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Asymptotic crossover in polymer blends

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Susceptibility and specific-heat data for a low-molecular-weight polymer blend near its critical point of unmixing are compared with a match-point renormalization-group theory which describes the crossover from classical mean-field to fluctuation-dominated behavior near the critical temperature. Using the Flory-Huggins form of the bare free-energy density, the crossover function requires only two free parameters.

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Until recently, the application of the concept of critical-point universality was limited to the region very close to the critical point, where the thermodynamic quantities are described by scaling laws with universal exponents depending only on the spatial dimension of the system and the symmetry of the order parameter. In the case of simple fluids, a large portion of the experimental data falls outside of this asymptotic scaling regime, and extends over a temperature window where mean-field (classical) theory is not valid. As the phase boundary is approached, the influence of the critical fluctuations first becomes apparent in the susceptibility, and the regime where any critical enhancement of the susceptibility is observed is referred to as the "global" critical region [1]. In the past, a quantitative description of the data in this region was achieved by introducing so-called "corrections to scaling." Now, a number of formulations based on the principle of critical-point universality have been used to derive an equation of state valid over the entire global critical regime. This has been accomplished by solving the problem of crossover, from pure mean-field to pure Ising critical behavior, as the critical point is approached [2–6]. The solution of this "asymptotic" crossover problem is most applicable to systems with a Ginzburg number that is sufficiently small, such that a crossover to classical behavior is actually observed a finite distance away from the critical point.

Binary polymer mixtures, or blends, of suitably low molecular weight exhibit a crossover from mean-field to critical behavior as the critical point is approached [7–10] and are thus ideal systems for studying this type of problem. From the Ginzburg criterion, the observed reduced temperature width of the global critical regime should be directly proportional to $(u_0 v_0)^2(a_0^4\xi_0^6)^{-1}$, where ξ_0 is the bare correlation length, v_0 is the reference cell volume, and the coefficients a_0 and u_0 appear in the Landau expansion of the free energy [8,10]. The constant of proportionality should be roughly the same in all polymer blends [8]. For the very-low-molecular-weight blend considered in this paper [10], we obtain a value of this constant which is a factor of 2 smaller than that reported in Ref. [8], provided we use the extrapolated value of the bare correlation length ξ_0, which guarantees consistency. Given the order-of-magnitude nature of the Ginzburg criterion, this agreement is reasonable. Using the theoretical form of ξ_0 suggested in Ref. [8], however, gives a value of this constant which is a factor of 20 smaller than that reported in Ref. [8]. This could explain the discrepancy reported by Janssen, Schwahn, and Springer for another very-low-molecular-weight blend [7]. Although this approach gives a universal description of the size of the crossover window, it does not give a quantitative description of the crossover itself. Motivated by this, we have used the asymptotic crossover formalism for a simultaneous description of the specific heat and susceptibility of the same critical blend described in Ref. [10]. Because a phenomenological form of the "bare" free energy is available from the Flory-Huggins model [11], the number of system-dependent parameters in the theory can be reduced from four to two.

The analysis starts with Ginzburg-Landau-Wilson free energy that follows from an expansion of the appropriate Flory-Huggins free energy. This is given as [10]

$$f[\Psi]=f_0+(k_B T/v_0)\int d^3x\left[\frac{1}{2}a_0\tau'\Psi^2+\left[\frac{1}{4!}\right]u_0\Psi^4+\frac{1}{2}c_0|\nabla\Psi|^2\right], \qquad (1)$$

where $\tau'=(1-T_c'/T)$ is the (mean-field) reduced temperature, $c_0=a_0\xi_0^2$, and the coefficients a_0 and u_0 are given in terms of the rescaled degrees of polymerization of the two species, the critical volume fraction, and the Flory-Huggins interaction parameter χ as derived in Ref. [10]. For the critical (deuterated)polystyrene-polybutadiene blend under consideration [10], the relevant parameters are $a_0=0.377$, $u_0=2.214$, and $\xi_0=9.4$ Å. It is worth noting that χ and ξ_0 are determined from a mean-field fit of the susceptibility and correlation length data far above the critical point [10], and thus a_0 and ξ_0 are fixed asymptotically. The parameter u_0 is obtained from the Flory-Huggins model. None of these parameters will be allowed to vary in the fit of the global critical region.

A description of the crossover to first order in $\varepsilon=4-d$, where d is the spatial dimension, that requires no adjustable parameters [2] can be derived from a renormalization-group analysis of Eq. (1). The Ginzburg number

$$G=(u_0 v_0)^2(32\pi^4 a_0^4 \xi_0^6)^{-1}$$

emerges as the relevant parameter in this $O(\varepsilon)$ analysis [2]. The Ginzburg criterion states that for $\tau' \gg G$, mean-field theory will be correct, while for $\tau' \ll G$, critical fluctuations will be important. For the system in question, $G \approx 0.003$, which is roughly an order of magnitude smaller than typical values in small-molecule fluids [1]. In Fig. 1, the vertical axis is proportional to the measured inverse susceptibility raised to the $1/\gamma$ power, where we have used the Ising value of the susceptibility exponent $\gamma=1.24$. The error bars are roughly the size of the data points. An asymptotic linear fit in the vicinity of the critical point yields the extrapolated value of the true critical temperature $T_c=41.15$ °C, which is in very good agreement with the value $T_c=41.2\pm0.1$ °C that we found in Ref. [10] using temperature jump light scattering. This suggests that $\gamma=1.24$ correctly describes the data very close to T_c, where there is a crossover to pure Ising behavior. Thus the $O(\varepsilon)$ solution to the crossover problem will not be quantitatively correct, because it does not give this correct Ising exponent very close to T_c (Refs. [1,2]).

Although a useful phenomenological version of the $O(\varepsilon)$ solution can be obtained by simply inserting the

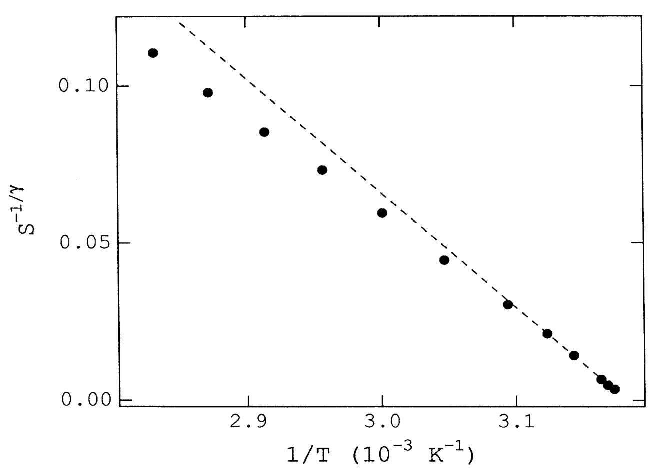

FIG. 1. Inverse susceptibility raised to the $1/\gamma$ power as a function of $1/T$. The linear region near T_c corresponds to pure Ising behavior.

correct Ising exponents [2], we have opted for a different approach. This is the so-called "match-point" solution of the nonlinear renormalization-group equations [12], which gives an effective free-energy density in terms of the bare parameters and a crossover function Y, from which the thermodynamic quantities may be derived [1,5]. From a renormalization-group matching procedure, it follows that the dimensionless renormalized singular free-energy density $\Delta A=(f-f_0)/k_B T$ can be written in the Landau form as [1,5]

$$\Delta A=(a_0/2)\tau\phi^2 Y^{(\gamma-1)/\Delta}+(u_0/4!)\phi^4 Y^{(2\gamma-3\nu)/\Delta} -(a_0^2/2u_0)\tau^2(\nu u^*/\alpha)[Y^{-\alpha/\Delta}-1]\ , \quad (2)$$

where $\gamma=1.24$, $\nu=0.63$, $\alpha=0.11$, and $\Delta=0.51$ are the usual Ising critical exponents, $\phi=\langle\Psi\rangle$ is the mean-field order parameter, and $u^*=0.472$ is the renormalization-group fixed-point value of the coupling constant u_0. The quantities a_0 and u_0 in Eq. (2) are as defined previously, but $\tau=(1-T_c/T)$ is now defined in terms of the true critical temperature. The crossover function Y is given by [1,5]

$$1-(1-u/u^*)Y=(u/u^*)(\Lambda/\kappa)Y^{\nu/\Delta}\ , \quad (3)$$

where

$$\kappa^2=(u\Lambda/u_0)^{1/2}[a_0\tau Y^{(2\nu-1)/\Delta}+(u_0/2)\phi^2 Y^{(\gamma-\nu)/\Delta}]\ . \quad (4)$$

The solution to Eqs. (3) and (4) subject to the constraint $\partial\Delta A/\partial\phi=0$ gives the crossover function Y in terms of τ and the two crossover parameters u and Λ, both above and below T_c. In the limit $\Lambda/\kappa\to1$, which corresponds to the classical mean-field limit, $Y\to1$ and Eq. (2) reduces to its mean-field form, if T is far enough above T_c so that the difference between T_c and T_c' has become insignificant. In the limit $\Lambda/\kappa\to\infty$, which corresponds to the asymptotic critical limit, $Y\to(\kappa u^*/u\Lambda)^{\Delta/\nu}$ and the asymptotic scaling laws with the first "correction to scaling" are recovered [1,5]. Because the blend under consideration exhibits pure mean-field behavior further than 15 K away from T_c, we can restrict ourselves to the asymptotic problem, and we do not need to modify Eq. (3) to account for an absence of (observed) mean-field behavior far above the phase boundary. In addition, there are usually four system-dependent parameters; the two introduced here, and two coefficients that determine the critical amplitudes. The other two parameters can be avoided if values of the parameters c_0, a_0, and u_0 are known.

The reduced (dimensionless) susceptibility for $T>T_c$ is found from Eq. (2) to be

$$\mathcal{S}^{-1}=[\partial^2\Delta A/\partial\phi^2]_{\phi=0}=a_0\tau Y^{(\gamma-1)/\Delta}\ . \quad (5)$$

Note that this reduces to the correct mean-field form far above T_c. A fit of our previously published [10] susceptibility data (rescaled to absolute units and then reduced to the correct dimensionless form) with Eq. (5) is shown in Fig. 2(a) as $\mathcal{S}^{-1}$ vs $1/T$. The solid line represents the global fit with $u=0.197$ and $\Lambda=0.09$. The dashed line is the asymptotic mean-field fit that intercepts the $1/T$ axis at T_c'. The same quantities are redisplayed in Fig. 2(b) as $\mathcal{S}$ vs T. As an order-of-magnitude check, the parameter u should be the same size as $3u^*(2G)^{1/2}$ (Ref. [1]), which is around 0.11. As can be seen from Fig. 2, the fit of the data is very reasonable.

The mean-field jump in the specific heat at constant pressure is easily calculated from Eq. (1) to be

$$\Delta C_p = (3a_0^2/u_0)(k_B/v_0) \ .$$

For the blend under consideration, this is roughly 0.016 $\mathrm{J\,cm^{-3}\,K^{-1}}$. Because the background specific heat is roughly two orders of magnitude larger than this anomaly, measurements of the critical contribution to C_p are difficult. Using a new differential ac calorimeter, we have recently achieved the level of resolution needed to reveal a peak of this size. A sample of the same critical blend used in the small-angle neutron-scattering measurements of the susceptibility [10] was placed in the calorimeter

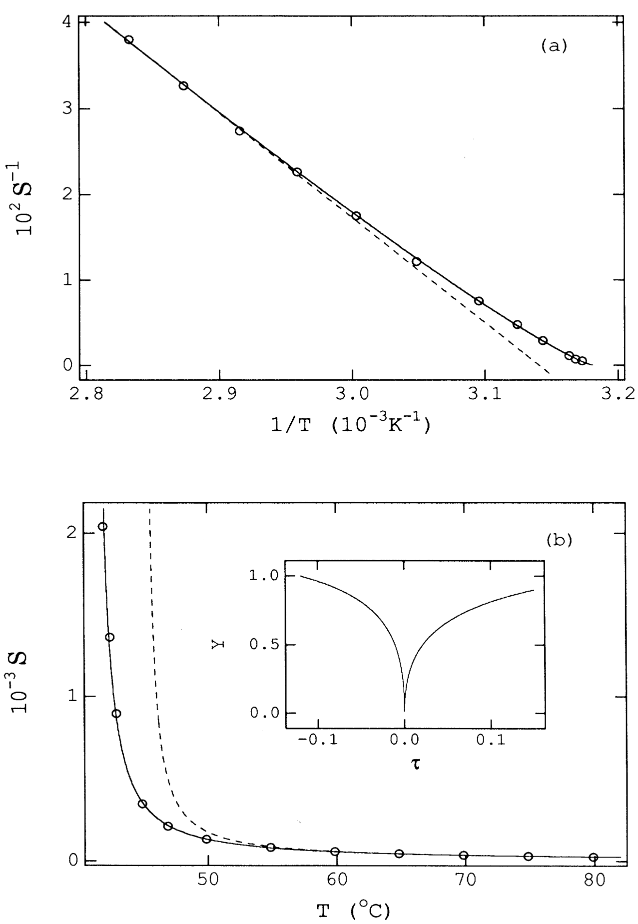

FIG. 2. Reduced inverse susceptibility (a) as a function of $1/T$ with both the global (solid line) and mean-field (dashed line) predicted behavior; (b) the reduced susceptibility as a function of T with both the global (solid line) and mean-field (dashed line) predicted behavior; and (inset) the crossover function Y as a function of τ both above and below T_c.

next to an off-critical sample (0.95 wt. % deuterated polystyrene) prepared from the same materials. Both samples were closely matched in thickness, which was around 2.5×10^{-2} cm, and had matched gold resistive heating films evaporated on the bottom of the sample cells. Connected in series, an ac voltage with a typical frequency of 0.4–0.5 Hz applied across the samples generated periodic heat pulses that were monitored on the other side with a pair of thermocouples. The ac signals from the two samples were connected to the differential input of a lock-in amplifier and locked in with the input signal, thus subtracting a large portion of the coherent noise as well as introducing a large offset. Another thermocouple was used to monitor the average temperature of the critical sample, which was ramped through the transition at a rate between 10 and 20 mK/min, after an initial annealing period of several hours at a temperature 20 K above T_c. The data was rescaled to absolute units, and an anomaly of the expected size was observed in three different samples, with an average peak temperature of 40.9 °C. There was, however, considerable scatter in the temperature at which the C_p anomaly was observed (as much as 3 K) and the exact behavior was not reproducible. Although this is not surprising, given the fact that this is an unmixing transition and it is difficult to ensure uniform mixing in the one phase region, this problem remains to be resolved. Because of this, the data shown here represent only a preliminary, order-of-magnitude measurement of the singular part of the specific heat.

Knowledge of the correct form of the crossover function Y allows us to calculate the expected global behavior of C_p. From Eq. (2), the reduced (dimensionless) specific heat $\mathcal{C}$ is given by

$$\mathcal{C} = -\partial^2 \Delta A/\partial\tau^2 + C_b \ , \tag{6}$$

where C_b is a background contribution. The free-energy density in Eq. (2) can be expressed in terms of Y by eliminating ϕ via the requirement that $\partial\Delta A/\partial\phi = 0$, which yields $\phi = 0$ as the stable solution for $T > T_c$, and

$$\phi^2 = \phi_0^2 Y^{(2\beta-1)/\Delta} \ , \tag{7}$$

with $\phi_0^2 = -(6a_0/u_0)\tau$ as the stable solution for $T < T_c$. The dependence of Y on τ above T_c is known from the fit of the susceptibility. Below T_c, $Y(\tau)$ can be found from Eqs. (3), (4), and (7), with the parameters u and Λ fixed from a fit of the susceptibility above T_c. The crossover function $Y(\tau)$ is shown in the inset of Fig. 2(b). Far away from the critical point, $Y \to 1$, while in the vicinity of the critical point, $Y \to 0$. The first term on the right-hand side of Eq. (6) can be calculated numerically to give the predicted form of the singular part of the specific heat.

The heat-capacity data from one of the samples was divided by k_B/v_0 to reduce it to the proper dimensionless form. A linear least-squares fit with Eq. (6) and a quadratic background of the form $C_b = B + AT + CT^2$ is shown in Fig. 3. The dashed line represents the same background with the predicted mean-field jump $\Delta\mathcal{C} = 3a_0^2/u_0$. In Fig. 3, the data have been shifted horizontally to achieve the best fit, thus introducing an additional pa-

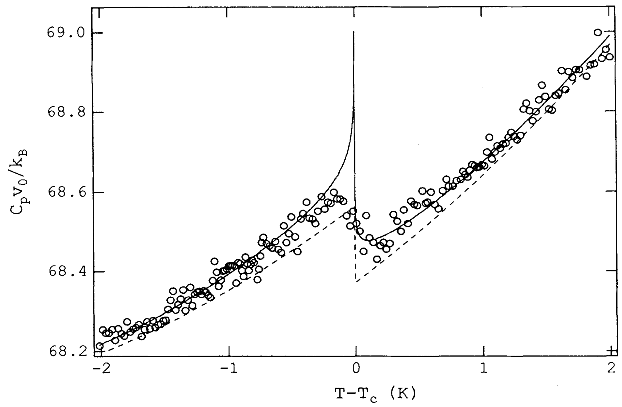

FIG. 3. Reduced specific heat in the vicinity of T_c. The solid line is the predicted global behavior, and the dashed line is the background with the predicted mean-field jump at T_c.

rameter to account for the scatter in the temperature at which the heat-capacity jump appeared. A simultaneous nonlinear fit of both $\mathcal{S}$ and $\mathcal{C}$ to determine u and Λ was not attempted because of the level of resolution in the C_p data. Although we are ultimately limited by polydispersity effects, significant improvement should be possible with modifications to the instrumentation and sample cell. Efforts are currently under way to resolve the apparent scatter in T_c and achieve a higher level of reproducibility.

In conclusion, we have used the "match-point" solution of the asymptotic crossover problem to describe the global critical behavior of both the susceptibility and specific heat of a low-molecular-weight binary polymer mixture. We report the observation of a critical anomaly in the specific heat in polymer blends. We find that the C_p data are in reasonable agreement with the behavior expected from a fit of the susceptibility, but it would be impossible to determine whether there is a crossover to critical behavior based on this heat-capacity data alone, as the size of the observed anomaly is the same size as the predicted mean-field jump. This is consistent with the fact that the susceptibility is the strongest measure of the importance of critical fluctuations. Perhaps the best measure of the width of the critical regime in this blend can be found in the response to shear flow as measured with small-angle neutron scattering, which very strongly suggests that critical fluctuations do not become significant until roughly 5 K away from T_c (Ref. [13]). To see the effect of critical fluctuations in the specific heat would require resolving the data within 200 mK of T_c, which could be extremely difficult. Polymer blends are an ideal system for studying this type of crossover phenomena, however, and a rigorous test of the theory will require precise measurements of more than one quantity.

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