

# RAPID COMMUNICATION

## Fluctuations in Highly Metastable Polymer Blends

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Metastable liquids play an important role in both biological and synthetic processes.<sup>1</sup> In spite of many decades of research, general principles for stabilizing metastable states remain elusive. For instance, laboratory experiments have demonstrated that liquid water at atmospheric pressure can be supercooled to  $-41^{\circ}\text{C}$ .<sup>1</sup> In contrast, the experimental protocol for avoiding liquid–liquid phase separation in supercooled mixtures has not been established.<sup>1–3</sup> The lifetime of metastable systems appears to be highly system-specific. It also depends on the care taken to minimize the presence of impurities, vibrations, irregularities at contained walls, and so forth. The word care indicates a certain lack of fundamental understanding. For example, the experimental protocol (or care) needed to widen the observable range of metastability of water is a matter of considerable debate.<sup>1</sup>

Fluctuations become increasingly important as the system is driven deeper into the metastable region. It is important to know if there are fundamental differences between the fluctuations in nonevolving metastable liquids, and those in stable liquids. One might, for example, find increased clustering in the metastable state, especially as the limit of instability is approached. On the other hand, Ising-like corrections may suppress clustering in highly metastable systems. To address such effects, one needs to characterize the fluctuations in the stable state, extrapolate these measurements to

the metastable region, and compare these extrapolations with direct measurements on metastable systems. For liquid mixtures on the verge of liquid–liquid phase separation, methods for extrapolating results from stable systems into the metastable region are well known.<sup>3</sup> However, direct measurements of fluctuations in highly metastable mixtures have not been reported. It is clear that model systems for systematic experiments on metastable liquid mixtures would be useful at this juncture.

In this article, we present the results of small-angle neutron scattering (SANS) experiments on stable and metastable polyolefin blends in the liquid state. The components were polymethylbutylene (PMB) and polyethylbutylene (PEB). We studied blends containing short PEB chains that were single phase at a given temperature and pressure ( $T, P$ ), as well as blends containing long PEB chains that were metastable at the same ( $T, P$ ). The concentration fluctuations in both the states were analyzed using the Random Phase Approximation (RPA).<sup>4</sup> This enables a quantitative comparison of fluctuations in stable and metastable systems without extrapolation. We demonstrate that our blends can be supercooled by  $50^{\circ}\text{C}$  (within  $4^{\circ}\text{C}$  of the stability limit) with great ease.

We restrict our attention to polymer blends that obey the Flory–Huggins theory, which gives the Gibbs energy density change of mixing,  $\Delta G$ , for a binary mixture of two polymers labeled 1 and 2,

$$\frac{\Delta G}{kT} = \frac{\ln \phi_1}{v_1 N_1} + \frac{\ln \phi_2}{v_2 N_2} + \frac{\chi}{v_0} \phi_1 \phi_2, \quad (1)$$

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**Table I.** Characteristics of Polymers at Ambient Conditions

Polymer	$N_i$	$v_i$ ( $\text{\AA}^3$ )	$b_i$ ( $\text{\AA}$ )	$l_i$ ( $\text{\AA}$ )
dPMB	2465	136.2	$5.95 \times 10^{-4}$	8.26
hPEB1	525	162.0	$-4.98 \times 10^{-5}$	7.93
hPEB2	2630	162.0	$-4.98 \times 10^{-5}$	7.93

where  $k$  is the Boltzmann constant,  $\phi_i$  is the volume fraction of component  $i$  in the mixture,  $N_i$  is the number of monomers per chain of component  $i$ ,  $v_i$  is the volume of each monomer of component  $i$ ,  $\chi$  is the interaction parameter, which we demonstrate to be a function of  $T$  and  $P$  only, and  $v_0$  is an arbitrary reference volume, which we set equal to  $100 \text{\AA}^3$ . The  $\chi$  parameter accounts for all of the nonidealities of mixing, including volume changes of mixing.<sup>5</sup> Equations for the boundary between the single-phase and two-phase regions (binodal), and the stability limit of the single-phase system (spinodal) are given in ref. 6. The coherent scattering intensity from concentration fluctuations in single-phase blends, based on the RPA, is given by

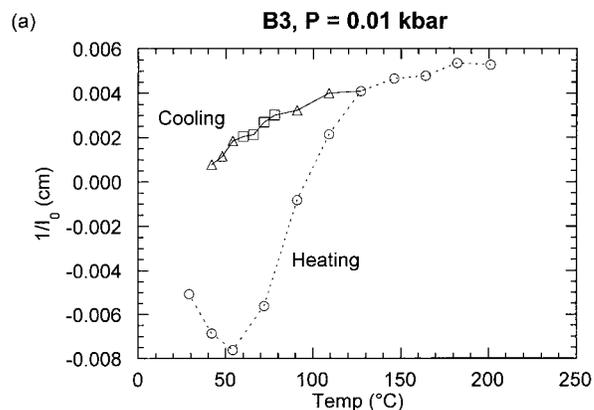
$$I(q) = \left( \frac{b_1}{v_1} - \frac{b_2}{v_2} \right)^2 \left( \frac{1}{S_{11}^0(q)} + \frac{1}{S_{22}^0(q)} - \frac{2\chi}{v_0} \right)^{-1} \quad (2)$$

where  $b_i$  is the scattering length of monomer  $i$ , and the ideal partial structure factors of chain  $i$ ,  $S_{ii}^0(q)$ , are well-known functions of  $N_i$ ,  $\phi_i$ ,  $v_i$ , and  $l_i$ , the statistical segment length of component  $i$ .<sup>4</sup>

Partially deuterated polymethylbutylene (dPMB) and hydrogenous polyethylbutylene (hPEB1 and hPEB2) homopolymers were synthesized and characterized using methods described in ref. 7. The characteristics of the polymers are given in Table I. The values of  $N_i$ ,  $b_i$ ,  $v_i$ , and  $l_i$  are based on C<sub>5</sub> and C<sub>6</sub> monomer units for PMB and PEB chains, respectively. Binary blends of PMB and PEB were made by dissolving the components in cyclohexane, and drying to a constant weight in a vacuum oven. The compositions of the blends used in this study, labeled B1 through B4, are given in Table II. SANS experiments were conducted on the NG3 beamline at the National Institute of Standards and Technology (NIST) in Gaithersburg,

**Table II.** Composition of Blends Studied

Sample	Components		$\phi_{\text{dPMB}}$
B1	dPMB	hPEB1	0.414
B2	dPMB	hPEB1	0.203
B3	dPMB	hPEB2	0.161
B4	dPMB	hPEB2	0.099

**Figure 1.** The extrapolated inverse absolute intensity as  $q \rightarrow 0$ ,  $1/I_0$ , versus temperature, during heating (circles; dashed line) and cooling (triangles and squares; solid line) runs, for blend B3 at  $P = 0.01$  kbar. See text for details.

Maryland, using the NIST pressure cell.<sup>8</sup> The time for data acquisition was 5–20 min, depending on the total detector counts, and data acquisition was started 5–10 min after the cell temperature and pressure had equilibrated. We report the azimuthally averaged, absolute coherent scattering intensity,  $I$ , as a function of  $q$  [ $q = 4\pi \sin(\theta/2)/\lambda$ ,  $\theta$  is the scattering angle and  $\lambda$ , the wavelength of the incident neutrons, was  $6 \text{\AA}$ ]. Details regarding instrumentation configuration and data reduction procedures are similar to our previous studies<sup>7</sup> and will be given in a full article.<sup>9</sup>

SANS results obtained immediately after blend B3 was loaded into the pressure cell are summarized in Figure 1 where we plot the temperature dependence of  $1/I_0$  ( $I_0$  is the extrapolated scattering intensity in the forward direction, using the Zimm equation). The blend was subjected to a heating run followed by a cooling run. During the heating run (circles in Fig. 1), the sample was heated from room temperature to  $201^\circ\text{C}$ . In all of the experiments, the sample was subjected to pressure scans from 0.01 to 1 kbar at each temperature. In Figure 1 we show data obtained at  $P = 0.01$  kbar. The negative values of  $I_0$ , obtained below  $100^\circ\text{C}$  during the heating run, are clear indications of phase separation at low temperatures. The true value of  $I_0$  must be positive; the negative values of  $I_0$  indicate the presence of large domains that cannot be resolved by our instrument. Based on previous studies on PMB/PEB blends,<sup>7</sup> we expected blend B3 to be phase-separated at atmospheric temperature and pressure (the state in which all of the blends were stored prior to the SANS experiments). The negative  $I_0$  values confirm our expectation. The abrupt change in the heating run data in Figure 1 at  $127^\circ\text{C}$  is a standard signature of homogenization. A more substantial confirmation of this is given below.

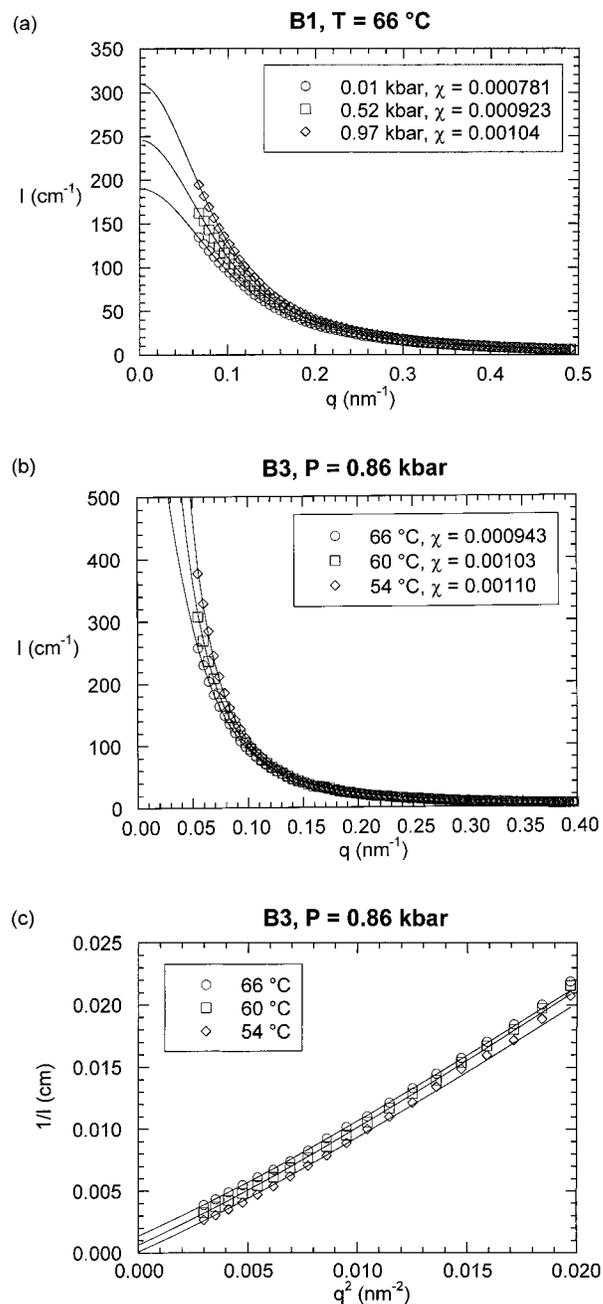
The cooling run was conducted in two segments. In the first segment, the sample was cooled from 201 to

109°C and studied as a function of decreasing temperature until  $T = 42^\circ\text{C}$  (triangles in Fig. 1). The sample was then reheated to  $91^\circ\text{C}$  and studied as a function of decreasing temperature from  $T = 78$  to  $60^\circ\text{C}$  (squares in Fig. 1). After homogenization at  $127^\circ\text{C}$ , the values of  $I_0$  become positive and independent of thermal history. The data in Figure 1 from the heating run and both segments of the cooling run fall on a smooth curve (within experimental error). Slow kinetics and irreversibility are obvious reasons for the differences between the heating and cooling runs. It is evident that  $127^\circ\text{C}$ , the temperature at which homogenization is achieved on experimental time scales, represents an upper bound for the binodal temperature at  $P = 0.01$  kbar.

We now study the  $q$ -dependence of the SANS profiles from our blends, which is related to the nature of the concentration fluctuations. We would like to use the RPA (eq 2) to estimate  $\chi(T, P)$  from the SANS data, but the RPA is only applicable to single-phase systems. We thus need to determine the  $(T, P)$  range over which our blends were single phase. As seen in the preceding paragraph, this is difficult in our system, due to slow kinetics and irreversibility. Our only alternative is to use the Flory–Huggins theory to compute the binodal, but to do this we need  $\chi(T, P)$ . We thus have a dilemma, because our original objective was to estimate  $\chi(T, P)$ . Our solution to this dilemma was to simply analyze all of the available data using the RPA and examine the validity of the analysis afterward.

In Figure 2(a) we show the pressure dependence of  $I(q)$  obtained from sample B1 at  $66^\circ\text{C}$ . The curves through the data represent least-squares RPA fits (eq 2) with  $\chi$  as the adjustable parameter. All other parameters were obtained from independent experiments and are summarized in Tables I and II; details will be presented in a full article.<sup>9</sup> (The statistical segment lengths were also adjusted but they were found to be within 6% of published values<sup>7</sup> for PMB and PEB chains.) It is evident that there is good agreement between theory and experimental data from sample B1 [Fig. 2(a)]. Knowing  $\chi$  as a function of  $T$  and  $P$ , we can show from eq 1 that blend B1 was in the single phase at  $T = 66^\circ\text{C}$  and  $0.01 \leq P \leq 0.97$  kbar. This validates the  $\chi$  parameters determined from this blend in Figure 2(a).

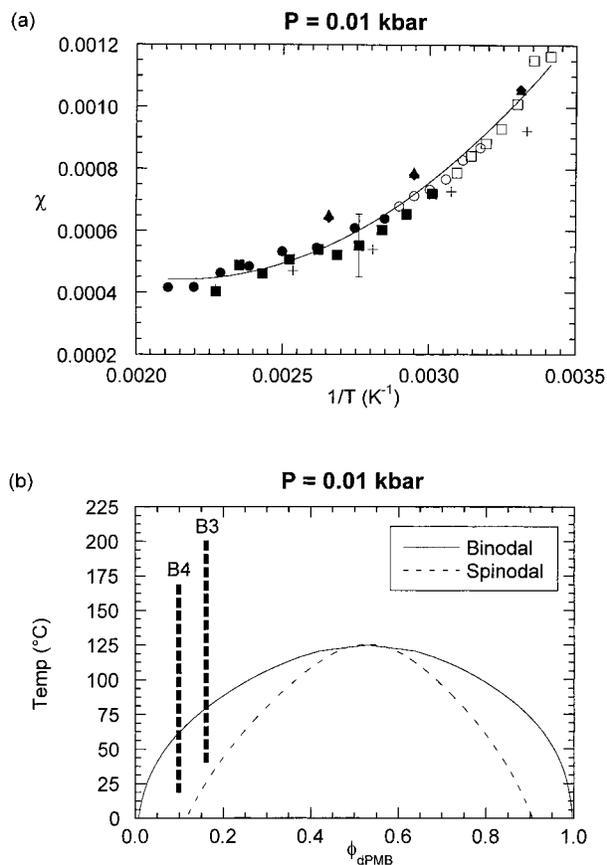
The method described above was used to analyze the data from all of our samples. In the case of B3 and B4 the data obtained during the cooling runs were used, because of our interest in the metastable single-phase state. In Figure 2(b) we show the comparison between the RPA and experiments on blend B3 at  $P = 0.86$  kbar and  $54 \leq T \leq 66^\circ\text{C}$ . Based on our previous estimates<sup>7</sup> of  $\chi$ , we expected B3 to be within the two-phase region under these conditions. In spite of this, the RPA works rather well; the quality of the fits obtained from B3 in Figure 2(b) is similar to that obtained from B1 in Figure 2(a). Due to proximity of blend B3 to the spinodal, the extrapolated intensity as  $q \rightarrow 0$  is very large. This is best seen in a Zimm plot where we plot  $1/I$  versus  $q^2$



**Figure 2.** Comparing experimental  $I$  versus  $q$  data with theory. The curves represent the RPA equation. (a) A stable blend, B1 at  $T = 66^\circ\text{C}$  and selected pressures; (b,c) A metastable blend, B3 at  $P = 0.86$  kbar and selected temperatures. In (c) the data in part (b) are shown in the  $1/I$  versus  $q^2$  format due to the proximity of B3 to the spinodal.

[Fig. 2(c)]. At  $54^\circ\text{C}$ ,  $I(q \rightarrow 0)$  is  $10^4 \text{ cm}^{-1}$  and the sample is estimated to be  $4^\circ\text{C}$  from the spinodal.<sup>10</sup>

In Figure 3(a) we show the results of our analysis on all of the samples at  $P = 0.01$  kbar in the form of  $\chi$

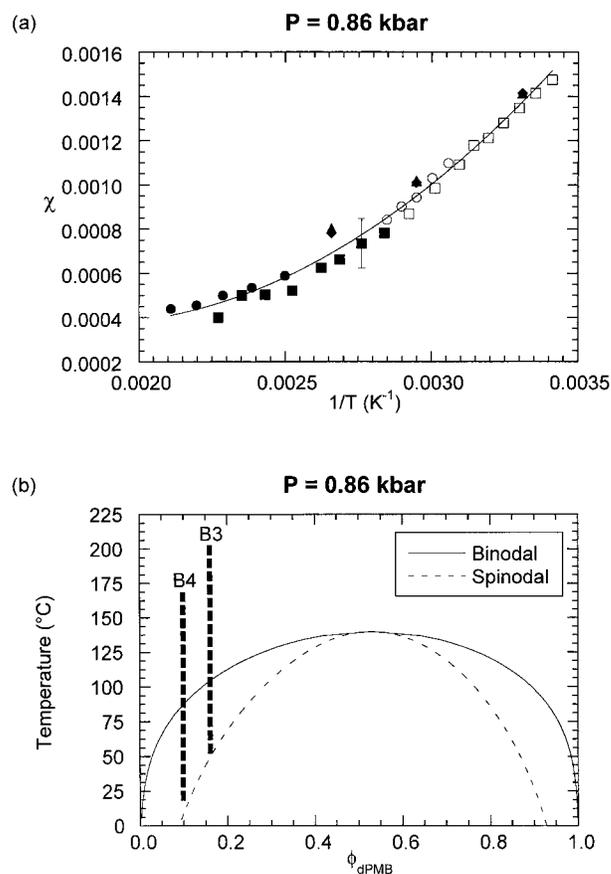


**Figure 3.** (a) The dependence of  $\chi$  on  $1/T$  at  $P = 0.01$  kbar. Diamonds: B1, triangles: B2, circles: B3, squares: B4. Filled symbols: stable blends. Open symbols: metastable blends. The crosses represent previously published data<sup>7</sup> from a stable blend (see text). The solid curve represents a least-squares quadratic fit through the data from blends B1 through B4. (b) The calculated phase diagram for dPMB/hPEB2 blends at  $P = 0.01$  kbar. The vertical dashed lines show the location of blends B3 and B4 where  $\chi$  was measured and reported in part (a).

versus  $1/T$ . The temperature dependence of  $\chi$  that we have obtained from samples B1 through B4 is in excellent agreement with each other. The crosses in Figure 3(a) are data from our previous study on a stable dPMB/hPEB blend with critical composition; see ref. 7 for details. The agreement between the previously published data and the present data is reassuring; some differences are expected because of differences in deuterium content of the PMB chains, and the fact that the old data were acquired on a SANS machine with significantly lower resolution.

We assumed that  $\chi$  was a quadratic function of  $1/T$ ,  $\chi = A + B/T + C/T^2$ , and estimated the parameters  $A$ ,  $B$ , and  $C$  by a best least-squares fit through the data in Figure 3(a). The solid curve in Figure 3(a) represents

the fit from which we get that  $A = 0.00253$ ,  $B = -1.929$  (K), and  $C = 446.01$  ( $\text{K}^2$ ). This allows us to calculate the binodal and spinodal curves of dPMB/hPEB2 blends, which we show in Figure 3(b). The vertical dashed lines represent the range of temperatures at which  $\chi$  values from blends B3 and B4 were reported in Figure 3(a). We can now distinguish between measurements from stable and metastable systems. The filled symbols in Figure 3(a) represent data taken from stable, single-phase systems, while the open symbols represent data taken from metastable systems. The fact that  $\chi$  measurements from samples B3 and B4 in the metastable state agree quantitatively with those obtained from stable, single-phase systems (B1 and B2), indicates the applicability of the RPA to metastable polymer blends. Note that using the data after homogenization (B3 after heating above  $127^{\circ}\text{C}$ ) was



**Figure 4.** (a) The dependence of  $\chi$  on  $1/T$  at  $P = 0.86$  kbar. Diamonds: B1, triangles: B2, circles: B3, squares: B4. Filled symbols: stable blends. Open symbols: metastable blends. The solid curve represents a least-squares quadratic fit through the data from blends B1 through B4. (b) The calculated phase diagram for dPMB/hPEB2 blends at  $P = 0.86$  kbar. The vertical dashed lines show the location of blends B3 and B4 where  $\chi$  was measured and reported in part (a).

essential for obtaining the collapse seen in Figure 3(a). The data obtained during the heating run at lower temperatures were in gross violation of the RPA.

In Figure 4(a) we show  $\chi$  versus  $1/T$  obtained at elevated pressures ( $P = 0.86$  kbar). We fit the data in Figure 4(a) using the same methodology as that used to analyze the data in Figure 3(a) to get  $\chi(T)$  at  $P = 0.86$  kbar [ $A = 0.00185$ ,  $B = -1.628$  (K), and  $C = 449.01$  ( $K^2$ )], and computed the phase diagram for dPMB/hPEB2 blends at  $P = 0.86$  kbar [Fig. 4(b)]. It is evident that the agreement between the  $\chi$  parameters obtained from stable and metastable systems, seen at atmospheric pressure (Fig. 3), also holds at elevated pressures (Fig. 4).

In summary, we have shown that the metastable state in PMB/PEB blends can be readily accessed. We present a direct comparison of the concentration fluctuations in stable and metastable polymer blends at the same temperature and pressure [filled and open symbols in Fig. 3(a) and 4(a)]. Such a comparison is only possible in polymeric systems because one can synthesize molecules with different chain lengths that are otherwise identical to each other. The ease with which we were able to obtain metastable states raises concerns about the interpretation of cloud point measurements on polymer mixtures. Our experiments provide the basis for further time-resolved studies, exploring the dependence of the lifetime of metastable systems on factors such as molecular motion and fluctuations.

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9. Lefebvre, A. A.; Lee, J. H.; Balsara, N. P.; Hammouda, B., manuscript in review.
10. Spinodals obtained by extrapolating data from stable systems are sometimes called pseudospinodals (refs. 1–3). In our analysis, we have used data from both metastable and stable systems and we thus have used the classical terminology.
11. Identification of equipment and materials does not imply recommendation by NIST.