 v_0^{2/3}$.

Asymptotically close to the critical point [$\Lambda/\kappa \gg 1$, $Y \to (\kappa/\bar{u}\Lambda)^{\Delta_{\mathrm{s}}/\nu}$] the crossover susceptibility (1) and correlation length (2) reduce to $\chi = \Gamma_0 \tau^{-\gamma}(1 + \Gamma_1 \tau^{\Delta_{\mathrm{s}}} + \ldots)$ and $\xi = \xi_0 \tau^{-\nu}(1 + \xi_1 \tau^{\Delta_{\mathrm{s}}} + \ldots)$ where $\xi_0 = \bar{\xi}_0 (N_{\mathrm{Gi}}/n_0)^{\nu - 1/2}$, $\Gamma_0 = g_0 N_{\mathrm{Gi}}^{\gamma-1} c_t^{-1} c_\rho^{-2} = g_0 \times N_{\mathrm{Gi}}^{\gamma-1} a_0^{-1}$, $\Gamma_1 = g_1 N_{\mathrm{Gi}}^{-\Delta_{\mathrm{s}}}(1 - \bar{u})$ with $N_{\mathrm{Gi}} = n_0 c_t^{-1} \times (\bar{u}\Lambda)^2 = n_0 u_0^2 v_0^2 (u^*)^{-2} a_0^{-4} \bar{\xi}_0^{-6}$, the Ginzburg number, and $\bar{\xi}_0 = c_t^{-1/2} v_0^{1/3} = (c_0/a_0)^{1/2} v_0^{1/3}$, the mean-field amplitude of the correlation length. The coefficients $g_0 \simeq 2.0$, $g_1 \simeq 0.10$, $n_0 \simeq 0.031$, and $\xi_1/\Gamma_1 \simeq 0.6$ are universal [10]. Far away from the critical point the susceptibility (1) approaches the mean-field limit ($\Lambda/\kappa \ll 1, Y \to 1$): $\chi^{-1} = a_0 \bar{\tau}$, $\xi = \bar{\xi}_0 \bar{\tau}^{-1/2}$ with $\bar{\tau} = \tau - \Delta T_{\mathrm{c}}/T$ where $\Delta T_{\mathrm{c}} \propto \bar{u}\Lambda^2/c_t$ is a shift of the critical temperature due to critical fluctuations. In the $\Lambda \to \infty$ approximation, $\bar{u} \to 0$ and the two crossover parameters $\bar{u}$ and $\Lambda/c_t^{1/2}$ collapse into a single one, namely, the Ginzburg number.

The results of the fit of our experimental data are presented in Figs. 1–3 and Table I. It is seen from

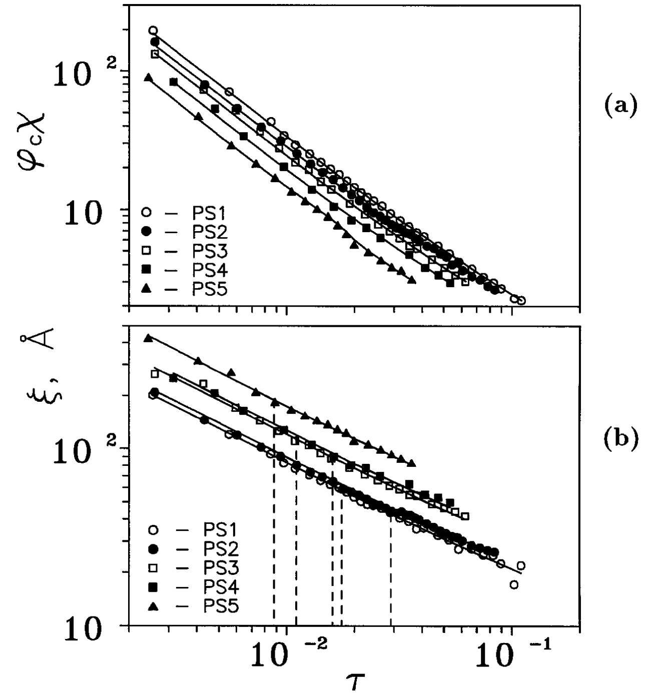

FIG. 1. (a) Normalized susceptibility of polystyrene-deuterocyclohexane solutions; the solid curves represent our crossover model, Eq. (1). (b) Correlation length of polystyrene-deuterocyclohexane solutions; the solid curves represent Eq. (2). Dashed lines indicate the temperatures at which $\xi = R_G$.

Fig. 2 that the crossover from mean field (dotted lines) to Ising (dashed lines) is clearly observed for two polymer solutions, PS1 and PS2, and it is well described by Eqs. (1)–(3) in the entire range of temperatures studied. Data for PS3 and PS4, although exhibiting more scatter at small τ, are consistent with the crossover function. The crossover is sharp and nonmonotonic for all the samples (Fig. 3). Moreover, the sharpness of the crossover increases with increase of molecular weight. The nonmonotonic behavior of $\gamma_{\rm eff}$ is caused by the play of $\bar{u}$ and $\Lambda/c_t^{1/2}$ and is directly related to large $\bar{u} > 1$ (negative Γ_1 and ξ_1) and small $\Lambda/c_t^{1/2} = \bar{\xi}_0/\xi_{\rm D} \ll 1$. Remarkably, the inverse cutoff $\xi_{\rm D} = v_0^{1/3}\Lambda^{-1}$ appears to be of the same order as $R_{\rm G}$ and scales as $M_{\rm W}^{0.5}$ as well (Table I).

Crossover between mean-field classical behavior and Ising asymptotic behavior has been reported for polymer blends [13–15]. In Ref. [14] $\chi(\tau)$ is described by a crossover model [16] which contains a single crossover parameter (Ginzburg number). We have found that such a single-parameter crossover model cannot describe the susceptibility of our polymer solutions, whereas the two-parameter model [Eqs. (1)–(3)] gives adequate fits for both susceptibility and correlation length. We note that fitting $\chi(\tau)$ of a polymer blend [15] to a simplified version of our crossover model resulted in $u^*\bar{u} \simeq 0.2$, as is typical for simple fluids [1].

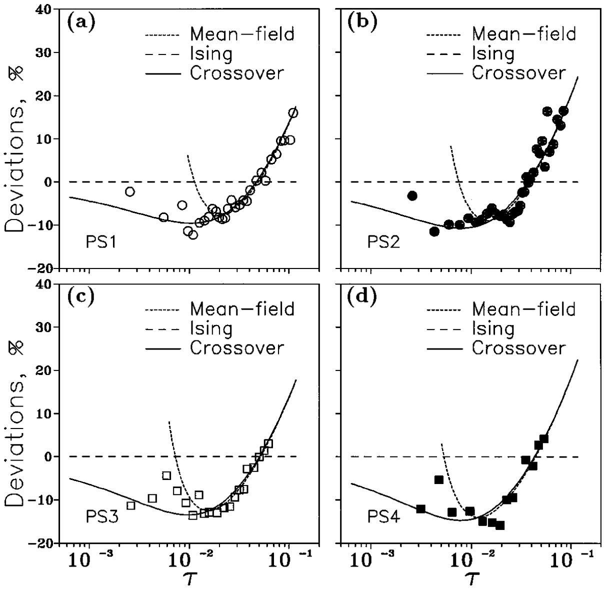

FIG. 2. Deviations of the experimental susceptibility data from the Ising asymptotic behavior (dashed line) for four samples [PS1 (a), PS2 (b), PS3 (c), PS4 (d)]. Solid curve represents the crossover model, Eq. (1). Dotted curve represents the mean-field asymptotic behavior. Note that the mean-field susceptibility diverges at a temperature above the actual critical temperature.

We define a crossover temperature $T_{\rm x}$ for each sample as the temperature of the inflection point in a plot of $\gamma_{\rm eff}$ vs $\log_{10}\tau$ (Fig. 3) which coincides within experimental accuracy with the temperature at which the correlation length becomes equal to the radius of gyration [6] (Fig. 2). The resulting temperature-concentration diagram of the polystyrene solutions is shown in Fig. 4. In the RG theory of polymer solutions [17] the Θ point is a tricritical point which divides specific critical singularities, associated with the self-avoiding-walk behavior of long ($M_{\rm W} \to \infty$) polymer chains at infinite dilution above the Θ temperature, and first-order phase transitions

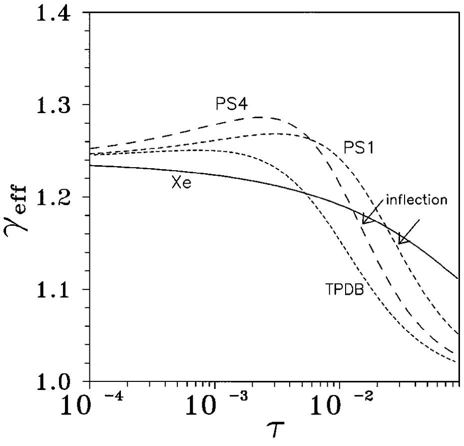

FIG. 3. Effective susceptibility exponent $\gamma_{\rm eff} = -\tau d \times \ln \chi/d\tau$ calculated from our crossover model for xenon and a nonaqueous ionic solution (TPDB) [1], and for two of the polymer solutions studied (PS1 and PS4).

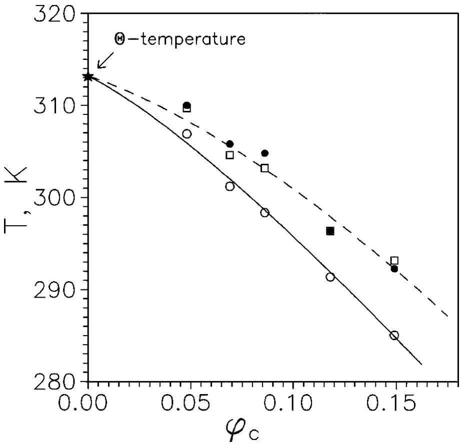

FIG. 4. Critical and crossover temperatures of the polystyrene-deuterocyclohexane solutions as a function of the critical concentration φ_c. The closed circles correspond to inflection points of $\gamma_{\mathrm{eff}}(\log_{10}\tau)$ (Fig. 3), the squares indicate temperatures at which $\xi = R_G$, and the open circles represent the experimental critical temperatures, while solid and dashed lines represent fits to Eq. (5) for T_c and T_x, respectively.

(phase separation). The region above the limiting phase separation is a tricritical domain for which the mean-field theory with logarithmic corrections is valid. This is why we identify the crossover temperature line with the limiting tricritical phase separation boundary which terminates at infinite dilution at the Θ point. Although the logarithmic corrections do not affect the mean-field values of the exponents $\gamma = 1$ and $\nu = 0.5$, they change the shape of the $M_W \to \infty$ phase boundary and critical temperature line.

While mean-field theory would imply a trianglelike tricritical phase boundary, the RG theory predicts that the phase boundary and the critical line should approach the Θ point with zero slope due to a logarithmic correction. As is seen in Fig. 4, the crossover temperatures T_x and the critical temperatures T_c are well described by nonanalytic equation of RG theory [17]

$$\frac{T - \Theta}{T} = A\varphi_c\left[\ln\frac{A}{\varphi_c}\right]^{-7/11}, \qquad (5)$$

with $A = 1.00 \pm 0.01$ for $T_c(\varphi_c)$ and $A = 0.58 \pm 0.02$ for $T_x(\varphi_c)$. On the other hand, if we try to interpolate both T_x and T_c to infinite dilution $\varphi_c = 0$, we obtain an intercept which exceeds the experimental observed value $\Theta \simeq 313$ K [18] by about 4 K. To our knowledge, this is the first experimental observation of the phase diagram behavior in the Θ region consistent with the RG theory.

In summary, we have found that the susceptibility and correlation length of polystyrene-deuterocyclohexane solutions manifest a sharp and nonmonotonic crossover from the mean-field tricritical behavior to asymptotic Ising criticality. Our model, represented by Eqs. (1)–(3), which was originally developed to describe crossover between *mean-field critical* and Ising critical behavior, appears to be applicable also for the crossover of the susceptibility and the correlation length from *mean-field tricritical* to Ising critical behavior in zero ordering field in the one-phase region. We have shown that the crossover length scale is equal to the characteristic size R_G of the polymer chains. The lower border of the tricritical domain for polymer solutions as well as the critical temperature at infinite dilution is a nonlinear function of concentration in agreement with the prediction of the RG theory.

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