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Authors

Knychala, Piotr

Timachova, Ksenia

Banaszak, Michal

et al.

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# 50th Anniversary Perspective: Phase Behavior of Polymer Solutions and Blends

Piotr Knychala,<sup>†</sup> Ksenia Timachova,<sup>‡</sup> Michał Banaszak,<sup>\*,||,⊥</sup> and Nitash P. Balsara<sup>\*,‡,#</sup>

<sup>†</sup>Faculty of Polytechnic, The President Stanislaw Wojciechowski State University of Applied Sciences, Kalisz, Poland

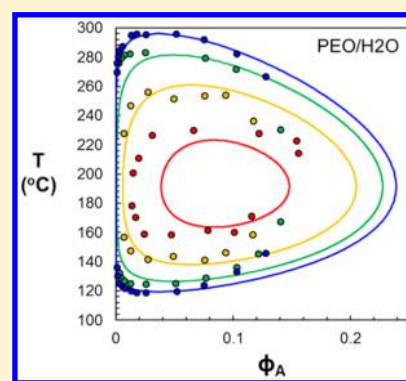
<sup>‡</sup>Department of Chemical and Biomolecular Engineering, University of California, Berkeley, Berkeley, California 94720, United States

<sup>||</sup>Faculty of Physics and <sup>⊥</sup>NanoBioMedical Centre, Adam Mickiewicz University, ul. Umultowska 85, 61-614 Poznan, Poland

<sup>#</sup>Materials Sciences Division, Lawrence Berkeley National Laboratory, Berkeley, California 94720, United States

## S Supporting Information

**ABSTRACT:** We summarize our knowledge of the phase behavior of polymer solutions and blends using a unified approach. We begin with a derivation of the Flory–Huggins expression for the Gibbs free energy of mixing two chemically dissimilar polymers. The Gibbs free energy of mixing of polymer solutions is obtained as a special case. These expressions are used to interpret observed phase behavior of polymer solutions and blends. Temperature- and pressure-dependent phase diagrams are used to determine the Flory–Huggins interaction parameter,  $\chi$ . We also discuss an alternative approach for measuring  $\chi$  due to de Gennes, who showed that neutron scattering from concentration fluctuations in one-phase systems was a sensitive function of  $\chi$ . In most cases, the agreement between experimental data and the standard Flory–Huggins–de Gennes approach is qualitative. We conclude by summarizing advanced theories that have been proposed to address the limitations of the standard approach. In spite of considerable effort, there is no consensus on the reasons for departure between the standard theories and experiments.



## INTRODUCTION

Our understanding of the thermodynamic underpinnings of the phase behavior of polymer solutions and blends began with the Flory–Huggins theory.<sup>1–3</sup> In this theory, the interactions between polymer chains of one type and another are governed by a parameter that is related to interactions on the monomer length scale and chain lengths. To model polymer blends, we consider two types of monodisperse polymer chains labeled A and B, with  $N_A$  and  $N_B$  repeat units, respectively. The monomer-scale interactions are governed by a nondimensional parameter,  $\chi$ , which is traditionally called the Flory–Huggins interaction parameter.

Most of the published derivations (e.g., refs 1–3) are restricted to the derivation of the Helmholtz free energy of mixing for polymer solutions. This is usually followed by generalization to polymer blends without a formal derivation. Research articles tend to focus on the temperature dependence of phase behavior of either solutions or blends; it is rare to see both solutions and blends discussed in the same paper. In this Perspective, we take a slightly different approach. We begin with a derivation of the Flory–Huggins Gibbs free energy of mixing for polymer blends, and solutions are treated as a special case. This is followed by comparing predictions based on Flory–Huggins theory with experimentally determined phase behavior of both solutions and blends. Our use of the Gibbs free energy enables addressing both temperature- and pressure-dependent phase diagrams. We discuss the nature of concentration fluctuations as described by the

mean-field theory of de Gennes and their effect on phase behavior.<sup>4,5</sup> We conclude by discussing the limitations of the Flory–Huggins–de Gennes approach and describe attempts to address these limitations.

## FLORY–HUGGINS THEORY

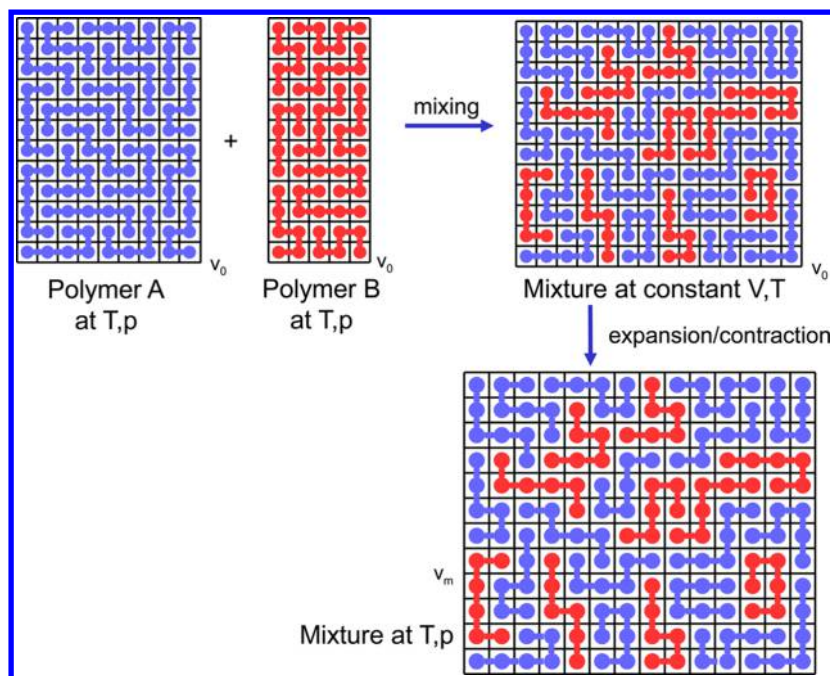
Our objective is to compute the Gibbs free energy of a homogeneous mixture of two polymers,  $\Delta G$ , relative to that of the pure polymers, following the Flory–Huggins approach.<sup>1–3</sup> The mixing process is conducted in two steps as shown in Figure 1. In the first step, the chains are mixed at constant volume ( $V$ ) and temperature ( $T$ ), and in the second step, the mixture is expanded or contracted to obtain the correct volume of the mixture, i.e., to account for the volume change of mixing. The pressure after step 1 is  $p_1$ , which will differ from  $p$  due to differences in the equations of state of the pure components and the mixture. In our analysis, we neglect the difference between  $p_1$  and  $p$ .

We begin by evaluating  $\Delta S$ , the entropy increase due to the mixing that occurs during step 1. The mixture comprises  $n_A$  indistinguishable polymer chains of type A, each with  $N_A$  segments per chain, on a lattice with  $n_t$  sites. Each segment occupies a volume  $v_0$ . The remainder of the sites are occupied by

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**Figure 1.** Schematic of mixing polymers A and B in two steps. In the first step, the polymer samples are mixed at constant  $V$  and  $T$ . The pressure after step 1 is  $p_1$ . In the second step volume of the mixture is changed to match the actual volume of the mixture at  $p$  and  $T$  of interest. The difference between  $p_1$  and  $p$  is neglected in the analysis.

polymer B; each B chain comprises  $N_B$  segments. The overall volume fractions of A and B chains,  $\phi_A$  and  $\phi_B$ , are given by  $n_A N_A / n_t$  and  $n_B N_B / n_t$ . We will assume that each lattice site has  $z$  nearest neighbors. If we label the  $n_A$  chains from 1 to  $n_A$  and sequentially place them in the lattice, then the total number of configurations is given by

$$\Omega'_A = \omega_1 \omega_2 \dots \omega_{n_A} = \prod_{j=1}^{n_A} \omega_j \quad (1)$$

where  $\omega_j$  is the number of configurations available to the  $j$ th chain.

The first monomer of the first chain has  $n_t$  possibilities. However, the second monomer only has  $z$  possibilities, as do all of the other monomers of this ideal chain.

$$\omega_1 = n_t z^{N_A - 1} \approx n_t z^{N_A} \quad (2)$$

The first monomer of the  $(j + 1)$ th chain has  $(n_t - jN_A)$  possibilities. On average, the probability of having an unoccupied neighboring site for the second monomer is  $1 - jN_A/n_t$ . Theories based on such averages are often referred to as mean-field theories. The term  $z$  in eq 2 is thus replaced by  $z(1 - jN_A/n_t)$ . Thus

$$\omega_{j+1} = (n_t - jN_A)(z(1 - jN_A/n_t))^{N_A} \quad (3)$$

The number of configurations available to indistinguishable A chains,  $\Omega_A$ , is given by  $\Omega'_A/n_A!$

$$\Omega_A = \frac{1}{n_A!} \prod_{j=1}^{n_A} n_t z^{N_A} (1 - jN_A/n_t)^{N_A} \quad (4)$$

The number of configurations that indistinguishable polymer B chains can adopt in the remaining  $n_t - N_A n_A$  sites is

$$\Omega_B = \frac{1}{n_B!} \prod_{j=1}^{n_B} n_t z^{N_B} (1 - \phi_A - jN_B/n_t)^{N_B} \quad (5)$$

The number of configurations that A chains can adopt in pure A,  $\Omega_{A,0}$ , is obtained by recognizing that a total number of sites in pure A is  $\phi_A n_t$  i.e., substituting  $\phi_A n_t$  for  $n_t$  in eq 4.

$$\Omega_{A,0} = \frac{1}{n_A!} \prod_{j=1}^{n_A} \phi_A n_t z^{N_A} \left(1 - \frac{jN_A}{\phi_A n_t}\right)^{N_A} \quad (6)$$

Similarly, the number of configurations that B chains can adopt in pure B is given by

$$\Omega_{B,0} = \frac{1}{n_B!} \prod_{j=1}^{n_B} \phi_B n_t z^{N_B} \left(1 - \frac{jN_B}{\phi_B n_t}\right)^{N_B} \quad (7)$$

and

$$\Delta S = k_B \ln \left( \frac{\Omega_A \Omega_B}{\Omega_{A,0} \Omega_{B,0}} \right) \quad (8)$$

It follows that

$$\begin{aligned} \frac{\Omega_A \Omega_B}{\Omega_{A,0} \Omega_{B,0}} &= \phi_A^{-n_A} \prod_{j=1}^{n_A} \left( \frac{1 - jN_A/n_t}{1 - jN_A/(\phi_A n_t)} \right)^{N_A} \\ &\times \phi_B^{-n_B} \prod_{j=1}^{n_B} \left( \frac{1 - \phi_A - jN_B/n_t}{1 - jN_B/(\phi_B n_t)} \right)^{N_B} \end{aligned} \quad (9)$$

and

$$\begin{aligned} \ln \frac{\Omega_A \Omega_B}{\Omega_{A,0} \Omega_{B,0}} &= -n_A \ln \phi_A - n_B \ln \phi_B \\ &+ N_A \left[ \sum_{j=1}^{n_A} \ln(1 - jN_A/n_t) - \sum_{j=1}^{n_A} \ln(1 - jN_A/(\phi_A n_t)) \right] \\ &+ N_B \left[ \sum_{j=1}^{n_B} \ln(1 - \phi_A - jN_B/n_t) - \sum_{j=1}^{n_B} \ln(1 - jN_B/(\phi_B n_t)) \right] \end{aligned} \quad (10)$$

It can be shown (see Supporting Information) that

$$N_A \left[ \sum_{j=1}^{n_A} \ln(1 - jN_A/n_t) - \sum_{j=1}^{n_A} \ln(1 - jN_A/(\phi_A n_t)) \right] = -n_t \phi_B \ln \phi_B \quad (11)$$

and

$$N_B \left[ \sum_{j=1}^{n_B} \ln(1 - \phi_A - jN_B/n_t) - \sum_{j=1}^{n_B} \ln(1 - jN_B/(\phi_B n_t)) \right] = n_t \phi_B \ln \phi_B \quad (12)$$

Equations 8 and 10 reduce to

$$\Delta S = -k_B [n_A \ln \phi_A + n_B \ln \phi_B] \quad (13)$$

because the last two terms in eq 10 cancel each other. It is easy to show that eq 13 is equivalent to the equation

$$\Delta S = -k_B n_t \left[ \frac{\phi_A}{N_A} \ln \phi_A + \frac{\phi_B}{N_B} \ln \phi_B \right] \quad (14)$$

The change in internal energy due to step 1,  $\Delta U$ , is given by the standard formula based on random mixing

$$\Delta U = n_t z \Delta \epsilon \phi_A \phi_B \quad (15)$$

where

$$\Delta \epsilon = \epsilon_{AB} - \frac{1}{2}(\epsilon_{AA} + \epsilon_{BB}) \quad (16)$$

where  $\epsilon_{AA}$ ,  $\epsilon_{BB}$ , and  $\epsilon_{AB}$  are the interaction energies between the segments. The change in the Helmholtz free energy in step 1 is  $\Delta A = \Delta U - T\Delta S$ . Combining eqs 15 and 14, we get

$$\Delta A = n_t k_B T \left[ \frac{\phi_A}{N_A} \ln \phi_A + \frac{\phi_B}{N_B} \ln \phi_B + \chi_u \phi_A \phi_B \right] \quad (17)$$

where

$$\chi_u = \frac{z \Delta \epsilon}{k_B T} \quad (18)$$

where  $\chi_u$  is the conventional Flory–Huggins interaction parameter that is related to internal energy.

The change in Gibbs free energy in step 2 is assumed to arise from  $p$ - $V$  work:

$$\Delta G_{\text{step 2}} = \Delta H_{\text{step 2}} = n_t p \Delta v \quad (19)$$

where  $\Delta v$  is the volume change of mixing per lattice site ( $v_m - v_0$ ). We assume that the dependence of  $\Delta v$  on composition is similar to that of  $\Delta U$

$$\Delta v = \eta \phi_A \phi_B \quad (20)$$

where the  $\eta$  is a parameter that is similar to  $\chi_u$ . Equation 20 is the simplest function that satisfies the constraint that the volume change of mixing must approach zero as  $\phi_A$  or  $\phi_B$  approaches zero.

The Gibbs free energy change for steps 1 and 2 is obtained by summing the contributions from the individual steps:

$$\Delta G = \Delta U - T\Delta S + \Delta H_{\text{step 2}} \quad (21)$$

or

$$\Delta G = n_t k_B T \left[ \frac{\phi_A}{N_A} \ln \phi_A + \frac{\phi_B}{N_B} \ln \phi_B + \chi \phi_A \phi_B \right] \quad (22)$$

where

$$\chi = \chi_u + \eta p / (k_B T) \quad (23)$$

Empirically it has been found that  $\chi_u$  is often a linear function of  $1/T$ :

$$\chi_u = A + \frac{B}{T} \quad (24)$$

In some cases  $\chi_u$  is a nonmonotonic function of  $1/T$ . In this case, one could use an expression of the form

$$\chi_u = A + \frac{B}{T} + \frac{C}{T^2} \quad (25)$$

While eq 24 is often used in the literature, there is no consensus on the expression that must be used in case the  $\chi$  versus  $1/T$  plot is not linear. In theory, this term will depend on the temperature dependence of the difference between the specific heats at constant pressure,  $C_p$ , of the pure components and the mixture,  $\Delta C_p$ , as  $\partial(\Delta H)/\partial T = \Delta C_p$ . Equation 24 is obtained when  $\Delta C_p$  is a constant. Equation 25 is obtained when the temperature dependence of  $\Delta C_p$  is dominated by a term proportional to  $1/T^2$ .<sup>6,7</sup> The full expression for  $\chi$  is

$$\chi = A + \frac{B}{T} + \frac{C}{T^2} + D \frac{p}{T} \quad (26)$$

where  $D = \eta/k_B$ . Parameters  $A$ ,  $B$ ,  $C$ , and  $D$  are obtained by fitting experimental data. In some cases, eq 26 must be augmented by other terms involving  $p$  alone or combinations of  $p$  and  $T$ ; for example, in ref 8 a term proportional to  $p$  is necessary to fit the data.

We illustrate the application of the Flory–Huggins theory by focusing on four specific systems: polystyrene/cyclohexane (PS/C6), poly(ethylene oxide)/water (PEO/H2O), polyisobutylene/deuterium-saturated polybutadiene with 63 mol % 1–2 units (PIB/DPB), and polyethylenebutylene/deuterium-labeled polymethyl butylene (PEB/DPMB). (In the DPB sample, the double bonds in the polybutadiene are saturated with deuterium gas to obtain a saturated hydrocarbon polymer.) The chemical structures of the components of interest are shown in Table 1. We also provide the volumes of the solvent molecules and monomers that we have used in our calculations. Parameters  $A$ ,  $B$ ,  $C$ , and  $D$  are given in Table 2. The approaches used to determine these parameters are discussed below.

The list of solvents and polymers in Table 1 is far from exhaustive. For the sake of brevity, important systems such as blends of polyethylene, propylene, and their copolymers,<sup>9</sup> natural rubber/benzene,<sup>10</sup> poly(isopropyl acrylate)/poly(isopropyl methacrylate),<sup>11</sup> and polystyrene/poly(vinyl methyl ether)<sup>12</sup> are not discussed.

Typical values of  $\Delta v/v_0$  range from  $10^{-4}$  to  $10^{-3}$  (e.g., refs 13 and 14), and thus the pressure-dependent term in eq 26 is typically unimportant when the pressure of interest is less than 0.1 kbar. Most of the experiments on polymer blends reported in the literature were conducted at atmospheric pressure.

If one takes Flory–Huggins theory literally, then  $\chi_u$  is given by eq 18, and  $A$  and  $C$  in eq 26 must be zero. It is apparent from Table 2 that this is seldom the case. The parameter  $A$  is often called the noncombinatorial entropic contribution to  $\chi$ . The rationale is simple: we have already assumed that the monomer-level

Table 1. Components and Monomer Volumes<sup>a</sup>

Component	Formula	$v_i$ (nm <sup>3</sup> )	$T$ (K)
PS		0.163	280
C6		0.177	280
PEO		0.071	450
H2O		0.034	450
PIB		0.109	413
DPB		0.117	413
PEB		0.162	300
DPMB		0.136	300

<sup>a</sup>Properties of the components of the polymer solution and blend systems examined in this paper: chemical formulas, monomer volumes,  $v_i$ , and the temperature,  $T$ , at which  $v_i$  values were determined. In the deuterated polymers, the locations of the D atoms are not known precisely.

Table 2. Flory–Huggins Interaction Parameters and Reference Volumes<sup>a</sup>

entry	system	$v_0$ (nm <sup>3</sup> )	$A$	$B$ (K)	$C$ (K <sup>2</sup> )	$D$ (K/kbar)	method
1	PEO/H2O	0.034	1.054	-200.4		7.183	PB
2	PS/C6	0.177	-0.3204	252.5			PB
3	PEO/H2O	0.034	-1.315	1782.2	-414008		PB
4	PIB/DPB	0.100	0.0150	-5.468			PB
5	PIB/DPB	0.100	0.0196	-7.467		-0.1314	NS
6	PEB/DPMB	0.100	0.0025	-1.929	446.01		NS

<sup>a</sup>Constants for calculating the Flory–Huggins interaction parameter,  $\chi$ , of the polymer solution and blend systems examined in this paper.  $v_0$  is the reference volume, the coefficients of Eq 26 that give the dependence of  $\chi$  on  $p$  and  $T$ , and the method used to determine  $\chi$  (phase boundaries or neutron scattering).

change of energy and volume due to mixing is of the form  $\phi_A(1 - \phi_A)$ . One could similarly assume that monomer-level differences in packing between the mixture and pure components is also given by a similar expression with  $A$  as the prefactor. While UCST behavior can be predicted even if  $A$  is 0 (or approximately so, see PS/C6 system data, entry 2, in Table 2) prediction of LCST behavior requires a nonzero value of  $A$  (see PEO/water system data, entry 1, in Table 2). Within the context of Flory–Huggins theory, nontrivial local entropic effects are essential for obtaining LCST behavior. The term  $C$  is obtained when the temperature dependence of the heat capacities of the mixture and pure components exhibits a nonlinear dependence on  $T$ .<sup>6</sup>

In the Flory–Huggins theory, the entropy of mixing,  $\Delta S$ , is always positive. Phase behavior is thus determined by the sign of  $\Delta U$ .  $\chi_w$  or equivalently  $\Delta\epsilon$ , can be either positive or negative (eq 16). In the case of positive  $\Delta\epsilon$ ,  $\epsilon_{AB} > (\epsilon_{AA} + \epsilon_{BB})/2$ , the interactions between unlike segments are unfavorable relative to those between like segments. These mixtures tend to be phase-separated at low temperatures. One-phase systems are obtained when the temperature is high enough for  $T\Delta S$  to dominate over  $\Delta U$ . In the case of negative  $\Delta\epsilon$ ,  $\epsilon_{AB} < (\epsilon_{AA} + \epsilon_{BB})/2$ , the interactions between unlike segments are favorable relative to those between like segments. These mixtures tend to be homogeneous at low temperatures, as both internal-energy-related and entropy-related terms favor mixing. Phase-separated systems are obtained at temperatures when the  $\Delta\epsilon/T$  contribution to  $\chi$  is small.

Depending on the composition of the mixture ( $\phi_A$ ,  $N_A$ , and  $N_B$ ) and  $\chi$ , a blend can be either single-phase or separated into two phases. One can distinguish between these scenarios by examining the chemical potentials of components A and B,  $\mu_A$  and  $\mu_B$ , with respect to those of the pure phases,  $\mu_A^0$  and  $\mu_B^0$ .<sup>6</sup>

$$\Delta\mu_A = \mu_A - \mu_A^0 = N_{AV} \frac{\partial \Delta G}{\partial n_A} \quad (27)$$

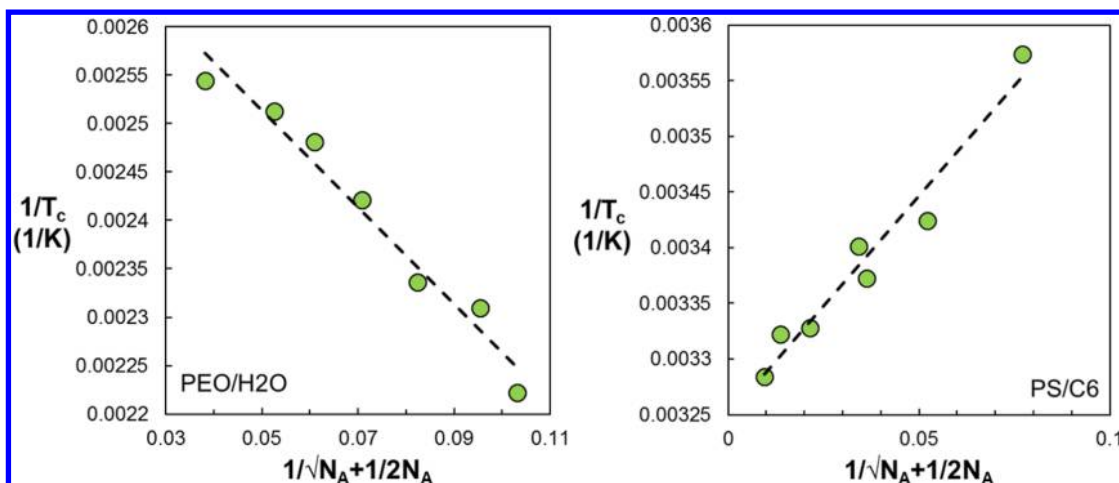
$$\Delta\mu_B = \mu_B - \mu_B^0 = N_{AV} \frac{\partial \Delta G}{\partial n_B} \quad (28)$$

where  $N_{AV}$  is Avogadro's number and  $R$  (used below) is the universal gas constant. Equations 22, 27, and 28 give

$$\Delta\mu_A = RT \left[ \ln \phi_A + (1 - \phi_A) \left( 1 - \frac{N_A}{N_B} \right) + N_A \chi (1 - \phi_A)^2 \right] \quad (29)$$

$$\Delta\mu_B = RT \left[ \ln \phi_B + (1 - \phi_B) \left( 1 - \frac{N_B}{N_A} \right) + N_B \chi (1 - \phi_B)^2 \right] \quad (30)$$

For phase-separated blends, the binodal curve, i.e., the locus of compositions of the two phases in thermodynamic equilibrium



**Figure 2.** (a) Lower critical solution temperature,  $T_c$ , for poly(ethylene oxide)/water (PEO/H<sub>2</sub>O) from Bae et al.,<sup>17</sup> Saeki et al.,<sup>18</sup> and Saraiva et al.<sup>19</sup> and (b) upper critical solution temperature,  $T_c$ , for poly(styrene)/cyclohexane (PS/C6) from Bae et al.<sup>17</sup> and Shultz and Flory<sup>20</sup> as a function of the number of monomers per chain,  $N_A$ . The dashed lines are linear fits through the data, consistent with eq 39.

with each other, can be obtained by equating the chemical potential of polymers A and B in the two coexisting phases

$$\mu_A^I = \mu_A^{II} \quad \mu_B^I = \mu_B^{II}$$

or by subtracting the chemical potentials of the pure phases

$$\mu_A^I - \mu_A^0 = \mu_A^{II} - \mu_A^0 \quad \mu_B^I - \mu_B^0 = \mu_B^{II} - \mu_B^0$$

The binodal curve is thus given by

$$\ln \left[ \frac{\phi_A^I}{\phi_A^{II}} \right] + (\phi_A^{II} - \phi_A^I) \left( 1 - \frac{N_A}{N_B} \right) + \chi N_A [(1 - \phi_A^I)^2 - (1 - \phi_A^{II})^2] = 0 \quad (31)$$

$$\ln \left[ \frac{1 - \phi_A^I}{1 - \phi_A^{II}} \right] - (\phi_A^{II} - \phi_A^I) \left( 1 - \frac{N_B}{N_A} \right) + \chi N_B [(\phi_A^I)^2 - (\phi_A^{II})^2] = 0 \quad (32)$$

Equations 31 and 32 are solved numerically to obtain the two quantities of interest. If  $\chi$  is known, then  $\phi_A^I$  and  $\phi_A^{II}$  can be determined. If  $\phi_A^I$  is known, then  $\chi$  and  $\phi_A^{II}$  can be determined. Examples of both types of calculations are given in this Perspective.

The critical point is conveniently obtained by setting the second and third derivatives of  $\Delta G$  with respect to  $\phi_A$  to zero. At the critical point

$$\chi_c = \frac{2}{N_{\text{AVG}}} \quad (33)$$

where  $\chi_c$  is the value of  $\chi$  at the critical point and

$$N_{\text{AVG}} = \frac{4}{\left( \frac{1}{\sqrt{N_A}} + \frac{1}{\sqrt{N_B}} \right)^2} \quad (34)$$

For polymer solutions, we set  $N_B = 1$ , and  $\chi_c$  is given by

$$\chi_c = \frac{1}{2} \left( 1 + \frac{1}{\sqrt{N_A}} \right)^2 \quad (35)$$

## DEFINITIONS OF MONOMERS AND REFERENCE VOLUMES

Both Flory and Huggins recognized that the monomers in the Flory–Huggins theory were unrelated to the chemical repeat units in the chains. In the discussion above, the chains are assumed to comprise monomers of volume  $v_0$ . We refer to  $v_0$  as the reference volume. When we describe polymer/solvent mixtures,  $v_0$  is set to the volume of a solvent molecule (molar volume divided by Avogadro's number) due to the assumption that  $N_B = 1$ . When we describe mixtures of two polymers, it is convenient to fix the reference volume; this enables comparison of the interactions between different pairs of chains on a common basis. In this paper, we set  $v_0 = 0.1 \text{ nm}^3$  for polymer blends. If the polymer chain comprises  $\hat{N}_i$  chemically identical repeat units each with volume  $v_i$ , then  $N_i$  is given by

$$N_i = \hat{N}_i \frac{v_i}{v_0} \quad (36)$$

where  $i = A$  or B.

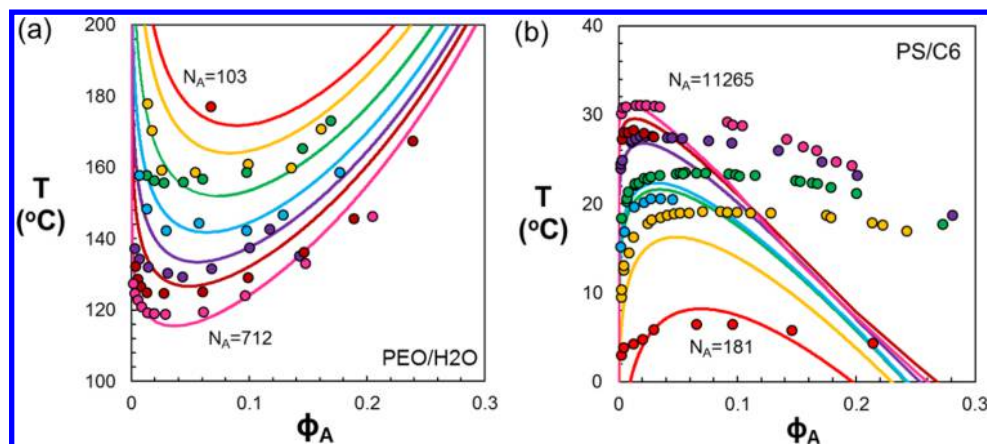
It is important to recognize that the Flory–Huggins Gibbs free energy of mixing (eq 22) does not explicitly depend on the value of  $v_0$ . However, the value of  $\chi$  that is reported depends on the chosen value of  $v_0$ . Since  $\chi$  is proportional to  $v_0$ , some may prefer to report  $\chi/v_0$ . However, even in this case, defining  $v_0$  is necessary. If  $v_0$  is not defined, then the relationship between  $\hat{N}_i$  and  $N_i$  is unknown. We thus recommend reporting both  $\chi$  and  $v_0$  when presenting data on the thermodynamics of polymer mixtures.

While we have used a lattice model to derive the Flory–Huggins free energy of mixing, as was done originally by Flory and Huggins, modern treatments have shown that the same expression can be obtained using off-lattice theories.<sup>15,16</sup> We also note in passing that defining  $v_0$  that is independent of  $T$  and  $p$  is essential for consistency between the Flory–Huggins theory and the stringent thermodynamic requirements that

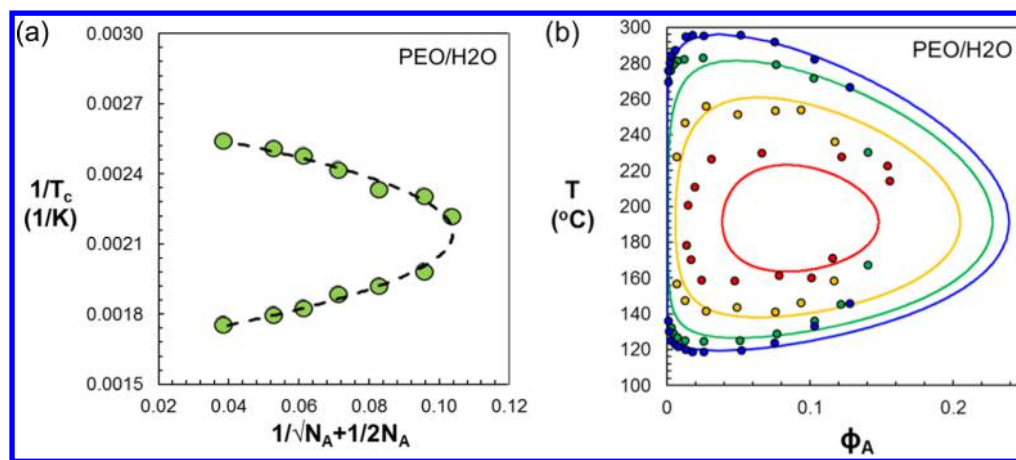
$$\left( \frac{\partial(\Delta G/T)}{\partial T} \right)_p = -\frac{\Delta H}{T^2} \quad (37)$$

and

$$\left( \frac{\partial \Delta G}{\partial p} \right)_T = \Delta V \quad (38)$$



**Figure 3.** Theoretical (curves) and experimental (markers) phase diagrams for (a) poly(ethylene oxide)/water (PEO/H<sub>2</sub>O) for  $N_A = 103$  (red),  $N_A = 120$  (yellow),  $N_A = 159$  (green),  $N_A = 213$  (blue),  $N_A = 285$  (purple),  $N_A = 380$  (maroon), and  $N_A = 712$  (pink) and (b) poly(styrene)/cyclohexane (PS/C6) for  $N_A = 181$  (red),  $N_A = 387$  (yellow),  $N_A = 789$  (green),  $N_A = 887$  (blue),  $N_A = 2218$  (purple),  $N_A = 5411$  (maroon),  $N_A = 11265$  (pink), using the fits reported in Figure 2. The data and curves correspond to the binodals (see eqs 31 and 32), and phase-separated regions are bounded by the convex curves.



**Figure 4.** (a) Both upper and lower critical solution temperatures,  $1/T_c$ , as a function of the number of monomers per chains,  $N_A$ , and (b) the resulting theoretical (curves) and experimental (markers) phase diagram for poly(ethylene oxide)/water (PEO/H<sub>2</sub>O) at  $N_A = 120$  (red),  $N_A = 213$  (yellow),  $N_A = 380$  (green), and  $N_A = 712$  (blue). The dashed curve in (a) is a quadratic fit through the data, consistent with eq 40.

where  $\Delta H$  is the enthalpy change of mixing.<sup>6</sup> For similar reasons, accounting for subtle changes in  $N_i$  with temperature and pressure is outside the scope of the Flory–Huggins theory.

### ■ EXPERIMENTS ON PHASE BEHAVIOR OF POLYMER SOLUTIONS AND BLENDS

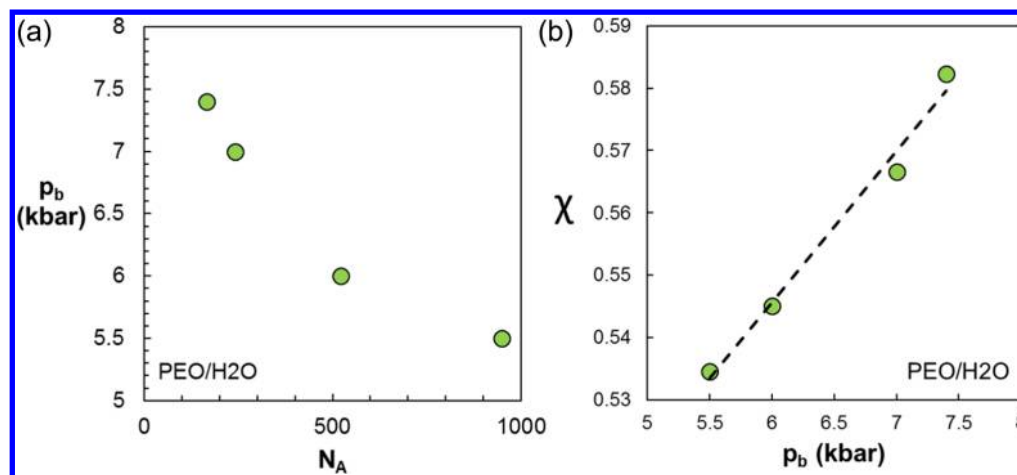
It is generally assumed that properties of polymer systems can be predicted using two sets of parameters: one set on the monomer length scale (independent of  $N_i$ ) and the other on length scales of the polymer chains (dependent on  $N_i$  only). The decoupling of these two sets is an important simplification that pervades polymer science. In the Flory–Huggins theory, the parameter that describes behavior on the monomer length scale is  $\chi$ , and the parameter that describes behavior on the chain length scale is  $N_i$ . A unique advantage polymer scientists have enjoyed is the ability to test molecular theories by conducting experiments as a function of chain length.

In Figures 2a and 2b we show the dependence of the critical temperature,  $T_c$ , on  $N_A$  for PEO/H<sub>2</sub>O and PS/C6 solutions.<sup>17–20</sup> The dependence of  $T_c$  on  $N_A$ , derived from eqs 24 and 35, is

$$A + \frac{B}{T_c} = \frac{1}{2} + \frac{1}{\sqrt{N_A}} + \frac{1}{2N_A} \quad (39)$$

The Flory–Huggins theory predicts that a plot of  $1/T_c$  versus  $1/(2N_A) + 1/\sqrt{N_A}$  for polymer solutions should be linear. This is approximately true for both polymer solutions (Figures 2a and 2b). The data are, however, qualitatively different in the two cases because PS/C6 mixtures phase separate upon cooling while PEO/H<sub>2</sub>O mixtures phase separate upon heating. These critical temperatures are referred to as upper critical solution temperatures (UCST) and lower critical solution temperatures (LCST), respectively. The lines in Figure 2 represent least-squares fits of eq 39 which give values of  $A$  and  $B$ ; we assume  $C = 0$  as this is consistent with the data in entries 1 and 2 in Table 2. The parameter  $B$  is positive for PS/C6, while it is negative for PEO/H<sub>2</sub>O.

The determination of  $A$  and  $B$  enables prediction of the phase behavior of PS/C6 and PEO/H<sub>2</sub>O mixtures as a function of chain length. The compositions of the coexisting phases as a function of temperature are determined by solving eqs 31 and 32 numerically. The experimental and theoretical phase diagrams for PS/C6 and PEO/H<sub>2</sub>O mixtures are compared in Figure 3. We see quantitative agreement between the Flory–Huggins theory and experiment in the case of PEO/H<sub>2</sub>O (Figure 3a). Deviations between theory and experiment are more substantial in PS/C6 solutions: the experimental boundaries of



**Figure 5.** (a) Binodal pressure,  $p_b$ , as a function of the number of monomers per chain,  $N_A$ , for mixtures with  $\phi_A^I = 0.05$  and  $T = 23$  °C. (b) Flory–Huggins interaction parameter,  $\chi$ , as a function of binodal pressure,  $p_b$ , for poly(ethylene oxide)/water (PEO/H2O) from Cook et al.<sup>21</sup> The dashed line is a linear fit through the data.

the two-phase mixtures are broader than theoretical predictions (Figure 3b).

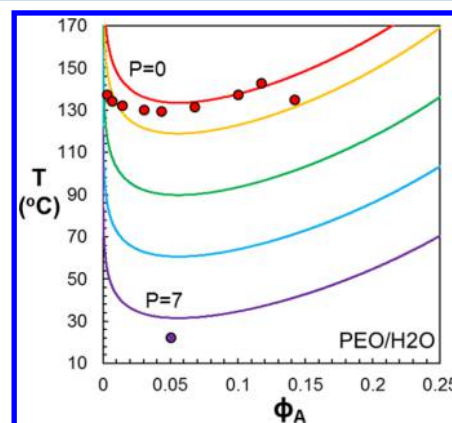
In Figure 2a, we focused on PEO/H2O data obtained over a limited temperature range. In Figure 4a we show the dependence of the critical temperature on chain length of the same mixtures over an extended temperature range. It is evident that in the high temperature regime heating results in homogenization. The opposite is seen in the low temperature regime. Modeling such data requires use of eq 25:

$$A + \frac{B}{T_c} + \frac{C}{T_c^2} = \frac{1}{2} + \frac{1}{\sqrt{N_A}} + \frac{1}{2N_A} \quad (40)$$

The curve in Figure 4a is a fit of eq 40 through the data that enables determination of  $A$ ,  $B$ , and  $C$ , and the parameters thus obtained are given in entry 3 of Table 2. The comparison of experimental and theoretical phase behavior of PEO/H2O systems over the full temperature range is shown in Figure 4b. The deviations between theory and experiment in the vicinity of both lower and upper critical temperatures are similar and rather small.

There are relatively few studies of the effect of pressure on the phase behavior of polymer solutions. In ref 21, Cook et al. determined the pressure at which PEO/H2O mixtures with  $\phi_A^I = 0.05$  and with different  $N_A$  values exhibited a transition from single-phase to two-phase systems; the temperature was held fixed at 23 °C. Their results are shown in Figure 5a where the binodal pressure  $p_b$  is plotted as a function of  $N_A$ . For each mixture, we used eqs 31 and 32 to determine  $\chi$  and  $\phi_A^II$ , and we were thus able to determine  $\chi$  as a function of  $p$ . This plot is shown in Figure 5b, and the slope of the line in that figure enables determination of  $D$ . The pressure dependence of the phase boundary of PEO/H2O mixtures with  $N_A = 285$  is shown in Figure 6 along with experimental data; ref 21 provides one data point at elevated pressures. The agreement between theory and experiment is better at large values of  $N_A$ .

One of the convenient features of polymer/solvent mixtures is that the critical temperature is a weak function of chain length. In the PS/C6 case, for example, changing the chain length by a factor of about 60 increased the absolute critical temperature by only a factor of 1.08 (from 278 to 303 K). It is much more challenging to study the phase behavior of polymer blends as a function of chain length as the critical temperature is a sensitive function of chain length. For the simple case of  $N_A = N_B$  and  $\chi = A/T$ , doubling



**Figure 6.** Theoretical (curves) and experimental (markers) phase diagram for poly(ethylene oxide)/water (PEO/H2O) at  $N_A = 285$  and  $T = 23$  °C at different pressures:  $p = 0$  kbar (red),  $p = 1$  kbar (yellow),  $p = 3$  kbar (green),  $p = 5$  kbar (blue), and  $p = 7$  kbar (purple).

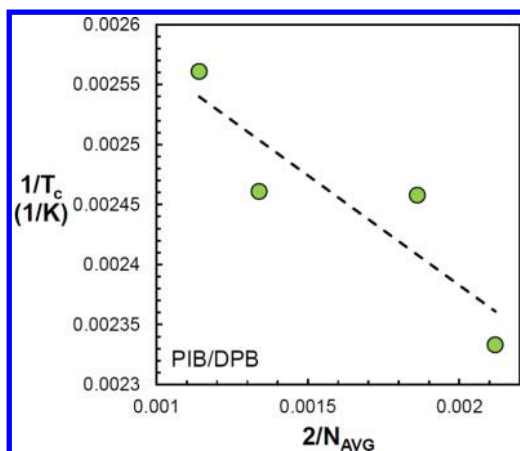
the chain length would double the absolute critical temperature. Since the Flory–Huggins theory is applicable to liquid polymers at equilibrium, the low temperature limit is dictated by the crystallization or glass transition temperatures of the mixtures. The upper limit is governed by the chain degradation temperature. The available temperature range for thermodynamic study is seldom larger than 200 °C. Consequently, there are relatively few examples of phase diagrams of polymer blends for a wide range of  $N_A$  and  $N_B$ . The parameter space for polymer blends is much larger than that for polymer solutions as many combinations of  $N_A$  and  $N_B$  could be used to obtain a single value of  $N_{AVG}$ .

In Figure 7, we plot  $1/T_c$  versus  $2/N_{AVG}$  for the PIB/DPB blends (entry 4, Table 2) taken from ref 22. To our knowledge, this is the only blend system of high molecular weight polymers where  $T_c$  is measured over a significant range of  $N_{AVG}$ , keeping chemical structure of the blend components fixed. The range of  $1/T_c$  values for this system is similar to that in Figure 2 for polymer/solvent systems, but the range of  $N_{AVG}$  is limited for reasons discussed above. Using the same approach that we used for solutions, we obtain

$$A + \frac{B}{T_c} = \frac{2}{N_{AVG}} \quad (41)$$

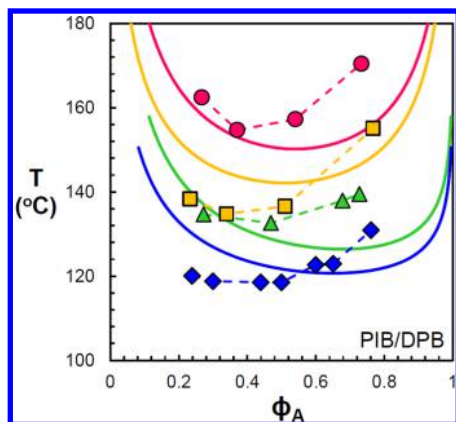
and linear fits through the data in Figure 7 enable determination of  $A$  and  $B$ . The values of  $A$  and  $B$  thus obtained are given in





**Figure 7.** Lower critical solution temperature,  $T_c$ , as a function of average chain length,  $N_{AVG}$ , defined by eq 34, for poly(isobutylene)/deuterium-saturated polybutadiene (PIB/DPB) from Nedoma et al.<sup>22</sup> The dashed line is a linear fit through the data, consistent with eq 41.

entry 4 of Table 2. The compositions of the coexisting phases as a function of temperature were determined by solving eqs 31 and 32 numerically for the parameters listed in Table 2. The experimental and theoretical phase diagrams for PIB/DPB mixtures are compared in Figure 8. It is evident that the phase



**Figure 8.** Theoretical (lines) and experimental (markers) phase diagram for poly(isobutylene)/deuterium-saturated polybutadiene (PIB/DPB) system (PIB = A and DPB = B) for four different blends:  $N_A = 810$ ,  $N_B = 1120$  (circles),  $N_A = 1030$ ,  $N_B = 1120$  (squares),  $N_A = 810$ ,  $N_B = 3589$  (triangles), and  $N_A = 1030$ ,  $N_B = 3589$  (diamonds). Data obtained from ref 22.

behavior of the four blends is only in qualitative agreement with the Flory–Huggins theory. We note in passing that the anomalous mixing behavior of PIB and other polyolefins was first noted by Krishnamoorti et al.<sup>23</sup>

One of the limitations of using the measured phase boundaries to estimate  $\chi$  is that  $\chi$  at the phase boundaries is always positive. It is evident from the values of A and B given in Table 2 that there are ranges of T where  $\chi$  is predicted to be negative. For the PIB/DPB blends,  $\chi$  is negative at temperatures below 90 °C. Probing thermodynamics in this regime requires study of single-phase systems.

It is well-known that concentration fluctuations in the one-phase region contain signatures of intermolecular interactions. This is especially true in the vicinity of the critical point,<sup>24</sup> and neutron scattering is a standard approach for studying these fluctuations in polymer blends. In pioneering work, de Gennes derived an expression for the scattered intensity from a homogeneous

mixture of polymers.<sup>4,5</sup> This theory, like the Flory–Huggins theory, is a mean-field theory. One advantage of this approach is that the T and p dependence of  $\chi$  can be obtained from temperature- and pressure-dependent experiments on one single-phase blend; phase-boundary-based methods require the preparation of several samples. Usually researchers choose the critical composition as the signal is strongest at this composition. The results of pioneering experiments using this approach are reported in refs 25–32. The  $\chi$  parameter determined using this approach for the PIB/DPB system as a function of 1/T at p = 0 is shown in Figure 9a, and the resulting values of A and B are given in entry 5 of Table 2.<sup>33</sup> It is interesting to contrast the wide range of positive and negative  $\chi$  parameters covered by Figure 9a with the narrow range of positive values covered in Figure 7. In spite of this, the A and B values determined by the two methods are similar (see PB and NS values of A and B for PIB/DPB blends, entries 4 and 5 of Table 2). In Figure 9b, we show the pressure and temperature dependence of  $\chi$  for p ranging from 0 to 3.1 kbar and T ranging from 30 to 167 °C. A reasonable collapse of the data is seen when  $\chi - A - B/T$  is plotted versus p/T, as suggested by eq 26. The slope of the linear fit in Figure 9b gives D.

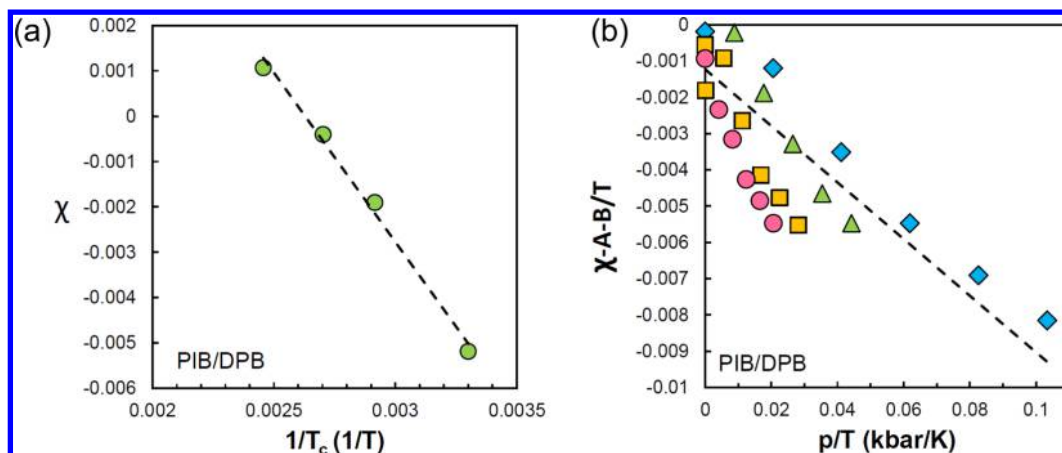
The predicted phase behavior of PIB/DPB blends with particular values of  $N_A$  and  $N_B$  as a function of T and p is shown in Figure 10. Here we cannot offer any comparison with experimental data; phase boundaries for this system have only been determined at atmospheric pressure (Figure 5).

While the data in Figure 9 were obtained from a particular homogeneous blend, i.e., particular values of  $\phi_A$ ,  $N_A$ , and  $N_B$ , one could repeat the measurements for several other blends. If the mean-field theories were accurate, then  $\chi$  measured from different blends at a given T and p would be identical. In most experiments,  $\chi$  obtained from different blends differ substantially. For the PIB/DPB blends,  $\chi$  obtained from such experiments could be empirically fit to the equation<sup>22</sup>

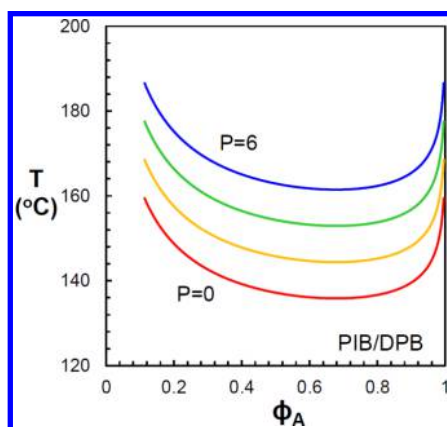
$$\chi(T, \phi_A, N_{AVG}) = -0.00622 + \frac{10.6}{T} - \frac{3040}{T^2} + \left[ -0.722 + \frac{638}{T} - \frac{229000}{T^2} \right] \frac{2\phi_A - 1}{N_{AVG}} \quad (42)$$

It was shown in ref 22 that using this expression results in excellent agreement between the predicted and measured phase boundaries. However, a particularly dissatisfying aspect of eq 42 is that the monomer length scale parameter  $\chi$  appears to be related to the chain length scale parameter,  $N_{AVG}$ . This is mainly a reflection of the fact that a quantitative understanding of concentration fluctuations and phase boundaries in polymer blends is lacking.

As a rule,  $\chi$  determined from polymer blends with different chain lengths and composition differ substantially from one another. For example, the simplest model system one can imagine is a blend of deuterated and nondeuterated polymers that are otherwise identical. The thermodynamic properties of such blends were examined in the pioneering work of Bates and co-workers.<sup>34</sup> Even in this system  $\chi$  was strongly dependent on blend composition.<sup>35</sup> The exception to the rule is poly(ethylbutylene)/deuterium-labeled poly(methylbutylene) (PEB/DPMB), entry 6 of Table 2.<sup>8</sup>  $\chi$  obtained from neutron scattering from homogeneous blends with different values of  $N_A$ ,  $N_B$ , and  $\phi_A$  are within experimental error. In Figure 11a, we show measurements of  $\chi$  for this system as a function of temperature for p = 0.01 and 0.86 kbar. At both pressures,  $\chi$  is independent of blend composition. The values of A, B, and C for this system, given in Table 2, were obtained by fitting the p = 0.01 kbar



**Figure 9.** (a) Flory–Huggins interaction parameter,  $\chi$ , as a function of inverse temperature,  $T$ , for poly(isobutylene)/deuterium-saturated polybutadiene (PIB/DPB) at atmospheric pressure ( $p = 0$ ). (b) Flory–Huggins interaction parameter,  $\chi - A - B/T$ , as a function of  $p/T$ , at  $T = 30^\circ\text{C}$  (circles),  $T = 70^\circ\text{C}$  (squares),  $T = 110^\circ\text{C}$  (triangles), and  $T = 150^\circ\text{C}$  (diamonds) from Ruegg et al.<sup>33</sup> The dashed lines are linear fits through the data.

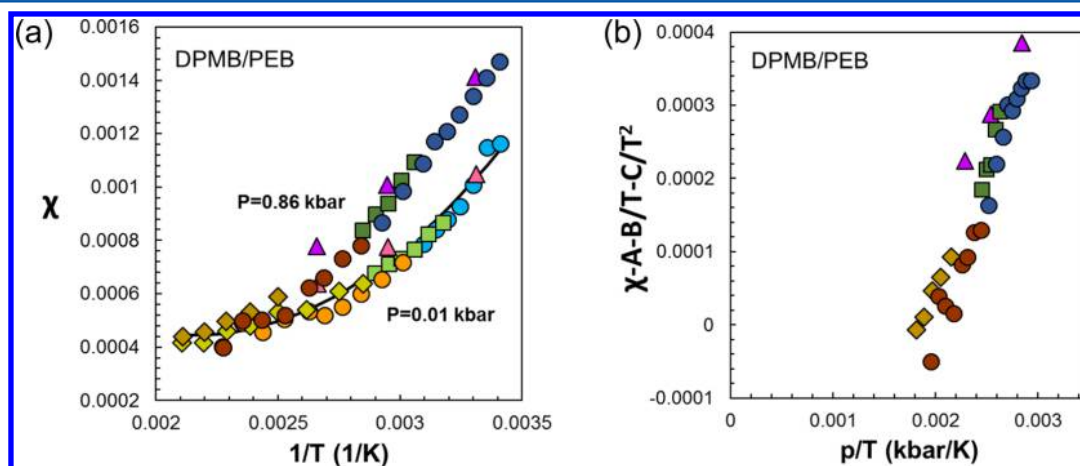


**Figure 10.** Theoretical phase diagrams for poly(isobutylene)/deuterium-saturated polybutadiene (PIB/DPB) at  $N_A = 810$ ,  $N_B = 3589$ , and  $T = 23^\circ\text{C}$  at different pressures:  $p = 0$  kbar (red),  $p = 2$  kbar (yellow),  $p = 4$  kbar (green), and  $p = 6$  kbar (blue).

data. In Figure 11b, we plot  $\chi - A - B/T - C/T^2$  obtained at  $p = 0.86$  kbar as a function of  $p/T$ . This is similar in spirit to

Figure 9b for the PIB/DPB system. As expected, the data in Figure 11b fall approximately on a straight line. It is worth noting, however, that unlike the case of the PIB/DPB blends, the data in Figure 11b do not go through the origin. This indicates that additional  $p$ -dependent terms are needed in eq 26. Within the context of eq 38, this is expected when  $\Delta V$  is dependent on  $T$  and  $p$ . Quantifying the thermodynamics of such systems is outside the scope of this Perspective. The fact that more than one parameter is needed to quantify the pressure dependence of  $\chi$  is not surprising, given that three parameters to describe the temperature dependence of  $\chi$  (at atmospheric pressure) in some cases. Another point worth noting is that  $\chi$  of PEB/DPMB blends increases with increasing pressure while the opposite is true for PIB/DPB blends. The phase-separation temperatures (and pressures) for PEB/DPMB blends have only been determined in a few cases, and these points are consistent with  $\chi$  determined from neutron scattering.<sup>36</sup>

In PIB/DPB blends (an LCST system) increasing pressure stabilizes the one-phase system (Figures 9 and 10), in contrast to PEB/DPMB blends where the opposite is observed (Figure 11). It is evident in Table 2 that for blends the sign of  $D$ , the parameter



**Figure 11.** (a) Flory–Huggins interaction parameter,  $\chi$ , as a function of inverse temperature,  $1/T$ , and (b) the reduced value  $\chi - A - B/T - C/T^2$  as a function of  $p/T$  for deuterated poly(ethylbutylene)/poly(methylbutylene) (PEB/DPMB) from Lefebvre et al.<sup>8</sup> Data at  $p = 0.01$  kbar from the one-phase region at  $\phi_A = 0.414$  (pink triangles),  $\phi_A = 0.161$  (yellow diamonds), and  $\phi_A = 0.099$  (orange circles) and data from the metastable two-phase region at  $\phi_A = 0.161$  (green squares) and  $\phi_A = 0.099$  (blue circles). Data at  $p = 0.86$  kbar from the one-phase region at  $\phi_A = 0.414$  (purple triangles),  $\phi_A = 0.161$  (mustard diamonds), and  $\phi_A = 0.099$  (maroon circles) and data from the metastable two-phase region at  $\phi_A = 0.161$  (forest squares) and  $\phi_A = 0.099$  (navy circles).

that quantifies volume change of mixing, appears to be related to the sign of  $\chi_w$ , the parameter that quantifies internal energy change of mixing. We offer a simple explanation for this observation. Attractive monomer–monomer energetic interactions (negative  $\chi_u$ ) are naturally accompanied by negative volume changes in mixing (negative  $D$ ). In this case,  $v_m$  (see Figure 1) is slightly smaller than  $v_0$ . Similarly when  $\chi_u$  is positive,  $v_m$  is slightly larger than  $v_0$ . Imre et al.<sup>37</sup> noted that the effect of pressure on polymer solutions differs qualitatively from that on polymer blends: in polymer solutions, increasing pressure usually stabilizes the homogeneous phase in both UCST and LCST systems. The PEO/H<sub>2</sub>O system (Figure 6) is an exception rather than the rule. More work is needed to obtain a comprehensive understanding of the molecular factors that govern the phase behavior of blends and solutions as a function of composition, temperature, and pressure.

In summary, the Flory–Huggins theory, developed in 1942, is remarkable: the phase behavior of a wide variety of polymer solutions and blends can be predicted with reasonable accuracy using a simple framework. All of the data in Figures 2–11 can be reproduced using two simple tables (Tables 1 and 2) and one easily derivable equation (eq 22). Over the past 50 years, this theory has provided the bedrock for interpretation of experimental data. It has, however, proven difficult to establish the molecular underpinnings of the measured  $\chi$  parameters. Numerous researchers have proposed approaches to go beyond Flory–Huggins theory. A few of these approaches are discussed below.

## ■ OTHER THEORIES FOR POLYMER SOLUTIONS

A class of theories that has gained significant acceptance in the broader community are referred to as equation-of-state theories. This approach was pioneered by Flory, Orwoll, and Vrij<sup>38</sup> in 1964. They argued that the properties of mixtures must be affected by the  $pVT$  properties (equations of state) of the pure components. Rigorous thermodynamic arguments were presented to assert that dissimilarity in equations of state of the components would give rise to phase separation. This approach provides a rational explanation for the LCST behavior of mixtures of normal paraffin hydrocarbons (oligomeric linear polyethylene) and alkane solvents such as octane. It is, perhaps, noteworthy that LCST behavior is not only observed in exotic mixtures like PEO/H<sub>2</sub>O.

A widely accepted equation-of-state model was that proposed by Sanchez and Lacombe<sup>39–41</sup> in 1976. This model maintains the lattice shown in Figure 1, but a key third component is introduced: voids. The application of pressure on both the pure components and the mixture squeezes out the voids, and the extent to which they are squeezed out depends on intermolecular interactions. While a significant number of parameters are required by the Sanchez–Lacombe model, most of them are related to the  $pVT$  properties of the pure components, and extensive tabulations of Sanchez–Lacombe parameters have been published.<sup>41</sup> There are fundamental differences between the  $pVT$  properties of solvents and polymers. For example, solvents have finite vapor pressures while the vapor pressure of polymers is negligible. It is interesting to note that this is captured by the Sanchez–Lacombe equation of state: the vapor pressure of a pure polymeric liquid approaches zero as the chain length approaches infinity. There is thus a correlation between the critical temperature of the solvent and observations of LCST behavior. LCSTs are observed well below the critical temperature as only modest differences in  $pVT$  properties are required to induce phase separation. Nevertheless, LCSTs are often found

above the normal boiling point of the solvent; see Figure 3 for example. (The small pressures needed to keep the solvent from boiling have a negligible effect on mixture thermodynamics.) Other popular equation-of-state theories are the statistical associating fluid theory (SAFT) and the theory of Patterson.<sup>42–44</sup>

Bekiranov et al.<sup>45</sup> developed an extension of Flory–Huggins theory wherein solvent monomers stick to the polymer chain. The picture provided in Figure 1 is still applicable, but now the solution contains many additional species which are clusters of  $m$  solvent molecules and a polymer chain. Minimization of the free energy of mixing gives the distribution of the clusters in solution. This allows for explicit prediction of the closed loop behavior seen in Figure 4. Panayiotou and Sanchez<sup>46</sup> extended the Sanchez–Lacombe model to include hydrogen-bonding and other intermolecular associations. Kisselev and Manias used this development to describe the phase behavior of PEO/H<sub>2</sub>O mixtures.<sup>47</sup>

One might ask if the observed phase behavior of PEO/H<sub>2</sub>O mixtures (Figures 2a, 3a, 4, 5, and 6) is due to (1)  $\Delta U$ ,  $\Delta S$ , and  $\Delta V$  determined using the Flory–Huggins analysis presented here (Figures 4, 5, and 6) or (2) due to clustering,<sup>45</sup> or (3) due to equation-of-state effects?<sup>47</sup> Are these three effects related, i.e., is the magnitude and sign of  $\Delta V$  inferred in (1) consistent with the clustering inferred in (2)? In an interesting study, Hammouda, Ho, and Kline studied concentration fluctuations in PEO/H<sub>2</sub>O mixtures by SANS.<sup>48</sup> While they observed an increase in scattering with increasing temperature, consistent with the observed phase behavior, they did not attempt to relate their scattering observations to molecular factors that govern phase behavior or clustering of water molecules with PEO chains. The ambiguity described above applies to many sets of data on polymer solutions and blends. Seemingly disparate theories are consistent with the data, and there is often no consensus on the molecular factors that underlie phase behavior.

## ■ OTHER THEORIES FOR POLYMER BLENDS

While the Sanchez–Lacombe theory can readily be used to study polymer blends (e.g., ref 49), we use this space to describe other approaches. Many microscopic theories assume a relationship between  $\epsilon_{AB}$ ,  $\epsilon_{AA}$ , and  $\epsilon_{BB}$ . A popular assumption is that  $\epsilon_{AB} = g\sqrt{\epsilon_{AA}\epsilon_{BB}}$  where  $g$ , the Bertholet parameter, is a number very close to 1. Some researchers use  $g$  as a fitting parameter. In the special case when  $g$  is set to 1, the internal energy as given by the Flory–Huggins theory reduces to regular solution theory. In this theory, the solubility parameter of component  $i$  is defined as,  $\delta_i = \sqrt{\epsilon_{ii}}$  and

$$\chi = \frac{v_0}{kT}(\delta_A - \delta_B)^2 \quad (43)$$

Equation-of-state parameters can also be used to estimate  $\delta_i$ <sup>50,51</sup>

$$\delta_i = \left( \frac{T\alpha_i}{\beta_i} \right)^{1/2} \quad (44)$$

where  $\alpha_i$  is the thermal expansion coefficient and  $\beta_i$  is the isothermal compressibility. This is perhaps the simplest approach for modeling mixture properties wherein  $\chi$  is predicted from pure component data. Equations 43 and 44 suggest that equation-of-state effects primarily affect  $A$ . Regular solution theory works reasonably well for simple mixtures, e.g., saturated hydrocarbon polymers that exhibit UCSTs.<sup>51</sup> A more elaborate theory wherein free volume is added to regular solution theory was proposed by

Ruzette and Mayes.<sup>52</sup> The phase diagrams of a number of blend systems were shown to be consistent with predictions of this theory. Like equation-of-state-based regular solution theory, there are no free parameters in the Ruzette–Mayes model.

Tambasco et al. have predicted  $\chi$  parameters for several polymer blends, using an equation-of-state model based on the Born–Green–Yvon lattice theory.<sup>53</sup> This theory accounts for nonrandom local mixing, an effect not accounted for in the Sanchez–Lacombe or Ruzette–Mayes models. The lattice cluster theory accounts for chemical complexity by including short branches along the backbone of the polymer chain in Figure 1.<sup>54</sup> In this theory DPMB will have a short branch at some frequency along the chain, PEB will have a long branch at the same frequency, while PIB will have two branches at each branch point, emanating at a higher spatial frequency (see Table 2). One expects this theory to provide a more accurate description of monomer-level effects such as entropic contributions and volume changes of mixing. Painter and Coleman developed models that accounted for hydrogen bonding and other associations in polymer blends.<sup>55</sup> In the polymer reference interaction site model (PRISM), mixture properties measured by SANS are calculated from monomer-level pair correlation functions of the constituents that may be determined from wide-angle neutron or X-ray scattering experiments or by simulations.<sup>56</sup> Excellent agreement between simulated and measured pair distribution functions is obtained in the case of simple polymers such as saturated hydrocarbons,<sup>57,58</sup> which enables robust predictions of  $\chi$ .

## CONCENTRATION FLUCTUATIONS AND PHASE SEPARATION IN POLYMER BLENDS

Modeling concentration fluctuations in homogeneous phases is important due to two reasons: (1) they are subtle “announcements” of the nature of intermolecular interactions and have been used to measure  $\chi$  (e.g., Figure 9), and (2) phase diagrams are affected by fluctuations, especially in the vicinity of the critical point.

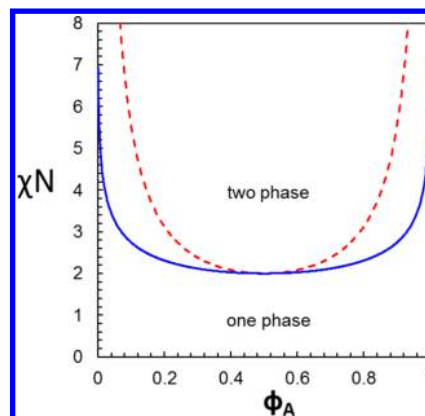
Concentration fluctuations in polymer mixtures occur naturally over a range of length scales that encompass monomer, molecular, and supramolecular length scales. In the theory of de Gennes,<sup>4,5</sup> the magnitude of fluctuations is calculated by the introduction of fluctuating fields that augment intermonomer interactions,  $\epsilon_{ij}$ 's (see eq 16). The fact that fluctuations of A and B are correlated (often referred to as the incompressibility assumption) is used to determine the fluctuating fields self-consistently using an approximation that de Gennes called the random phase approximation (RPA). De Gennes did not publish a detailed derivation of the RPA equation but generously provided handwritten notes on the derivation when asked. A copy of his notes that he sent to one of us (N.P.B.) in 1989 is included in the Supporting Information (a formal derivation of the RPA result is given in ref 59). The final result of the RPA is a deceptively simple relationship between scattering from fluctuations and  $\chi$ . An additional parameter that enters discussions of concentration fluctuations is the statistical segment length,  $a$ . The radius of gyration of chains that are approximated as random walks is given by  $R_{g,i} = \sqrt{N_i a_i^2/6}$  ( $i = A$  or B). For chains located on the lattice pictured in Figure 1,  $a$  is given by  $\nu_0^{1/3}$ , i.e.  $a = 0.464$  nm. It turns out that the statistical segment length of many common polymers is  $0.5 \pm 0.1$  nm, when  $N_i$  is defined based on a  $\nu_0 = 0.1$  nm<sup>3</sup>.<sup>60</sup> In the discussion below we thus assume  $a_i = \nu_0^{1/3}$ . It is perhaps remarkable that neutron scattering data from all

homogeneous blends are quantitatively consistent with the theory of de Gennes<sup>4</sup> provided  $\chi$  and  $a_i$  are treated as adjustable parameters.

The magnitude and characteristic size (length) of the concentration fluctuations diverge as the spinodal is approached; the spinodal curve is defined by

$$\left( \frac{\partial^2(\Delta G)}{\partial \phi_A^2} \right)_{T,p} = 0 \quad (45)$$

The calculated phase diagram for symmetric blends with  $N = N_A = N_B$  on a  $\chi N$  versus  $\phi_A$  plot is shown in Figure 12,



**Figure 12.** Binodal (solid) and spinodal (dashed) curves for blends with  $N_A = N_B = N$ , calculated using the Flory–Huggins theory.

where both the binodal and spinodal are shown. For blends at the critical composition, the spinodal is exposed and can be approached from the one-phase side with relative ease. Away from the critical point, the spinodal lies within the two-phase window, and the extent to which one can approach the spinodal depends on factors like nucleation barriers; one-phase systems are metastable in the window between the binodal and spinodal. Our understanding of nucleation barriers in polymer solutions and blends is far from complete. While some theories have been written on the subject,<sup>24</sup> we are not aware of any experiment that has attempted to measure the height of nucleation barriers in either polymer solutions or polymer blends. The extent to which these barriers affect the measured phase diagrams is unclear. It appears that in the case of UCST blends nucleation barriers are large enough that the spinodal can be approached from the one-phase side in relatively simple experiments wherein the sample is quenched (using pressure changes) to locations inside the binodal but outside the spinodal.<sup>8</sup>

The issue of the kinetics of phase separation and dissolution is an important one. While we do not dwell on the subject, it directly affects our ability to determine phase boundaries. Most phase boundaries are determined from the one-phase side. Classical theories due to Cahn and co-workers suggest the existence of two phase separation mechanisms: nucleation and growth in the metastable region and spinodal decomposition in the unstable region.<sup>61,62</sup> The signature of the initial stages of spinodal decomposition is the presence of a scattering peak due to selective amplification of fluctuations with a characteristic length scale. Polymer blends are ideally suited for studies of the kinetics of phase separation because chain entanglement<sup>63</sup> slows down kinetics of phase separation, and the early stage can be readily captured by time-resolved scattering experiments.

Pioneering early work on polymer blends demonstrated the connection between experimental data and Cahn's predictions.<sup>64–68</sup> In particular, the dependence of the dominant length scale of spinodal decomposition on quench depth was in excellent agreement with the predictions.

Less is known about the initial stages of nucleation. In the classical theories, nucleation occurs when an isolated region in space crosses the nucleation barrier. Such an event will have no scattering signature as scattering from any single object will be overwhelmed by scattering from concentration fluctuations of a sufficiently large metastable system. In experiments, however, the scattering from polymer blends quenched into the metastable region contain scattering peaks that are qualitatively similar to those obtained in the spinodal region.<sup>69–71</sup> In addition to scattering peaks, the time-dependent scattering profiles from blends merged at a particular scattering vector,  $q_c$ ; the scattering intensity was independent of time for scattering vectors larger than  $q_c$ . Since the lack of increase in scattering at a given  $q$  indicates the absence of growing structures with characteristic length scales  $1/q$ ,  $1/q_c$  was taken as a measure of the critical nucleus.<sup>70</sup> The experiments reported in refs 69–71 were done on PEB/DPMB blends, the system that exhibited near-perfect agreement with the Flory–Huggins–de Gennes framework. This facilitated determination of the dependence of critical nucleus size on quench depth.

The effect of fluctuations on phase diagrams, particularly the location of the spinodal, is a subject of long-standing interest. In a classic study, de Gennes compared the average magnitude of the fluctuations with the width of the coexistence window.<sup>72</sup> He concluded, based on scaling arguments, that fluctuations were only important in the vicinity of the critical point. A formal derivation of the effect of fluctuations on polymer blend thermodynamics for polymers with identical statistical segment lengths was worked out by Olvera de la Cruz et al.<sup>73</sup> Important entropic corrections arising from inequality of statistical segment lengths were derived by Fredrickson et al.<sup>74</sup> Wang used the one-loop renormalization approach to obtain a more complete picture of the effect of fluctuations.<sup>16</sup> This theory naturally encompasses terms derived in refs 73 and 74 and leads to the conclusion that the spinodal does not formally exist for polymer blends in three dimensions (or lower dimensions). It also provides prefactors for the scaling originally obtained by de Gennes. The prefactors are much larger than anticipated by de Gennes and the community, suggesting that fluctuations may be more important than originally anticipated. It is perhaps worth mentioning that the one-loop approach was first used by Fredrickson and Helfand<sup>75</sup> to compute fluctuation corrections in the block copolymer phase diagram, a subject that is outside the scope of this Perspective. While few experimental studies aimed at addressing fluctuation effects in polymer blends have been carried out,<sup>76,77</sup> many important questions such as the existence of the spinodal have not been addressed by experiments. Qin and Morse<sup>78</sup> used this approach to predict that the critical temperature (for symmetric polymer blends) is suppressed by concentration fluctuations in accordance with the following equation:

$$\chi N = 2 + 3.7N^{-1/2} \quad (46)$$

Strictly speaking,  $N$  on the right-hand side of eq 46 (and eq 47) should be replaced by  $Nv_0^2/a^6$ , where  $a$  is the average statistical segment length of the two polymers. As discussed above, we have chosen  $v_0$  is such that  $v_0^2/a^6$  is approximately unity for a number of polymers.<sup>60</sup> In 2016, Spencer and Matsen tested this theory by detailed computer simulations.<sup>79</sup> This paper provides an

excellent overview of attempts to address the issue of concentration fluctuations and critical behavior in polymer blends. Included in this work is careful consideration of the relationship between the intermonomer interactions used in simulations and  $\chi$  measured by experimentalists. They obtained

$$\chi N = 2 + 0.79N^{-1/2} \quad (47)$$

The correction to the Flory–Huggins theory is so small that for practical  $N$  values they recommend using the mean-field theory for interpreting experiments. For example, for  $N = 1000$  (typical value used in the blends reported in Figure 10), Spencer and Matsen obtain  $\chi N = 2.025$  instead of 2.0. An additional fact that is reported in ref 79 is that the scattering from polymer blends is indistinguishable from predictions of de Gennes. It is perhaps noteworthy that the most recent study of fluctuation corrections in 2016 takes us back to Flory, Huggins, and de Gennes.

## CONCLUDING REMARKS

Our understanding of phase behavior of polymer solutions and blends has grown steadily since the development of the Flory–Huggins theory in 1942.<sup>1–3</sup> The theory contains one parameter,  $\chi$ , that must be determined experimentally. In the early days,  $\chi$  was determined by fitting the experimentally observed phase behavior to theory. In 1970, de Gennes demonstrated that  $\chi$  could be determined from measurements of scattering from concentration fluctuations in homogeneous mixtures.<sup>5</sup> While the theory can be applied to any mixture containing flexible chains,<sup>59</sup> it has mainly been used to determine  $\chi$  in polymer blends. It also presented the community with a new and powerful framework for modeling the thermodynamics of more complex polymer systems such as block copolymers.<sup>80</sup>

Mean-field theories are based on the assumption that  $\chi$  is independent of chain length and mixture composition. Experimentally, we find this is the exception rather than the rule. In most systems studied thus far, the experimentally determined  $\chi$  parameter is found to vary as chain length and composition are varied. While there is little doubt that the Flory–Huggins theory is an appropriate starting point, there is no consensus on how to improve upon it. The reasons for departure from Flory–Huggins theory must be nonuniversal as there is at least one system wherein the measured  $\chi$  follows the Flory–Huggins stipulation. In cases where departures are evident, e.g., PEO/H<sub>2</sub>O, different researchers have proposed different hypotheses that are all consistent with experimentally determined phase behavior. Since the unanswered questions are related to monomer-level mixing effects, probing the local structure of mixtures using approaches such as wide-angle X-ray scattering, nuclear magnetic resonance, and X-ray absorption spectroscopy may be useful for determining the underlying reason for departure from Flory–Huggins theory. Traditional methods for studying the thermodynamics of polymer blends (those that have been the focus of this Perspective) are not sensitive to monomer-level structure. Independent measurements of thermodynamic functions that affect  $\Delta G$  such as  $\Delta V$ ,  $\Delta S$ ,  $\Delta C_p$ , and  $\Delta H$  will also help discriminate between different theoretical frameworks that predict similar values of  $\chi$ .

While we have focused on mixtures of polymers and low molecular weight solvents, there is a growing interest in mixtures of polymers and a new kind of additive: salt. One might think of salt as a “solvent” that can dissociate into oppositely charged species or cluster. Accounting for Coulombic interactions<sup>81</sup> led to effects that are qualitatively different from those discussed in this Perspective.

## ■ ASSOCIATED CONTENT

### 📄 Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.macromol.6b02619.

A copy of de Gennes's handwritten notes on the RPA derivation (PDF)

## ■ AUTHOR INFORMATION

### Corresponding Authors

\*E-mail [balsara@berkeley.edu](mailto:balsara@berkeley.edu); phone (510) 642-8937 (N.P.B.).

\*E-mail [mbanasz@amu.edu.pl](mailto:mbanasz@amu.edu.pl); phone +48 (61) 8295-065 (M.B.).

### ORCID

Ksenia Timachova: 0000-0001-8200-3552

Michał Banaszak: 0000-0003-0106-632X

Nitash P. Balsara: 0000-0002-0106-5565

### Author Contributions

K.T. and P.K. contributed equally to this work.

### Notes

The authors declare no competing financial interest.

### Biographies



Piotr Knychala received an MSc degree in Computer Science in 2007 and a Ph.D. degree in Physics in 2012 from the Adam Mickiewicz University in Poznan, Poland, under Professor Michał Banaszak. He is currently a lecturer in the Department of Computer Science in the Faculty of Polytechnic of the President Stanisław Wojciechowski University School of Applied Sciences in Kalisz, Poland. His main research interests include polymer melts and solutions, block copolymer nanostructures, ionic copolymers, and coarse-grained models of biopolymers investigated by lattice simulations.



Ksenia Timachova received her bachelor's degree in chemical engineering from the Massachusetts Institute of Technology in 2013

where she studied the dynamics of diffusion of rod-coil block copolymers under Professor Brad Olsen, who introduced her to the fundamentals of polymer chemistry and polymer thermodynamics. She is currently a Ph.D. candidate at the University of California, Berkeley, under Professor Nitash P. Balsara, studying the connections between microscopic and macroscopic transport of ions through polymer electrolytes for lithium batteries. Her main interests are in the fields of polymer science and clean energy technologies, particularly the application of novel polymer materials to energy generation, efficiency, and storage.



Michał Banaszak graduated in 1985 with a degree in theoretical physics from Adam Mickiewicz University in Poznan, Poland. He received his PhD degree in Physics, under the guidance of Professor Mark Whitmore in 1991 from Memorial University in St. John's, Canada, specializing in polymer physics and went on to work as postdoctoral fellow with Professor Maciej Radosz in Exxon Research & Engineering Co. in Annandale, NJ, from 1992 to 1995 on the theory and modeling of polymer solutions. From 1995 to 1997 he worked as a research associate with Professor Julian Clarke at the Chemistry Department of UMIST in Manchester, UK, specializing in large-scale computer simulations of ionic copolymers. In 1997, he joined the associate faculty of the Adam Mickiewicz University, obtaining a DSc degree in Physics in 2004 with a specialty in soft matter and computer simulations. He is currently a Professor and Head of the High Pressure Physics Division of the Faculty of Physics at Adam Mickiewicz University and is involved in a variety of research on polymer modeling using large-scale computing. His main interests are in developing new models and theories for nanoscale self-assembly of various copolymer systems. He also works with experimentalists in order to verify computational predictions and develop novel efficient algorithms and codes.



Nitash P. Balsara is a chemical engineer with a bachelor's degree from the Indian Institute of Technology (IIT) in Kanpur, India, in 1982, a master's degree from Clarkson University in Potsdam, NY, in 1984, and

a Ph.D. from Rensselaer Polytechnic Institute (RPI) in Troy, NY, in 1988. He was introduced to the field of polymers by Professor K. S. Gandhi at IIT. He worked on polymer blends during his Ph.D. under the mentorship of Professor Bruce Nauman. While he was completing his Ph.D., he learned polymer thermodynamics from Professor Sonja Krause. He did postdoctoral research at the University of Minnesota in Minneapolis under the guidance of Professors Tim Lodge and Matt Tirrell, where he learned about scattering and microphase separation in block copolymers. He returned to polymer blends when he did his second postdoc at Exxon Research and Engineering Company in Annandale, NJ, working under the guidance of Dr. Dave Lohse and Professor Bill Graessley, alongside Ramanan Krishnamoorti. His more recent education in the field of polymer thermodynamics is mainly due to his students. In 1992, he joined the faculty of Department of Chemical Engineering at Polytechnic University in Brooklyn, NY. He was promoted to associate professor in 1996 and professor in 1998. In 2000, he joined the faculty at the Department of Chemical Engineering at the University of California, Berkeley, and Lawrence Berkeley National Laboratory as a faculty scientist. He has managed to hang on to both jobs. He cofounded two start-ups, Seo and Blue Current.

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## NOTE ADDED AFTER ASAP PUBLICATION

This paper was published ASAP on April 6, 2017, with errors in Table 1 and Figures 4 and 5. The corrected version was reposted on April 13, 2017.