Fluctuation-Induced First-Order Transition of an Isotropic System to a Periodic State

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Small-angle neutron-scattering data, obtained from a near-symmetric isotropic diblock copolymer, demonstrate non-mean-field behavior over a wide temperature range ($\geq 57\,^\circ$C) above the weakly first-order microphase-separation transition. These results are quantitatively explained by a fluctuation theory based on the Hartree approximation employed by Brazovskii to describe such phase transitions.

Numerous interesting condensed systems possess phase transitions between a spatially homogeneous phase and a periodic ordered phase with broken rotational and translational symmetry. The most familiar example of such a system, and one in which the transition is strongly first order, is the crystallization of a simple liquid. There are other equilibrium systems, however, in which the phase transition is believed to have a weak first-order character[1] and are those relevant to the present study. Examples of such systems include weakly anisotropic antiferromagnets,[2] the isotropic-cholesteric and nematic-smectic C transitions in liquid crystals,[3,4] pion condensates in neutron stars,[5] and block copolymer melts.[6,7] Additionally, certain pattern-forming nonequilibrium systems exhibit transitions of a similar nature.[8]

A characteristic feature of the above systems is that they possess an inherent (or experimentally accessible) symmetric point at which the cubic coefficient in an appropriate Landau theory vanishes, resulting in the mean-field prediction of a second-order (continuous) transition. Various treatments of order-parameter fluctuations, however, have demonstrated that the continuous transition is an artifact of mean-field theory and indicate the presence of a fluctuation-induced first-order phase transition at a temperature lower than the mean-field critical temperature.[2,9] In a seminal paper, Brazovskii[2] introduced a simple model Hamiltonian to describe such behavior. For the case of a one-component order-parameter field, $\phi(\mathbf{q})$, and at the symmetric condition, the Hamiltonian can be written ($d=3$)

$$H[\phi] = \frac{1}{2!}\int\frac{d\mathbf{q}}{(2\pi)^3}[\tau+(q-q^*)^2]\phi(\mathbf{q})\phi(-\mathbf{q})+\frac{\lambda}{4!}\int\frac{d\mathbf{q}_1}{(2\pi)^3}\int\frac{d\mathbf{q}_2}{(2\pi)^3}\int\frac{d\mathbf{q}_3}{(2\pi)^3}\phi(\mathbf{q}_1)\phi(\mathbf{q}_2)\phi(\mathbf{q}_3)\phi(-\mathbf{q}_1-\mathbf{q}_2-\mathbf{q}_3),$$

$$(1)$$

where τ is proportional to the distance from the mean-field critical temperature and $\lambda>0$ is a coupling coefficient that must be computed from a microscopic theory for the particular system of interest. Unlike conventional antiferromagnets, where the underlying lattice plays a role in selecting the low-temperature periodic phase, isotropic systems describable by Eq. (1) condense to a spatially periodic state with reciprocal-lattice vectors that are selected from the *continuous* surface $|\mathbf{q}|=q^*$. Brazovskii[2] showed that field fluctuations become singular in amplitude as $\tau\to 0$, but that for sufficiently weak coupling (small λ) these singularities can be controlled with a self-consistent Hartree approximation. His analysis predicts a fluctuation-induced first-order phase transition to a one-dimensional (lamellar) periodic structure at a temperature $\tau_t \sim -[(q^*)^2\lambda]^{2/3}$. Renormalization-group calculations on a model similar to Eq. (1) suggest the lack of a stable fixed point in three dimensions and are thus consistent with Brazovskii's results.[9]

In spite of these interesting predictions, there has been limited experimental work on such systems. Lowering of the transition temperature has been observed in studies of cholesteric liquid crystals[10] and in several experiments near the nematic-smectic C boundary.[4] Although there is strong evidence that the transition is weakly first order in such systems, we are unaware of any quantitative test of Brazovskii's theory.

It was pointed out by Leibler[6] that Brazovskii's theory should be applicable to A-B diblock copolymer melts. An A-B diblock copolymer is a linear (flexible) polymer that consists of a linear chain (i.e., block) of A polymer attached to a block of B polymer. At sufficiently high temperatures, bulk diblock copolymers exist in an isotropic, disordered phase, while various ordered structures (e.g., lamellar, hexagonal, cubic) arise at low temperatures (see Fig. 1). The lattice constants in such periodic phases scale with the copolymer radius of gyration [$R_g^2 = a^2 N/6$, where a and N are the length and number
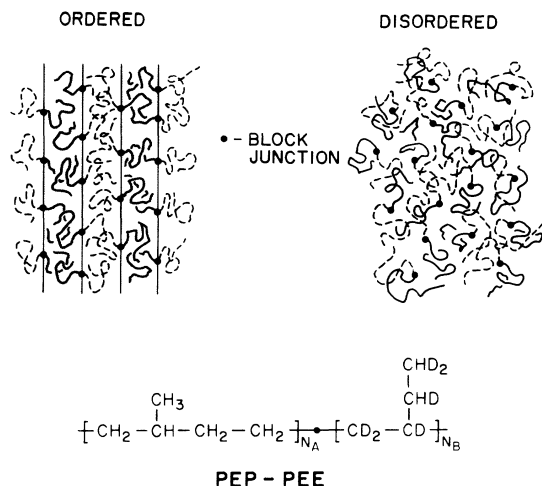
FIG. 1. Schematic illustration of ordered (lamellar) and disordered A-B diblock copolymer. The solid and dashed segments correspond to sequences of A and B repeat units. Also shown is the molecular structure of the PEP-PEE diblock copolymer discussed in this work.
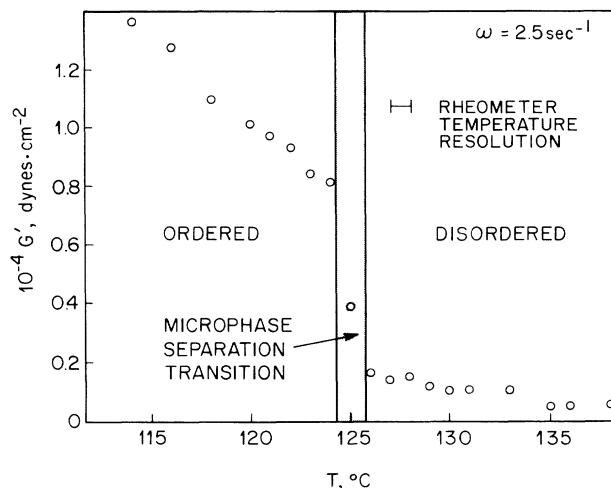

FIG. 2. Temperature dependence of the low-frequency dynamic elastic modulus for sample PEP-PEE near the weakly first-order MST. An uncertainty of $\pm 1\,°C$ in $T_{MST} = 125\,°C$ (shaded area) derives from the temperature resolution of the rheometer.

of block copolymer statistical (Gaussian) units] and, thus, can be as large as several hundred angstroms. Which ordered phase is selected depends primarily on the volume fraction, f, of component A. The symmetric point described by Eq. (1) corresponds to the case of $f = \frac{1}{2}$; here $\phi(\mathbf{q})$ represents fluctuations in composition about f. For future reference, we note that the order-disorder transition in block copolymers is traditionally referred to as the microphase separation transition (MST).[6]

In this Letter we present, to our knowledge, the first experimental test of Brazovskii's theory. In particular, we report small-angle neutron-scattering (SANS) and dynamical-mechanical experiments on a nearly symmetric model A-B diblock copolymer and compare the results with a recent application of Brazovskii's theory to the case of block copolymers.[7]

A PEP-PEE [poly(ethylene-propylene)-poly(ethylethylene)] diblock copolymer containing a partially deuterated PEE block was prepared and characterized as described elsewhere[11]; an illustration of the PEP-PEE structure is given in Fig. 1. The overall molecular weight, polydispersity, and PEP volume fraction are, $M_W = 57\,500$, $M_W/M_N = 1.05$, and $f = 0.55$, respectively.

We have determined the MST for this sample using a Rheometrics System IV rheometer operated in an oscillatory mode with a cone-and-plate geometry. As described elsewhere,[12] the low-frequency rheological properties of amorphous diblock copolymers are strongly dependent on the phase state, thereby providing a sensitive method for the determination of the MST. Figure 2 illustrates the temperature dependence of the dynamic elastic modulus, G', for the PEP-PEE copolymer at a

particular low frequency of 2.5 sec^{-1}. The distinct discontinuity in $G'(T)$ at $125 \pm 1\,°C$ identifies the MST; the full frequency dependence of the modulus, which closely resembles that reported previously for another copolymer,[12] will be reported separately.[13]

SANS data were obtained for the PEP-PEE sample with use of the 8-m instrument at the National Bureau of Standards.[14] Experiments were conducted with 8.0-Å wavelength (Λ) neutrons ($\Delta\Lambda/\Lambda = 0.25$) and a pinhole collimation geometry. Scattering cell preparation followed previously described procedures.[15] The sample cell was contained within a large, temperature controlled, copper block fitted with a thin copper window. A thermocouple, mounted in the scattering cell, was used to monitor the sample temperature ($\pm 0.2\,°C$). The azimuthally symmetric two-dimensional scattering patterns were reduced to one-dimensional form [intensity verses scattering wave vector, $q = 4\pi\Lambda^{-1}\sin(\theta/2)$, where θ is the scattering angle] in units of absolute scattering intensity (cm^{-1}), following established procedures.[16] Three sets of representative SANS results, obtained at temperatures above the MST, are presented in Fig. 3.

The coherent elastic neutron-scattering intensity from a homogeneous fluid containing two distinct types of scattering centers is given by

$$I(q) = v^{-1}(b_i - b_j)^2 S(q), \qquad (2)$$

where b_i and b_j are the coherent scattering lengths per unit volume v of scattering species i and j, respectively; partial deuteration of PEE (see Fig. 1) introduces a large difference between b_{PEE} and b_{PEP} for the present sample. Leibler[6] has shown that, within the random-phase approximation, the structure factor for a disor-
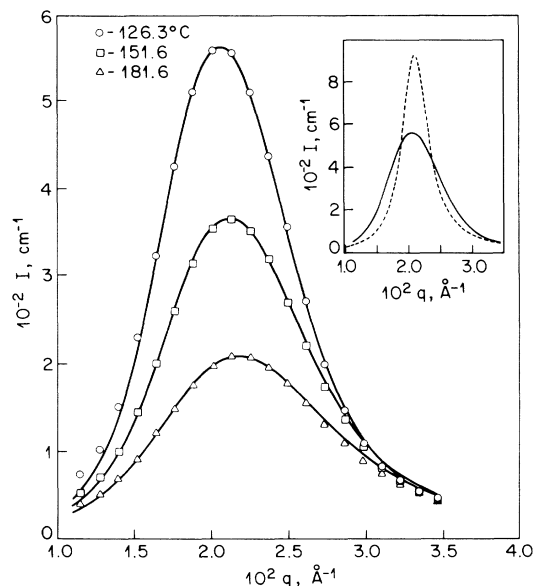
FIG. 3. SANS results at three representative temperatures above T_{MST}. Solid curves were calculated by convoluting Eqs. (2) and (3) (dashed curve) with the instrumental resolution function as illustrated for the $T = 126.3\,^\circ\text{C}$ result in the inset.
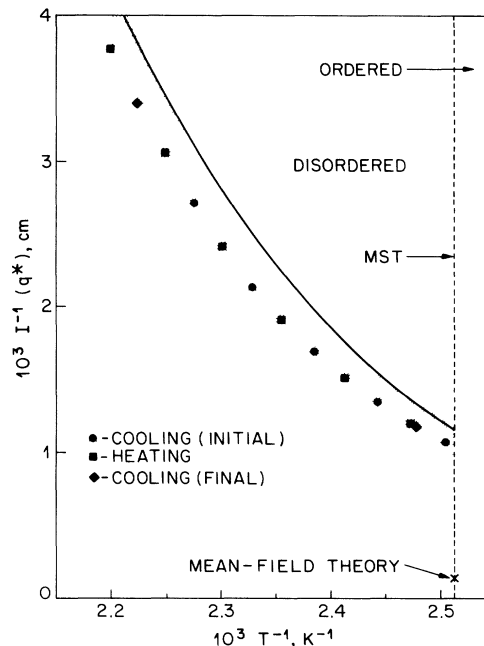

FIG. 4. Reciprocal peak intensity obtained from the (desmeared) SANS results; the shaded area identifies the estimated systematic uncertainty. The mean-field prediction ($\times$) was calculated from Leibler's theory (Ref. 6), while the solid curve was obtained by a single-parameter fit (Ref. 17) by the BLFH fluctuation theory (Ref. 7).

dered diblock copolymer melt is given by

$$S^{-1}(q) = N^{-1}F(x,f) - 2\chi_{\text{eff}}, \qquad (3)$$

where χ_{eff} is an effective interaction energy parameter, $F(x,f)$ is a function related to the correlation functions of a noninteracting (Gaussian) copolymer chain,[6] and $x = (qR_g)^2$. $F(x,f)$ attains a minimum at $x = x^* = (q^*R_g)^2$; expansion of Eq. (3) about x^* gives the form of the quadratic coefficient in Eq. (1), where $\tau \propto N^{-1}F(x^*,f) - 2\chi_{\text{eff}}$. We have fitted Eqs. (2) and (3) to the disordered phase SANS data by adjustment of χ_{eff} and R_g as shown by the solid curves in Fig. 3. These calculations include corrections for instrumental smearing, which primarily derives from the wavelength distribution, as illustrated in the inset. The fitting procedure allows us to extract the unsmeared peak intensity, $I(q^*)$, which is plotted as inverse intensity against inverse temperature in Fig. 4. Within mean-field theory,[6] linearity is expected in such a plot because $\chi_{\text{eff}} = \chi$, where χ (Flory-Huggins parameter) is linear in T^{-1} for dispersion interactions, e.g., hydrocarbons.[15] The shaded region in Fig. 4 indicates the estimated systematic error in $I^{-1}(q^*)$, which emerges from the uncertainty in absolute intensity calibration.[16]

Examination of Fig. 4 reveals that $I^{-1}(q^*)$ is nonlinear in T^{-1} over the entire experimental temperature range above the MST. This result is in marked contrast with binary polymer mixtures, which exhibit mean-field behavior [i.e., $I^{-1}(0)$ is linear in T^{-1}], except for a narrow range of temperatures near the critical point.[18] Furthermore, the peak intensity at the MST,

$I(q^*)_{\text{MST}} = 950 \pm 95$ cm^{-1}, is significantly less than that predicted by mean-field theory, $I(q^*)_{\text{MST}} = 7552$ cm^{-1}. Here we note that all our calculations include a small contribution from a cubic term added to Eq. (1) in order to account for the slightly asymmetric composition ($f = 0.55$) of the PEP-PEE sample.[6,7] Within the context of Leibler's mean-field theory,[6] this modification leads to the prediction of a weak first-order transition [i.e., finite $I(q^*)_{\text{MST}}$] to a cubic phase for $f \neq \frac{1}{2}$. Clearly, the results shown in Fig. 4 are qualitatively inconsistent with the mean-field theory.

Recently, Fredrickson and Helfand[7] have implemented Brazovskii's approach to treat fluctuation effects in diblock copolymers near the MST. The theory relies on microscopic calculations of the coefficients in Eq. (1) by Leibler[6]; hence we refer to this treatment as the Brazovskii-Leibler-Fredrickson-Helfand (BLFH) theory. For the present case ($f = 0.55$) a fluctuation-induced first-order transition is predicted to occur at $(\chi N)_{\text{MST}} = 10.70 + 43.16\bar{N}^{-1/3}$, where the term containing $\bar{N} = a^6 N/v^2$ is the fluctuation correction to the mean-field stability limit. Thus, the fluctuation corrections diminish with increasing N and in the limit $N \to \infty$ the mean-field theory is exactly recovered. The BLFH theory also provides values of f at which the lamellar, hexagonal, and cubic phases can be directly accessed from the disordered state. For the degree of polymeriza-

tion considered here ($\bar{N}=9548$), a disordered-to-lamellar transition is predicted over $0.42 \lesssim f \lesssim 0.58$. In fact, sample PEP-PEE exhibits such a transition; this will be discussed is a separate report.

In the BLFH theory for the disordered phase the form of Eq. (3) is preserved, except that χ_{eff} is renormalized from the mean-field χ and satisfies

$$\chi_{\text{eff}} = \chi - \frac{v}{2a^3} C(f) N^{-2} [N^{-1} F(x^*, f) - 2\chi_{\text{eff}}]^{-1/2}. \quad (4)$$

Here, $C(f)$ is a constant that depends weakly on composition, e.g., $C(0.5)=257$ and $C(0.55)=277$. At the order-disorder transition the peak height of the structure factor is predicted to be[7]

$$S^{-1}(q^*)_{\text{MST}} = 0.2008[C(f)v]^{2/3} N^{-4/3} a^{-2}, \quad (5)$$

leading to $I(q^*)_{\text{MST}} = 867$ cm^{-1} for sample PEP-PEE (intersection of solid curve and dashed line in Fig. 4), which within experimental error agrees with that determined by SANS.

We have compared the BLFH prediction for $I(q^*, T)$ [Eqs. (2)-(4)] with our experimental data based on the usual assumption[15] that $\chi = AT^{-1} + B$ (see previous comment). By varying a single parameter (T_{MST} and χ_{MST} have been independently determined), the theoretical prediction (solid curve in Fig. 4) can be brought into near coincidence with the SANS results, within the systematic experimental uncertainty.[17]

Among the various systems described by Eq. (1), diblock copolymers may be the best suited for a careful study of fluctuation effects. The experimenter has the ability (through synthetic chemistry) to systematically vary molecular weight, which governs the wavelength and amplitude of the dominant fluctuations, and the composition, f, which controls the symmetry of the underlying ordered phase.

In summary, a small-angle neutron-scattering study of a nearly symmetric model diblock copolymer has revealed non-mean-field behavior over a wide temperature range ($\geq 57\,^\circ$C) above the microphase separation transition (MST) temperature. The fluctuation theory of Fredrickson and Helfand, based on the Brazovskii treatment of systems exhibiting a weakly first-order transition from an isotropic to a nonuniform state and on Leibler's block copolymer Hamiltonian, quantitatively accounts for the results.

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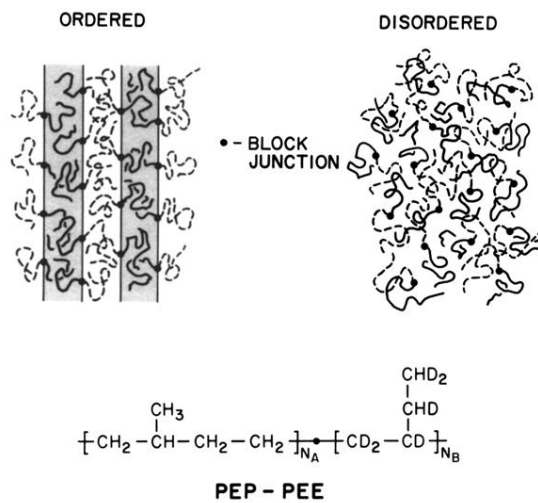
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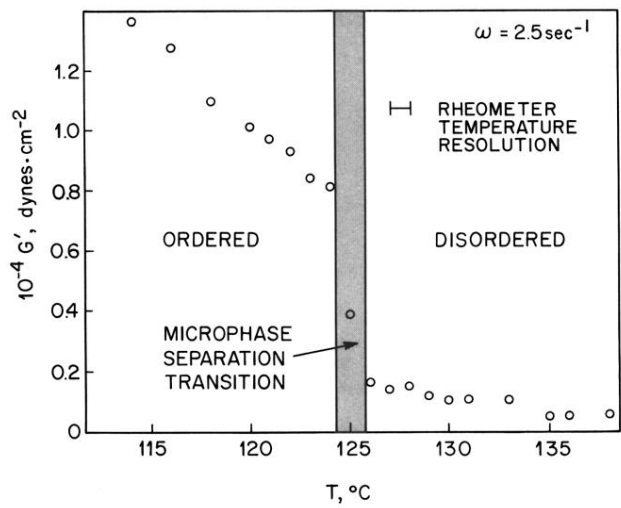
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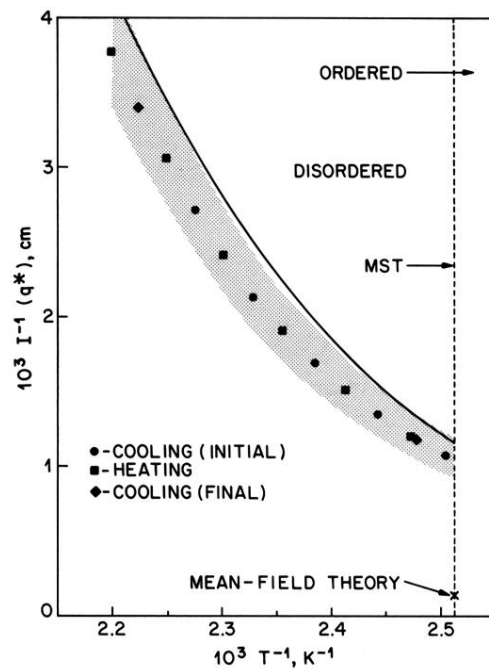
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