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Analyzing and Predicting Polymer Fluid and Blend Properties Using Minimal Pure Component Data

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ABSTRACT: We find that it is possible to use a sparse data set, consisting of as few as three data points per fluid, and produce a quantitative description of both pure component and blend behavior. Making use of isothermal compressibilities (κ_T) and thermal expansion coefficient data (α_P) for a variety of polymer fluids, as well as experimentally determined critical temperatures for several blends, we apply the lattice Born−Green−Yvon (BGY) theory to the analysis and characterization of polymeric fluids and blends. In particular, we focus on polystyrene (PS), poly(vinyl methyl ether) (PVME), polybutadiene (PB), and poly(2,6-dimethyl-1,4-phenylene oxide) (PPO) as well as the mixtures PS/PVME, PS/PB, and PS/PPO. In the first section of the paper we use the analytic expressions derived from the lattice BGY theory to analyze experimental data for the two mechanical coefficients. In the second portion of the paper we investigate the accuracy and consistency of the predictions made with each set of characteristic parameters.

1. Introduction

In using experimental data to characterize the thermodynamic properties of polymeric fluids, there is a fine line between requiring enough data to draw meaningful connections between theory and experiment and having so much data that the theory is no longer a predictive tool. Indeed, testing the predictive potential of a theory becomes a more stringent challenge as the amount of available experimental data is decreased. In this paper we discuss the advances we have made toward the goal of testing the confines of theory when using a dearth of experimental data, with our focus being on pure polymers and, to a lesser extent, polymer blends. The work is motivated by the expectation that theories should be useful in understanding and predicting the behavior of systems which, albeit poorly characterized, may have properties of great interest.

The theoretical aspect of our research utilizes the Born−Green−Yvon (BGY) lattice theory for compressible fluids developed by Lipson and co-workers.[1−5] This approach has previously been applied to n-alkane liquids and mixtures[1] as well as polymer fluids, solutions, and blends.[2−5] The theory yields tractable expressions for all the thermodynamic properties of a system (which may have an arbitrary number of components); in fact, we have applied it to compressible fluids and compressible binary mixtures.[2] These expressions reveal their statistical mechanical origins by the presence of characteristic parameters whose values must be determined before the theory can be applied. For a one-component system these are the nonbonded nearest-neighbor interaction energy, ϵ, the number of contiguous lattice sites needed per molecule, r, and v, the volume per mole of lattice sites. For a binary mixture the mixed-segment interaction energy, ϵ_{12}, must also be determined. Our initial applications of the theory made use of a well-followed route: values for the pure component parameters were optimized by fitting the lattice BGY equation of state to pressure−volume−temperature (*PVT*) data. In the case of mixtures, the mixed interaction energy was determined by matching a theoretical critical temperature (such as that for phase separation, for example, an upper critical solution temperature (UCST)) to an experimental datum point. However, the critical point is difficult to describe using a mean field theory (such as BGY), and thus it would be valuable to have alternate routes to the mixed interaction energy which bypass this traditionally problematic region altogether. In fact, we have extended the application of the lattice BGY theory to the characterization and analysis of polymeric mixtures by developing two new routes, each using data in the one-phase region; this work has been recently published.[5] We showed that mixture *PVT* surfaces and zero-angle neutron scattering (NS) intensities (as a function of temperature) could be fit using the BGY theory to yield a complete set of characteristic parameters for the pure components and the mixture. Both of these routes avoid the necessity for any pure component data, and each requires a smaller data set (substantially smaller in the case of the NS results) than does the original route described above. In this work we turn our attention back to the characterization of pure polymer melts, expanding the number of routes available for the characterization of pure polymeric fluids through the use of pure component isothermal compressibility and thermal expansion coefficient data.

As the above discussion implies the most widely followed path to the characterization of a polymer fluid involves use of *PVT* data, which requires measurements made over a wide range of pressures, volumes, and temperatures. It is certainly not the case that one can rely on the availability of these data for a given polymer of interest. That being true, it would be very useful to have alternate routes to characterization which necessitate fewer, more readily available data points. In addition, comparing the results from following several different routes would provide information about the consistency of a theory. Given that the primary criterion is that the data be more readily available than *PVT* results, a natural choice is to turn to the so-called mechanical coefficients of a liquid. The available literature focuses primarily on two of the most easily measured quantities: the coefficient of thermal expansion α_P ($= (1/V)(\partial V/\partial T)|_P$) and the coefficient of isothermal compressibility κ_T ($= (1/V)(\partial V/\partial P)|_T$). These two coef-

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ficients are often applied in the characterization of polymeric materials and are quite useful in determining possible engineering applications.[6]

The isothermal compressibility is generally used in the calculation of engineering quantities such as the bulk or shear moduli. Both κ_T and α_P undergo rather extreme behavioral changes for temperatures above the glass transition (T_g), in some cases experiencing an approximately 50% increase for the melt, with typical values on the order of 10^{-5} bar^{-1} for κ_T and 10^{-4} K^{-1} for α_P. As both coefficients exhibit a sharp decline in value for the glass vs the melt, this trend can be utilized to give a qualitative understanding of how rubbery or glassy the polymer is. A more rubbery polymer will generally exhibit a higher value for the coefficient of interest.[7] Furthermore, by applying these coefficients in the determination of characteristic parameters, a polymer may be suitably investigated with as few as three data points.

In this paper, we present a route whereby the BGY theory is used to analyze α_P and κ_T data on pure polymers in order to obtain the characteristic parameters of the fluid. We use the results of each analysis to predict other pure fluid properties, and we also combine the pure fluid results with a fit to a mixture critical temperature in order to predict coexistence curves for several blends. This latter procedure is analogous to the one described above for polymer blends; however, it obviates the need for pure component *PVT* data. We have chosen four pure polymeric fluids for investigation, along with three diverse polymer mixtures: a blend of polystyrene and poly(vinyl methyl ether) (PS/PVME),[8–10] polystyrene blended with poly(butadiene) (PS/PB),[8,9,11] and a mixture of polystyrene and poly(2,6-dimethyl-1,4-phenylene oxide) (PS/PPO).[8,9] These blends respectively display a lower critical solution temperature (LCST), upper critical solution temperature (UCST), and miscibility across the entire composition range.

In section 2 we provide experimental and theoretical background. Section 3 describes the fitting procedures. The predictions are presented in section 4, and in section 5 we summarize our results.

2. Experimental and Theoretical Background

Experimental Data. All of the experimental data used to generate BGY results were obtained from the literature. The typical methodology for determining coefficient values (both κ_T and α_P) is outlined as follows:[12,13] high-precision volumetric data for compressible fluids are obtained using flexible bellows which contain the sample and also serve to isolate the sample from the pressure-transmitting (or temperature-transmitting, dependent upon the coefficient being measured) liquid. Mercury is the pressure-transmitting liquid that is implemented with the greatest frequency. Pressures are reached by forcing the bellows to contract, until the internal pressure of the sample is equilibrated to the applied pressure. The change in sample volume is obtained by measuring the change in length of the bellow. The average accuracy of the displacement is reported as ±1 μm. To monitor and maintain thermal equilibrium, the bellows are placed in a heat bath, which can control variations in temperature with an estimated error of ±0.1 K.

Coexistence data for the PS/PB blend were measured at Imperial College in London, where an apparatus was used to determine polymer compatibility at temperatures up to approximately 430 K. The experimental apparatus consisted of a sample holder mounted on a platform which allotted for control of the sample's position. The sample was viewed through a sapphire window, allowing for a visual determination of the cloud point at a heating rate of 1 K/h. The examination vessel was mounted in a thermostatic bath, which was fit with controlled cooling, heating, and stirring devices. The individual samples were contained within Pyrex tubes inverted in a mercury bath. Magnetic stirring was used in order to ensure homogeneous mixing. The accuracy of the sample temperature was approximated as ±0.1 K, while the cloud point was accurate to ±0.5 K.

The coexistence curve for the PS/PVME blend was obtained by optical evaluation of the phase separation point. Additional information regarding the experimental steps made in discerning the phase diagram of this blend can be located in ref 10. The accuracy for the coexistence data was reported as ±1 K.

Experimental *PVT* results were taken from Zoller and Walsh's extensive compilation of data. The accuracy of the density determinations are reported as ±0.002 cm^3/g for all values. Pressure values are reported with an accuracy of 0.1 MPa.

Theory. In this work, Born–Green–Yvon (BGY) theory[1] is applied to a simple cubic lattice model with a coordination number z, which is held at a fixed value of six for all calculations. The total lattice volume is given by $V = v(N_0/N_A)$, where v is the volume per mole of lattice sites, N_0 is the total number of lattice sites, and N_A is Avogadro's number. The parameter r_i represents the number of contiguous lattice sites occupied by a single molecule of species i. For a binary mixture (where $i = 1, 2$) the site fractions are defined as $\phi_i = r_iN_i/N_0$, $\phi_h = N_h/N_0$, and $\phi = 1 - \phi_h$, where N_i is the total number of molecules of i and N_h is the number of holes (unoccupied lattice sites). The product r_iz is the maximum number of interactions possible for r_i separate segments. However, the maximum number of interactions available to a molecule occupying r_i contiguous lattice sites is given by $q_iz = r_i(z - 2) + 2$, which leads to the definition of alternate concentration variables $\xi_i = q_iN_i/(N_h + \sum_j q_jN_j)$ and $\xi_h = N_h/(N_h + \sum_j q_jN_j)$ reflecting the molecule's nearest-neighbor connectivity. The energy term ϵ_{ii} is the interaction energy of the nonbonded nearest neighbors of the same species, while unlike nearest-neighbor interactions are denoted by ϵ_{ij}.

The theory is described in detail in the literature.[1–5] Here we outline the premise and then give the results for several thermodynamic quantities of interest. The BGY integral equation hierarchy links distribution functions (pair to triplet, and so on) and for our purposes is closed off at the level of pair interactions using the Kirkwood superposition approximation. All pairs of segments, except for the particular pair of interest, are then assumed to act independently. The results for the remaining pair probabilities represent the probability of having different types of nearest-neighbor interactions.[14] The summation of the product of these probabilities multiplied by the associated energetic contribution yields an expression for the internal energy of the blend, which is a function of temperature and (for a multicomponent system) composition. Since the systems are compressible at finite (experimental) pressures, which encompass all of the results in this study, each of the interaction energies contributes to the blend's internal energy, not just a simple combination as is found in Flory–Huggins theory.[15] A Gibbs–Helmholtz relationship is used to obtain the free energy from the internal energy; for the purposes of integration we assume that in the case of a mixture there is random mixing (as described by Guggenheim) at infinite temperature.[16] At finite temperatures there are important nonrandom contributions to the entropy of the mixture. The lattice BGY result for the dimensionless configurational Helmholtz free energy, $\hat{a}$, of a K-component blend is given by

$$\hat{a} = \sum_{i=h,1}^{K} \left(\frac{\phi_i}{r_i} \ln \phi_i + \frac{q_i z \phi_i}{2 r_i} \left\{ \ln\left[\frac{\xi_i}{\phi_i}\right] - \ln[\xi_\mathrm{h} + \sum_{j=1}^{K} \xi_j \exp(-\beta\epsilon_{ij})] \right\} \right) \quad (1)$$

where $\beta = 1/(k_\mathrm{B}T)$, k_B is Boltzmann's constant, and T is the temperature. Accordingly, the Helmholtz free energy density, A/VT, is given by

$$A/VT = k_\mathrm{B}\hat{a}/v + a_0 \quad (2)$$

where a_0 is a caloric background not necessary for this work. The blend's thermodynamic properties are extracted from this derivative of the Helmholtz free energy density:

$$\mathrm{d}(A/VT) = \frac{U}{V}\,\mathrm{d}(1/T) + \sum_{j=1}^{K} \frac{\mu_j}{T}\,\mathrm{d}(\rho_j) \quad (3)$$

where U is the internal energy of the system, ρ_j is the number density of component i, and μ_j is the chemical potential of species i. The chemical potential of component i is given by

$$\mu_i = \frac{r_i}{\beta}\left(\frac{\partial \hat{a}}{\partial \phi_i}\right)_{\beta,\varphi_{k\neq i}} \quad (4)$$

Phase transitions for binary mixtures are usually represented in terms of the molar density ($\rho = \rho_1 + \rho_2$) and mole fraction ($x = \rho_2/\rho$). Conjugate to the mole fraction is the difference between the chemical potential of each component (where $\mu = \mu_2 - \mu_1$). These terms allow for the critical line for the blend to be expressed as[17]

$$\left(\frac{\partial \mu}{\partial x}\right)_{T,P} = 0, \quad \left(\frac{\partial^2 \mu}{\partial x^2}\right)_{T,P} = 0 \quad (5)$$

where the initial term defines the spinodal line and the second equation defines a critical point as an extremum of the spinodal. The lower critical solution temperature (LCST) represents the minimum of the spinodal, and conversely, the upper critical solution temperature, or UCST, represents the maximum. Hence, for a pressure P, the coexisting phases satisfy both of the expressions $\mu(T,P,x_1) = \mu(T,P,x_2)$ and $\mu_1(T,P,x_1) = \mu_1(\mathrm{T},P,x_2)$.

For a pure, compressible fluid the BGY equation of state is given by[1]

$$P = -\frac{1}{\beta v}\left\{\ln \phi_\mathrm{h} + \frac{z}{2}\ln\left(\frac{\xi_\mathrm{h}}{\phi_\mathrm{h}}\right) + \phi\left(1 - \frac{1}{r}\right) + \frac{z\phi}{2}\left(\frac{q}{r} - 1\right) + \frac{z\xi^2}{2}\left[\frac{\exp(-\beta\epsilon) - 1}{\xi\exp(-\beta\epsilon) + \xi_\mathrm{h}}\right]\right\} \quad (6)$$

This may be fit to experimental pressure–volume–temperature (*PVT*) data so as to ascertain values for the characteristic parameters r, v, and ϵ. Similarly, when determining parameters from α_P and κ_T data only r_1, r_2, v, ϵ_{11}, and ϵ_{22} are established. The equation used to calculate the coefficient of thermal expansion is

$$\alpha_P = \rho\,\frac{\partial\left(\frac{1}{\rho}\right)}{\partial T} = \frac{\frac{\partial P}{\partial T}}{\rho\,\frac{\partial P}{\partial \rho}} \quad (7)$$

where ρ is density, P is pressure, and T is temperature. The equation used for the coefficient of isothermal compressibility is given by

$$\kappa_T = \rho\,\frac{\partial\left(\frac{1}{\rho}\right)}{\partial P} = \left(\rho\,\frac{\partial P}{\partial \rho}\right)^{-1} \quad (8)$$

Equations 7 and 8 illustrate the similarities and differences between the two coefficients. Characteristic parameters calculated from coefficients of thermal expansion might be challenged in terms of making predictions for how a system will respond as a function of pressure since the data are typically only collected at atmospheric pressure (0.1 MPa). Indeed, all of the experimental results were collected under atmospheric pressure (0.1 MPa). However, parameters obtained from isothermal compressibility data should be able to capture the effects of changing pressure as well as of changing temperature. Thus, our initial expectation was that parameters obtained from isothermal compressibilities would be more adept at predicting *PVT* surfaces, while both coefficients might be expected to be equally effective in calculating coexistence curves (almost always only reported at $P = 0.1$ MPa) with an approximately equal accuracy.

The mixed interaction energy, ϵ_{12}, may be estimated several ways. In rare cases (e.g., mixtures of n-alkanes or solutions of polyethylene in n-alkanes) it is appropriate to calculate it using the Lorentz–Berthelot mixing rule (geometric mean approximation)

$$\epsilon_{12} = g(\epsilon_{11}\epsilon_{22})^{1/2} \quad (9)$$

where g is a fit parameter which describes the nature of the mixed interactions. Alternatively, g may be determined by analyzing one or more kinds of experimental data, as described in the Introduction in the context of discussing ϵ_{12}.

3. Analysis of Experimental Data

Pure Component Data. Previous results using the BGY theory have illustrated the capacity of this approach to accurately capture the effects of pressure and temperature on the density of both pure fluids and mixtures as well as the molecular weight and pressure dependence on miscibility. In this paper we investigate the ability of the BGY theory to make predictions using characteristic parameters obtained from both the coefficient of thermal expansion and the isothermal compressibility. The potential advantage of these two new routes is that far fewer data points would be required than in previous analyses. Reducing the amount of *PVT* data used to obtain pure fluid parameters may provide comparable results; however, an analysis of this type

Table 1. Characteristic Parameters for Several Data Types

polymer	ϵ (J/mol)	r	v (L/mol)	M_w (g/mol)
Characteristic Parameters from α_P Data				
PS[9]	−2412.9	21997.6	0.011 010	279 000
PVME[9]	−1930.5	9537.9	0.009 200	99 000
Characteristic Parameters from κ_T Data				
PS[9]	−2403.9	24185.2	0.010 040	279 000
PB[9]	−2202.5	11839.2	0.008 474	95 000
PVME[9]	−2021.4	9637.9	0.009 204	99 000
PPO[9]	−2246.1	9995.4	0.008 343	100 000

Blend Parameters

blend	v (L/mol)	g	T_c fit using
PS/PB[11]	0.009 257	0.993 56	α_P
PS/PVME[8,10]	0.010 105	1.007 51	α_P
	0.009 622	1.004 98	κ_T
PS/PPO[8]	0.009 192	1.000 04	κ_T
	0.009 192	1.000 02	ϵ_{geo}
	0.009 192	1.000 00	g set to unity

would still require more data points than a study involving either coefficient. Details concerning the polymers under investigation are given in the first two parts of Table 1, along with values for the characteristic parameters obtained using each method. The r values in the table are associated with the molecular weights which are listed. In making use of these results to predict behavior for a sample of different molecular weight, the ϵ and v values would remain constant, while the r value would be scaled according to the relationship $r_{new} = r_{old}\ (MW_{new}/MW_{old})$. While the analysis for each pure fluid results in a characteristic v value, to avoid using a lattice with composition-dependent site volumes when describing mixtures a single v value is used for both the components and the blend. There are several routes by which single v may be determined: making a conjecture as to a "reasonable" value, using the arithmetic average of the two pure values, or choosing the v of one of the pure components. When fitting to mixture data alone, all of the pure component parameters are determined, along the mixed interaction energy as well as a single v which the applies to the pure and mixed states. For the results reported here, optimized v values are obtained from the pure component fits. We then use the arithmetic average of the pure fluid v values as the sole v for describing each component as well as the mixture, so that in both the pure and mixed states the same lattice is used. In doing this, we rescale the value of r for each component so as to maintain a constant hard-core volume, which is given by r^*v.

Figure 1 displays the results for the thermal expansion coefficient, wherein $\alpha_P T$ is plotted as a function of temperature. The symbols represent the experimental data (all collected at 0.1 MPa), and the curves show the optimized BGY fit. Results on the left are for PS and on the right for PVME. The experimental temperatures associated with the data points are given in the figure caption. The figure illustrates some of the difficulty in analyzing thermal expansion behavior. In fact, the BGY theory was more than able to produce a much closer fit to the data, but at the cost of some unrealistic parameter values. In particular, the "optimized" volume per mole of lattice sites was 2 orders of magnitude too large. The most prominent reason for the error is the very slight temperature dependence of the coefficient. When the analysis is constrained so as to obtain parameter values within a reasonable range ("reasonable" being judged by the results of PVT analysis on many polymer fluids), the BGY calculations overestimate the dependence of α_P on temperature for both polymers. A similar conclusion was reached by Flory and Orwoll in their detailed study of a homologous series of n-alkane systems.[18] Using equation-of-state parameters determined using thermal expansion and thermal pressure coefficients as a function of volume and temperature, they were able to qualitatively predict the thermal expansion behavior but had difficulty obtaining quantitative agreement.

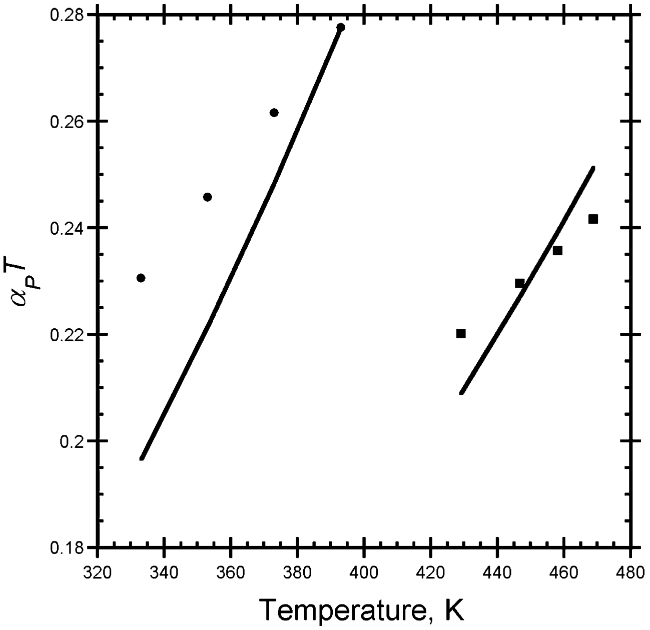

Figure 1. Thermal expansion coefficient (times temperature) as a function of temperature; symbols represent experimental data,[9] and the lines show the optimized BGY fit. The left line represents PS, and the right line is PVME. Temperatures refer to the results from left to right: for PS (333, 353, 373, and 393 K) and for PVME (429, 446, 458, and 468 K).

Figure 2 depicts the analogous results for the isothermal compressibility. From left to right the lines represent the results for PS, PVME, PB, and PPO. The theory was able to capture the temperature dependence of the compressibility data with a higher degree of accuracy than the thermal expansion data, and this was done without constraining the analysis. All of the experimental results were in the melt region of the polymers, and the theory was well able to fit the compressibilities which were both more (PPO) and less (PS) dependent on temperature. Noting the differences between the scales of the two plots, it is observed that κ_T values are considerably more sensitive to changes in temperature than α_P, which reinforces the argument presented previously.

Blends. *Critical Solution Temperatures.* As noted above, to make predictions about mixture behavior, a value for the mixed interaction energy or equivalently the g parameter is needed. In the case of phase-separating blends we follow two routes: One involves using the pure component parameters obtained through the analysis of α_P data and then fixing g so that the BGY result for the critical temperature (not composition) agrees with experiment; the other is analogous but uses the parameters from the κ_T analysis. Once this single temperature is set, the rest of the coexistence curve is predicted using the theory. The blend parameters are listed in Table 1.

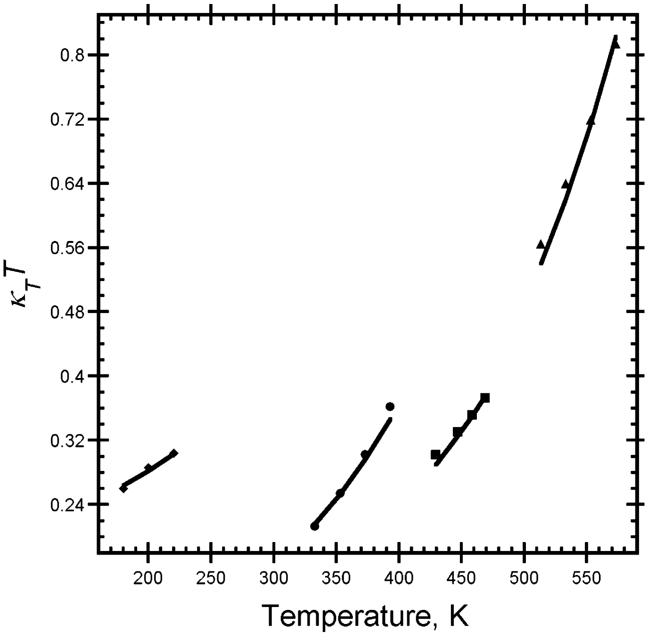

Figure 2. Isothermal compressibility (times temperature) as a function of temperature; symbols represent experimental data,[9] and the lines show the optimized BGY fit. Following from left to right, the results are for PS, PVME, PB and PPO, respectively. Temperatures refer to the results from left to right: for PB (180, 200 and 220 K), for PS (333, 353, 373, and 393 K), for PVME (429, 446, 458, and 468 K), and for PPO (513, 533, 553, and 573 K).

4. Predictions for Melt and Blend Behavior

Melt Pressure−Volume−Temperature Surfaces. One might reasonably expect that predicting the *PVT* results for the pure fluids would be a greater challenge for the characteristic parameters determined from the thermal expansion coefficient data than for those from the isothermal compressibilities, in that the latter spans three dimensions, as does the *PVT* surface. Figure 3 shows the predictions for the *PVT* surface of PS using α_P (part a) and for poly(vinyl methyl ether) using α_P (part b) and κ_T (part c). The figure shows pressure plotted as a function of volume for a series of temperatures (with the temperatures given in the figure captions). The symbols represent the experimental data, and the curves represent the *predictions* of BGY theory. The *PVT* surfaces were also predicted for both PS and PB using κ_T parameters, but these results were similar in quality to those of Figure 3 and so are not included. As can be seen from this figure, using the characteristic parameters obtained from both types of coefficient data yield predictions that are in good to excellent agreement with experimental data, with the κ_T parameters performing slightly better.

Blend Pressure−Volume−Temperature Surfaces. Along with the pure fluid *PVT* data, experimental results were also obtained for a blend of PS and PVME. Predicting the blend *PVT* surface is an even more demanding task for these parameters, as the behavior now becomes a function of four variables: pressure, volume, temperature, and composition. Two compositions for this blend were examined, 30 and 70 wt % PS. For this blend, the molecular weights of the polymers are 114 200 g/mol for PS and 99 000 g/mol for PVME. The experimental LCST was 394.17 K, and a fit to this temperature yielded a *g* value of 1.007 51 using the α_P results and 1.004 98 using the κ_T results.[10] In Figure 4,

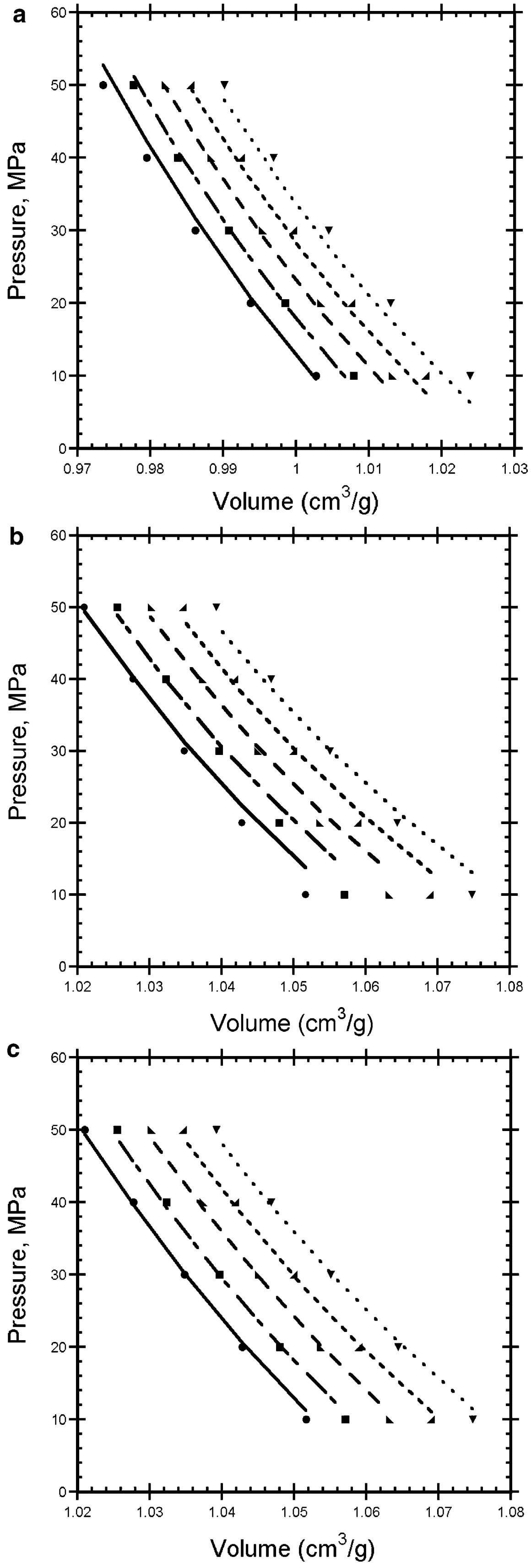

Figure 3. BGY *predictions* for the PVT behavior of (a) PS using α_P parameters, for (b) PVME using α_P parameters, and for (c) PVME using κ_T parameters. The symbols represent experimental data,[8] and the lines represent BGY calculations. Temperatures refer to the results from left to right: for PS (492, 500, 509, 517, and 526 K) and for PVME (440, 448, 457, 465, and 473 K).

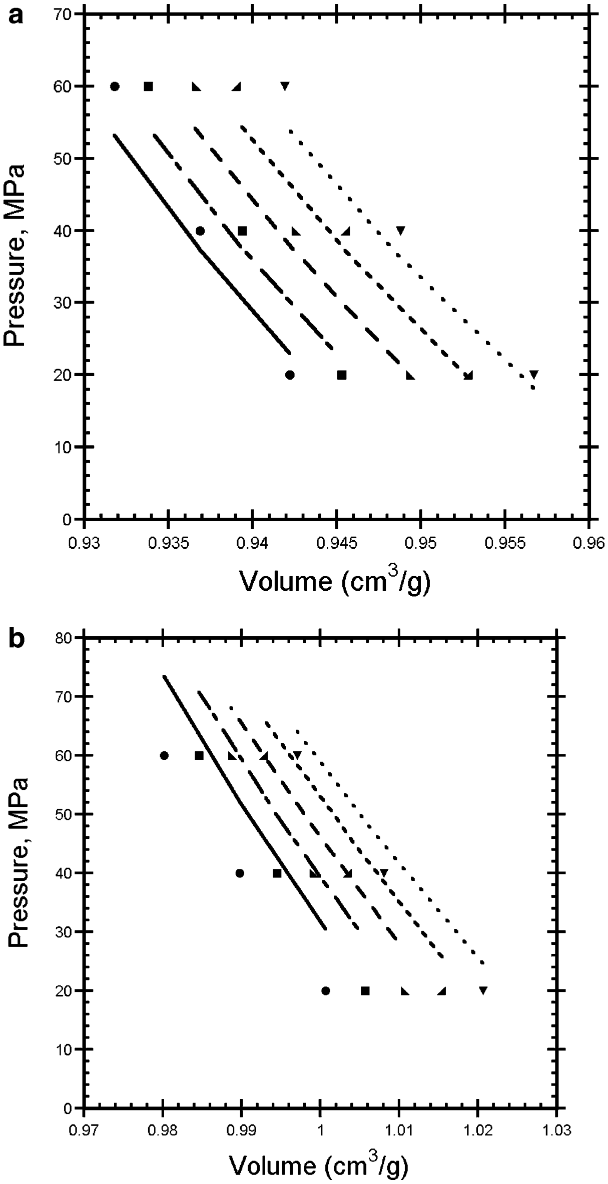

Figure 4. BGY *predictions* for the PVT behavior of PS/PVME (experimental data from ref 8): (a) for the 30% PS surface using κ_T parameters and (b) for the 70% PS surface using α_P parameters. The temperatures used in (a), from left to right, are 327, 335, 343, 351, and 359 K, while those used in (b) are 367, 375, 382, 391, and 398 K.

the isothermal compressibilities were used to predict the 30% PS surface (part a), and in part b the thermal expansion parameters were used to predict the 70% PS surface. For this figure, the symbols represent the experimental data, and the curves are the BGY *predictions*. Both sets of parameters were used to predict each of the 30% and 70% PS surfaces, but because of the similar nature of the results, not all the plots are included. Consistent with the previous results, the predictions using the isothermal compressibility parameters were closer to the experimental results than those using the thermal expansion parameters for both the 30% PS (shown in (a)) and 70% PS (not shown) mixture surfaces. A closer examination of the lower pressure region (which is the primary region of interest, given the nature of the coefficient data) shows a higher accuracy for the 30% PS blend. The pure fluid parameters were obtained from analyzing data for the polymer in the melt region. However, the experimental state of the 70% blend is such that *some* of the *PVT* data are apparently associated with a glassy, phase-separated blend. This discrepancy in the state of the system is reflected in the differences observed between predicted and experimental results.

In Figure 5 we turn to the miscible blend of PS and PPO. The figure illustrates three different sets of predictions for a 50/50 blend of PS/PPO (MW ratio of 244 000/100 000 g/mol) using the κ_T pure fluid parameters in all three cases and a *g* parameter determined respectively from (a) a fit to the blend *PVT* surface, (b) using the pure component energies as determined from analysis of pure *PVT* data and then adjusting *g* so that the mixed interaction energy would have the same value as in (a), and (c) set to unity, thereby considering the mixed interaction energy to be the geometric mean of the pure component energies as determined by the analysis. As usual, the symbols represent the experimental data, and the curves are the BGY predictions. It is worth noting that this blend is completely miscible in all proportions. In addition, given the glass transition temperatures of the two components (PS $T_g = 373$ K, PPO $T_g = 483$ K), we expect that this 50/50 blend will not be glassy or phase separated, as was the concern for the PS/PVME 70/30 blend. Not surprisingly the fit to the blend *PVT* surface (Figure 5a) produced the best correlation to the experimental data. The second route (Figure 5b) shows somewhat better agreement than the third (Figure 5c); from Table 1 we see that the fairly small differences in BGY results are reflected in very small differences in *g*.

Coexistence Curves. In Figure 6, the predictions for the spinodal and binodal curves are compared with experimental data for PS/PVME using the κ_T parameters (a) and α_P parameters (b). For both plots, the filled symbols represent the experimental data, the calculated spinodal is given by the dashed line, and the solid line shows the predicted binodal curve. The *g* parameter was determined by fitting to the lower critical solution temperature only, not the critical composition. Therefore, with the exception of the critical temperature, the entire curve represents a BGY prediction. Consistent with previous results, the compressibilities produce a more accurate plot, yielding a slightly better approximation of the critical composition and showing closer agreement with the experimental data for most of the binodal curve. Indeed, the binodal prediction using isothermal compressibility parameters generally is within ±5 K of the experimental results for the entire blend composition. In terms of the critical composition, the experimental coexistence curve is rather flat near the LCST, a feature which would not be captured using a mean-field (classical) theory such as lattice BGY.

In Figure 7 we turn to the coexistence curve for PS/PB, a UCST blend with a critical temperature of 296.85 K. As for the results of Figure 6, here the BGY prediction is generated using the pure component parameters determined from the κ_T fits and a *g* value from optimizing agreement with the experimental critical temperature. In addition to the change from LCST (PS/PVME) to UCST (PS/PB) behavior, the coexistence curve for PS/PB is substantially narrower than that for PS/PVME, a feature which is correctly captured in the BGY predictions.

These results show that a relatively small set of pure component data may be utilized to great effect, even in the determination of blend properties. In fact, as few

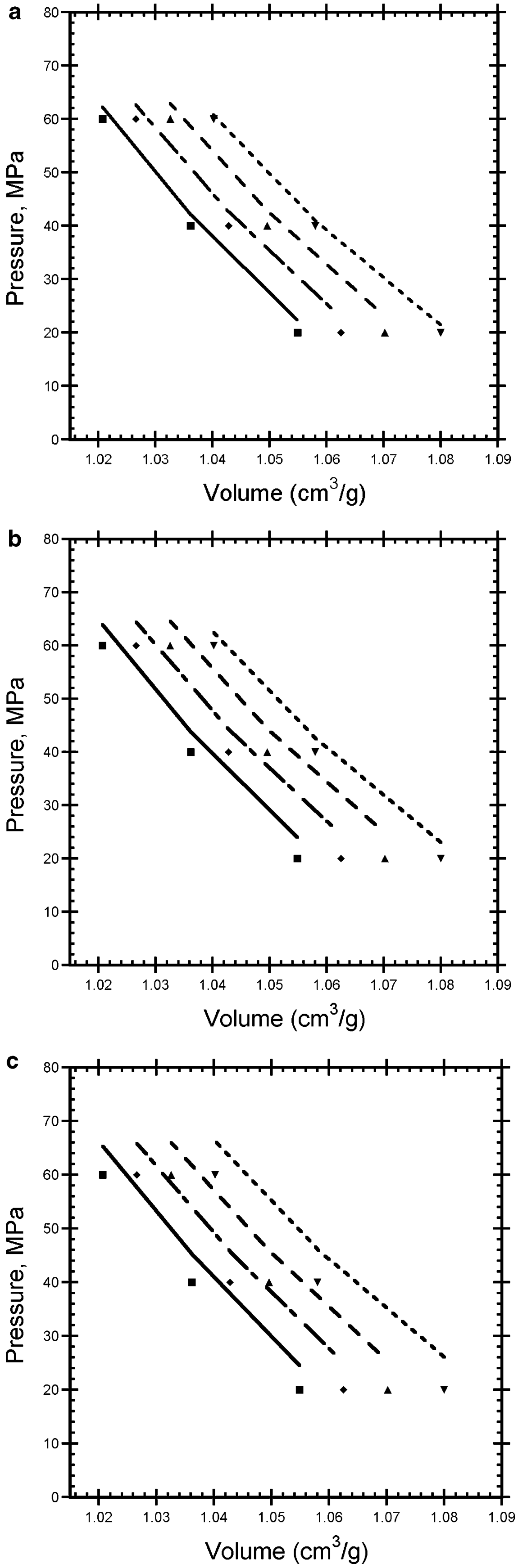

Figure 5. BGY *predictions* for the PVT behavior of the 50/50 PS/PPO surface, using κ_T parameters and a g factor determined by (a) fitting, (b) calculating from the geometric mean, and (c) having a g value of unity. The experimental results were obtained from ref 8. For all figures, the temperatures refer to the results from left to right: 411, 423, 435, and 447 K.

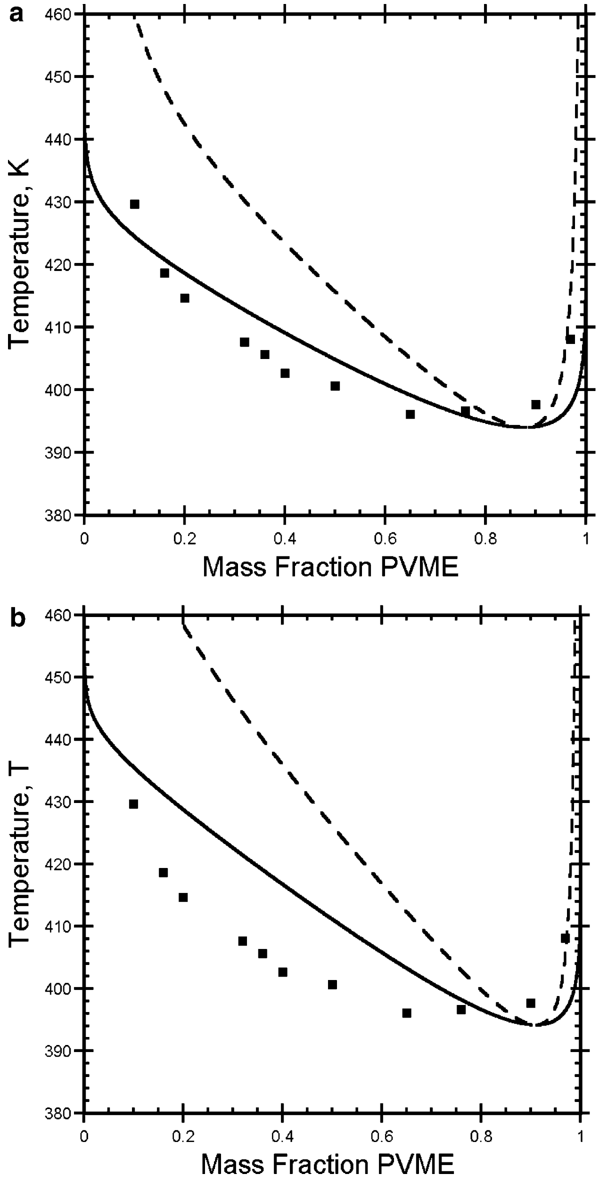

Figure 6. Coexistence results for PS/PVME using the isothermal compressibility parameters (a) and the parameters from the coefficient of thermal expansion (b). The symbols represent experimental data.[10] The curves show the BGY *predictions* for the binodal (the solid line) and spinodal (the dashed line), where in each case the critical temperature was used to fit for the g parameter, characterizing the mixed interaction energy.

as three temperature-dependent data points may be enough to generate a useful set of characteristic parameters for a fluid. While both thermal expansion coefficients and isothermal compressibility data can be used as a viable alternative to *PVT* data, we find that the thermodynamic properties of the polymers under investigation (and their blends) are more accurately captured by the parameters obtained from analyzing isothermal compressibility data.

5. Summary

In this work we have proposed two routes for the characterization of pure polymers, each of which minimizes the amount of experimental data required. Prior to the research described here, we had analyzed pure fluid pressure–volume–temperature (*PVT*) surfaces in order to determine ϵ, v, and r, the characteristic

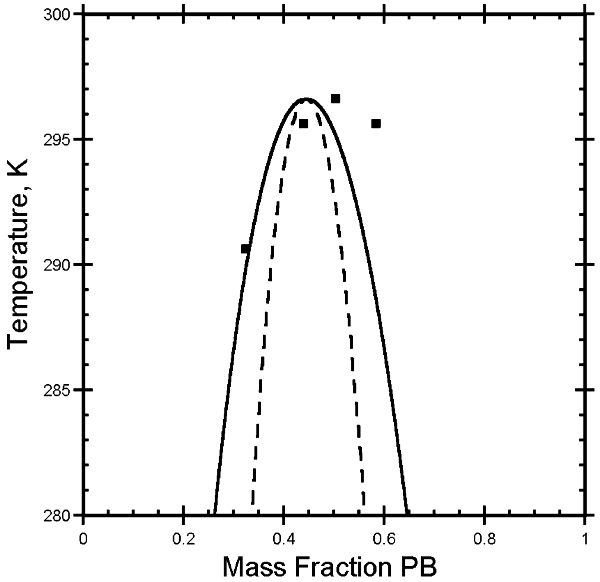

Figure 7. As in Figure 6, for the PS/PB blend. The experimental coexistence data are given in ref 11.

parameters of a polymer. However, determination of an experimental *PVT* surface typically requires 30 measurements or more, usually spanning a considerable range of temperatures and pressures. One of the methods presented here involves use of thermal expansion coefficients, and the other implements isothermal compressibilities (each measured at several temperatures); only three to five data points were required. We found that in the case of the former it was necessary to constrain the fit so that v was required to be in a “reasonable” range; otherwise, the optimized value was likely to be 1−2 orders of magnitude too large. No such constraints were required in analyzing the compressibility data, making that a somewhat preferable route. We then tested the results by using each set of characteristic parameters so obtained to generate a predicted *PVT* surface for each of four polymer melts (PS, PB, PVME, and PPO) and compared the BGY predictions with experimental data. We found that both routes to the predicted *PVT* surfaces yielded good quantitative agreement with experiment; however, the compressibility parameters produced slightly more accurate results.

In previous work our main goal in analyzing *PVT* data on pure fluids was to combine the sets of characteristic parameters along with an estimate of the mixed segment interaction energy so as to make predictions about mixture behavior. We therefore tested the new routes proposed here by following a similar procedure. The characteristic parameters for the two polymers in the mixture of interest were combined with a fit to the critical temperature of the mixture in order to make blend predictions. We were interested in three blends: PS/PVME, which exhibits an LCST, PS/PB, a UCST blend, and PS/PPO, a miscible blend. In the case of PS/PVME there are *PVT* data for the blend surface. Thus, we began our comparison with blend data by using the BGY theory along with the parameters as described above to predict the blend surface at two compositions. We found that using the compressibility parameters the predicted results were in close agreement for the 30 wt % PS surface. On the other hand, the thermal expansion parameters yielded a 70 wt % PS surface which was noticeably different from experiment. However, we attribute at least some of the disparity to inherent difficulties with this composition of blend, as it would seem that both the LCST and the blend glass transition appear to fall within the experimental temperature range studied. We also studied the *PVT* surface of the miscible blend PS/PPO and found that assuming the mixed interaction to be the geometric mean of the pure component interactions yielded surface predictions which were very close to the surface fits.

We then turned to predictions on the coexistence curves for PS/PVME and PS/PB. Recall that we have chosen to use the respective critical temperatures to characterize the mixed interactions, so the BGY predictions are effectively “pinned” at the critical points. However, every other point on the binodal and spinodal plots shown represents prediction using the BGY theory. For PS/PVME we found that using the compressibility parameters yielded a binodal which was noticeably closer to the experimental data than that predicted using the thermal expansion parameters, although the latter was still in very reasonable agreement with experiment. The agreement between experiment and theory was similarly impressive for PS/PB. Here it is noteworthy that the BGY theory accurately predicts the much narrower PS/PB coexistence curve relative to that for PS/PVME.

As a result of this research, we conclude that a rather small amount of thermal expansion or isothermal compressibility data—as few as three data points—can yield pure component parameters which may be successfully implemented in the prediction of pure fluid and mixture behavior. This is in contrast to the *PVT* route, which necessitates the acquisition of a significantly larger data set. One drawback with using thermal expansion coefficient data is the need to constrain the analysis so as to obtain a reasonable value for v, the volume per mole of lattice sites. On the other hand, our experience in determining v values has shown that “reasonable” may be reliably thought of as meaning that v lies somewhere in the range of 0.006−0.015 L/mol. Thus, while one might prefer to use compressibility data if there is a choice, the use of isothermal expansion data is not precluded. It is our belief that isothermal compressibilities and thermal expansion coefficients present an attractive alternative to *PVT* data in the analysis of pure fluid polymer thermodynamics. This implies that the BGY theory (and others) may now be used to understand and predict the behavior of a wide range of polymers for which characteristic data are rather sparse.

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