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**Liquid-Liquid Equilibria and Theta Temperatures in
Homopolymer-Solvent Solutions from a Perturbed
Hard-Sphere-Chain Equation of State**

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LIQUID-LIQUID EQUILIBRIA AND THETA TEMPERATURES IN HOMOPOLYMER-SOLVENT SOLUTIONS FROM A PERTURBED HARD-SPHERE-CHAIN EQUATION OF STATE

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ABSTRACT

The perturbed hard-sphere-chain (PHSC) equation of state is used to calculate liquid-liquid equilibria of binary nonpolar solvent/homopolymer systems exhibiting both an upper critical solution temperature (UCST) and a lower critical solution temperature (LCST). Systems studied include polyisobutylene, polyethylene, and polystyrene solutions. Equation-of-state parameters of homopolymers are obtained by regressing the pressure-volume-temperature data of polymer melts. In polymer solutions, however, theory overestimates the equation-of-state effect which causes the LCST at elevated temperature. To correct the overestimated equation-of-state effect, an empirical adjustable parameter is introduced into the perturbation term of the PHSC equation of state. An entropy parameter is also introduced into the Helmholtz energy of the mixture to correlate quantitatively the dependence of critical temperatures on polymer molecular weight. For systems exhibiting either an UCST or a LCST, theory requires two adjustable parameters to obtain quantitative agreement of theoretical critical temperatures with experiment as a function of polymer molecular weight. For systems exhibiting both an UCST and a LCST, theory often requires three adjustable parameters.

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INTRODUCTION

Equation-of-state theories for polymer systems such as the Flory-Patterson-Prigogine theory of corresponding states¹⁻³ and the lattice-fluid theory⁴ by Sanchez and Lacombe are able to represent the simultaneous occurrence of an upper critical solution temperature (UCST) and a lower critical solution temperature (LCST) in a temperature-composition diagram for solvent/polymer systems. In the absence of specific interactions such as hydrogen bonding between unlike molecules, intermolecular interactions in polymer solutions are energetically unfavorable relative to intramolecular interactions. The mixture therefore exhibits UCST behavior at low temperature where the energetic effect is dominant. As the temperature exceeds the UCST, the mixture forms a single homogeneous phase because the combinatorial entropy of mixing, which favors mutual miscibility, starts to dominate over the energetic effect. At further elevated temperature, however, the entropically unfavorable equation-of-state effect becomes dominant and the mixture again exhibits phase separation. It is now well-known that the equation-of-state effect in polymer solutions results from the compressibility disparity between compressible solvent molecules and relatively dense polymers⁵. The compressibility disparity in these systems is mainly due to the difference in molecular sizes. While qualitative features of the temperature-composition diagram are understood, it is often difficult to obtain quantitative agreement between theory and experiment.

Equation-of-state theories for binary mixtures require fitting parameters to describe the thermodynamic properties of pure fluids as well as an adjustable binary parameter which characterizes the magnitude of interaction energy between unlike segments. To apply equation-of-state theories to polymer systems, equation-of-state parameters of homopolymers are often obtained by regressing the pressure-volume-temperature (*PVT*) data of polymer melts. Equation-of-state theories have been successfully used to interpret quantitatively the LCST behavior in polymer/polymer systems⁶⁻⁸. These theories also qualitatively describe the simultaneous occurrence of an

UCST and a LCST in solvent/polymer systems. As yet, however, quantitative representation by equation-of-state theories has not been possible for liquid-liquid equilibria of polymer-solvent solutions. This work discusses a semiempirical method toward obtaining such representation.

The critical points in solvent/polymer systems lie in a dilute or semidilute polymer concentration range where polymer molecules do not overlap significantly with each other. In a polymer solution, equation-of-state theories predict a LCST at a temperature lower than experiment when the equation-of-state parameters of homopolymers are obtained by fitting the *PVT* data of polymer melts. In applying the lattice-fluid theory to polyisobutylene solutions, Sanchez and Lacombe⁴ showed that the predicted theta temperatures associated with LCST are lower than experiment. Sanchez and Lacombe⁴ also found that theta temperatures cannot be raised by simply making the intermolecular interaction more energetically favorable by adjusting the binary parameter. Here, theta temperature is defined as the asymptotic critical temperature of a solvent/polymer system in the limit of infinite polymer molecular weight. In typical polymer solutions, there are two theta temperatures; the theta temperature associated with LCST and that associated with UCST. Extensive applications of Patterson-Delmas corresponding-states theory³ to polymer solutions⁹⁻¹³ also show that calculated LCSTs are often lower than experiment. These observations indicate that equation-of-state theories tend to overestimate the equation-of-state (unfavorable entropic) effect when applied to liquid-liquid equilibria in polymer-solvent systems.

Recently, Song *et al.*¹⁴⁻¹⁹ presented a perturbed hard-sphere-chain (PHSC) equation of state applicable to polymer systems including copolymer systems. The PHSC equation of state describes the *PVT* data of homopolymers better than the lattice-fluid equation of state¹⁵. Although the PHSC equation of state quantitatively describes the LCST behavior in copolymer blends¹⁸, the model overestimates the equation-of-state effect when applied to liquid-liquid equilibria of binary solvent/polymer systems.

Lambert *et al.*¹⁹ obtain PHSC parameters of pure polymers as adjustable parameters obtained from the mixture data; in Lambert's work, equation-of-state parameters of pure polymers depend on the solvent type. Lambert's procedure, however, is not suitable for solvent/copolymer systems if the same set of intersegmental parameters between the segments comprising the copolymer molecule are used in various solvents because in that event, equation-of-state parameters of copolymers need to be independent of the solvent type.

In this paper we first show that the PHSC equation of state overestimates the equation-of-state effect when applied to liquid-liquid equilibria of real polymer solutions. An empirical adjustable parameter is introduced into the perturbation term of the PHSC equation of state to correct the overestimated equation-of-state effect. The equation-of-state parameters of homopolymers are not adjusted; they are obtained by fitting the *PVT* data of polymer melts. Theory, however, often fails to correlate quantitatively the dependence of consolute solution (critical) temperatures on polymer molecular weight. An entropy parameter is therefore introduced into the Helmholtz energy of the mixture to obtain quantitative agreement of theory with experiment for molecular-weight dependence of critical temperatures. The adjustable parameters presented in this paper give flexibility in correlating data for polymer solution liquid-liquid equilibria because equation-of-state parameters for pure polymers are not adjusted; they are independent of the solvent.

THEORY

Equation-of-State for Mixtures of Homonuclear Chains. Details of the perturbed hard-sphere-chain (PHSC) equation of state for homopolymer systems are given in References 14 to 17. The PHSC equation of state is expressed in terms of the radial distribution function at contact prior to forming the chain molecule¹⁴ and through parameters which

represent attractive and repulsive interactions between segments as given by the Song-Mason method¹⁵.

The PHSC equation of state uses the modified Chiew equation of state for athermal mixtures of hard-sphere chains¹⁴ as the reference state and the van der Waals-type perturbation term¹⁵. Consider a mixture containing m species where the mole fraction of component i is x_i . The PHSC equation of state for mixtures of homonuclear chain molecules, where each molecule consists of effective hard spheres of equal size and potential energy, is given by¹⁶

$$\begin{aligned} \frac{p}{\rho k_B T} &= \left(\frac{p}{\rho k_B T} \right)_{\text{ref}} + \left(\frac{p}{\rho k_B T} \right)_{\text{pert}} \\ &= 1 + \rho \sum_{i=1}^m \sum_{j=1}^m x_i x_j r_i r_j b_{ij} g_{ij} - \sum_{i=1}^m x_i (r_i - 1) (g_{ii} - 1) - \frac{\rho}{k_B T} \sum_{i=1}^m \sum_{j=1}^m x_i x_j r_i r_j a_{ij} \end{aligned} \quad (1)$$

where the last term is the perturbation term, p is the pressure, $\rho \equiv N/V$ (N is the number of molecules and V is the volume) is the number density, k_B is the Boltzmann constant, T is the absolute temperature, and r_i is the number of effective hard spheres per molecule of component i . In Eq. (1), g_{ij} is the radial distribution function at contact prior to bonding and a_{ij} and b_{ij} are parameters which represent attractive and repulsive interactions, respectively, on a segment basis. Subscript ij denotes a pair of effective hard spheres comprising components i and j . In the perturbation term, the term $r_i r_j a_{ij}$ can be interpreted as the parameter which represents the attractive interaction on a molecule basis between molecule i and molecule j .

In the PHSC equation of state, the Boublik-Mansoori-Carnahan-Starling expression is used¹⁴:

$$g_{ij} = \frac{1}{1-\eta} + \frac{3}{2} \frac{\xi_{ij}}{(1-\eta)^2} + \frac{1}{2} \frac{\xi_{ij}^2}{(1-\eta)^3} \quad (2)$$

where η is the packing fraction given by

$$\eta = \frac{\rho}{4} \sum_{i=1}^m x_i b_{ii} \quad (3)$$

and

$$\xi_{ij} = \frac{\rho}{4} \left(\frac{b_{ii} b_{jj}}{b_{ij}} \right)^{1/3} \sum_{i=1}^m x_i b_{ii}^{2/3} \quad (4)$$

The Helmholtz energy of the mixture, $A(T, V, N, x_i)$, is calculated from the equation of state for the mixture¹⁶, Eq. (1), as

$$\begin{aligned} \frac{A}{Nk_B T} &= \sum_{i=1}^m x_i \frac{A_i^0}{Nk_B T} + \int_0^\rho \left(\frac{p}{\rho k_B T} - 1 \right) \frac{d\rho}{\rho} + \sum_{i=1}^m x_i \ln(x_i \rho k_B T) \\ &= \sum_{i=1}^m x_i \frac{A_i^0}{Nk_B T} + \sum_{i=1}^m \sum_{j=1}^m x_i x_j r_i r_j b_{ij} \left(\int_0^\rho g_{ij} d\rho \right) - \sum_{i=1}^m x_i (r_i - 1) \left[\int_0^\rho (g_{ii} - 1) \frac{d\rho}{\rho} \right] \\ &\quad - \frac{\rho}{k_B T} \sum_{i=1}^m \sum_{j=1}^m x_i x_j r_i r_j a_{ij} + \sum_{i=1}^m x_i \ln(x_i \rho k_B T) \end{aligned} \quad (5)$$

where A_i^0 is the Helmholtz energy of N molecules of component i in the reference state. The reference state is pure ideal gas at unit pressure and at the temperature of the mixture. The athermal entropy of mixing calculated from Eq. (5) reduces to that of the incompressible Flory-Huggins lattice model²⁰ when mixing is at constant temperature and constant volume, assuming that the segment diameter is the same for all components and that the packing fractions of pure components before mixing are the same as those in the mixture^{14,16}; within the context of an equation of state, the incompressible Flory-Huggins theory is briefly discussed elsewhere^{14,16}.

We consider binary solvent/homopolymer systems where components 1 and 2 represent solvent and polymer molecules comprising segments A and B, respectively; these systems are denoted as A_{r_1}/B_{r_2} . (Segment type A should not be confused with the Helmholtz energy A .) In the following equations, subscripts of parameters denote the type of segments.

In the PHSC equation of state, parameters a_α and b_α ($\alpha=A,B$) for pure fluids consisting of segments of type α are scaled in terms of the minimum of the nonbonded segmental pair potential ϵ_α at the center to center distance σ_α by

$$a_\alpha = \frac{2}{3}\pi\sigma_\alpha^3\epsilon_\alpha F_a(k_B T/\epsilon_\alpha) \quad (\alpha=A,B) \quad (6)$$

$$b_\alpha = \frac{2}{3}\pi\sigma_\alpha^3 F_b(k_B T/\epsilon_\alpha) \quad (7)$$

where F_a and F_b are universal functions of the reduced temperature $k_B T/\epsilon$ as given by the Song-Mason method¹⁵. The essential roles of universal functions F_a and F_b are to provide temperature dependences to parameters a and b , respectively.

Parameters for a pair of unlike segments A and B are given by

$$a_{AB} = \frac{2}{3}\pi\sigma_{AB}^3\epsilon_{AB}\sqrt{F_a(k_B T/\epsilon_A)F_a(k_B T/\epsilon_B)} \quad (8)$$

$$b_{AB} = \frac{1}{8}(b_A^{1/3} + b_B^{1/3})^3 \quad (9)$$

$$\sigma_{AB} = \frac{1}{2}(\sigma_A + \sigma_B) \quad (10)$$

$$\epsilon_{AB} = (1 - \kappa_{AB})\sqrt{\epsilon_A\epsilon_B} \quad (11)$$

where κ_{AB} is an adjustable intersegmental parameter. In Eq. (9), additivity of hard-sphere diameters may be relaxed by introducing an additional intersegmental parameter into Eq. (9)¹⁸.

Universal functions F_a and F_b can be determined from available configurational thermodynamic property of a simple fluid ($r=1$) if σ and ε are accurately known¹⁵. Originally, these functions were determined by fitting the vapor pressures and the densities of saturated liquid and vapor for methane and argon¹⁵. The gas-liquid critical temperature of pure fluids, however, increases as the molecular weight of fluid rises. Therefore, for molecular fluids ($r>1$), it was necessary to introduce a scaling parameter¹⁵ into the reduced temperature to keep the magnitude of reduced temperature within the range used to determine F_a and F_b . Later, to cover a much wider reduced temperature range without using the scaling parameter, new universal functions were determined by using the *PVT* data for liquid methane and argon as well as the thermodynamic properties used in determining the original universal functions. The new universal functions are given by¹⁹

$$F_a(k_B T/\varepsilon) = 1.8681 \exp[-0.0619(k_B T/\varepsilon)] + 0.6715 \exp[-1.7317(k_B T/\varepsilon)^{3/2}] \quad (12)$$

$$F_b(k_B T/\varepsilon) = 0.7303 \exp[-0.1649(k_B T/\varepsilon)^{1/2}] + (1 - 0.7303) \exp[-2.3973(k_B T/\varepsilon)^{3/2}] \quad (13)$$

References 15 and 19 give details of computation procedures for the regression of PHSC equation-of-state parameters.

Phase Equilibrium Calculation. The critical points and coexistence curves of mixtures can be computed from the Helmholtz energy of the mixture, $A(T, V, N, x_i)$, given by Eq. (5). The chemical potential per molecule of component i , μ_i , is found from $A(T, V, N, x_i)$:

$$\mu_i = \left(\frac{\partial A}{\partial N_i} \right)_{T, V, N_{j \neq i}} \quad (14)$$

The expression for the chemical potential is given in References 16 and 18. For a fixed temperature, the coexistence curve is calculated by equating the pressure and, for each component, chemical potentials of coexisting phases. The conditions for critical points are given in References 16 and 18. The pressure of the mixture is computed by equating the chemical potential of a solvent molecule in the vapor phase to that in the liquid phase. At low pressures considered here, the vapor phase is pure solvent.

RESULTS AND DISCUSSION

Tables I and II give the PHSC equation-of-state parameters for the universal functions defined by Eqs. (12) and (13). For each system, Table III gives the range of polymer molecular weight used in experiment by the original investigators.

Overestimation of the Equation-of-State Effect. When applied to liquid-liquid equilibria of polymer solutions, the PHSC equation of state overestimates the equation-of-state effect which is responsible for the lower critical solution temperature (LCST). Theoretical LCST is significantly lower than experimental. Quantitative agreement of theoretical LCST with experiment cannot be obtained by adjusting the intersegmental parameter κ_{AB} defined by Eq. (11).

Overestimation of the equation-of-state effect may be caused by an erroneous implicit assumption in the perturbation term. This assumption becomes apparent when the equation of state is expressed in terms of segment fraction ϕ_i and segment number density ρ_r defined by

$$\phi_i \equiv \frac{N_i r_i}{N_r} \quad (i=1, \dots, m) \quad (15)$$

$$\rho_r \equiv \frac{N_r}{V} \quad (16)$$

where N_i is the number of molecules of component i and N_r is the total number of segments given by

$$N_r = \sum_{i=1}^m N_i r_i \quad (17)$$

With T , ϕ_i , and ρ_r as intensive variables, Eq. (1) is given by¹⁶

$$\frac{p}{\rho_r k_B T} = 1 + \rho_r \sum_{i=1}^m \sum_{j=1}^m \phi_i \phi_j b_{ij} g_{ij} - \sum_{i=1}^m \phi_i \left(1 - \frac{1}{r_i}\right) g_{ii} - \frac{\rho_r}{k_B T} \sum_{i=1}^m \sum_{j=1}^m \phi_i \phi_j a_{ij} \quad (18)$$

Equation (18) indicates that the perturbation term neglects chain connectivity. The PHSC theory approximates the perturbation term of the hard-sphere-chain system by that of a system obtained by first breaking the bonds between bonded hard spheres and then randomly mixing non-bonded spheres. In the latter system, the segment density of a particular segment is uniform throughout the system. This assumption is reasonable in pure polymer melts and concentrated polymer solutions where the polymer-segment density as well as the solvent-segment density are essentially uniform, that is, when the mean-field assumption is valid.

In dilute polymer solutions, however, the assumption of uniform polymer-segment density is not valid. Mean-field theory fails in dilute solutions because, in these systems, polymer segments are localized inside isolated polymer molecules. In addition, the polymer-segment density near the periphery of a spherical volume element occupied by a polymer molecule is smaller than that near the center of the sphere. The interaction between two polymer molecules in dilute solutions may be modeled better by the interaction between weakly overlapping spheres. The extent of interpenetration depends

on various factors including the polymer's molecular weight, polymer concentration, and solvent quality. In a dilute solution, all polymer segments of a polymer molecule are not available for interaction with polymer segments of another polymer molecule²⁰⁻²³.

In dilute polymer solutions, the number of segments of a polymer molecule interacting with those of another polymer molecule is smaller than the number of polymer-polymer interactions in pure polymer melts. Using the incompressible Flory-Huggins theory, Inagaki *et al.*²⁴⁻²⁷ showed that in ternary dilute polymer1/polymer2/solvent systems, the contact frequency between segments of polymer1 and those of polymer2 is smaller than that given by the mean-field theory.

In the PHSC equation of state, the term $r_i r_j a_{ij}$ in Eq. (1) represents attractive interaction between a pair of molecules of components i and j . Because all polymer segments are not available for interactions in a dilute polymer solution, it is not correct to assume that the parameter which represents the interaction between two polymer molecules in a dilute polymer solution is the same as that in a pure polymer melt whose properties were used to obtain equation-of-state parameters for a polymer.

For binary mixtures of type A_{r_1}/B_{r_2} , the perturbation term in Eq. (1) is given by

$$\left(\frac{p}{\rho k_B T}\right)_{\text{pert}} = -\frac{\rho}{k_B T} (x_1^2 r_1^2 a_A + 2x_1 x_2 r_1 r_2 a_{AB} + x_2^2 r_2^2 a_B) \quad (19)$$

where components 1 and 2 represent solvent and polymer, respectively. In Eq. (19), $r_2^2 a_B$ represents attractive interaction between two polymer molecules. Intersegmental parameter κ_{AB} enters the equation of state through parameter a_{AB} . Due to neglect of chain connectivity, overestimation of the equation-of-state effect in dilute polymer solutions probably follows from the overestimated contribution of the term associated with the polymer molecule in the perturbation term, $r_2^2 a_B$.

The calculated LCST is readily raised by decreasing the magnitude of the last term in Eq. (19). Here, we propose to replace r_2 in Eq. (19) by r_2^* defined by

$$r_2^* \equiv r_2 v_B \quad (v_B \leq 1) \quad (20)$$

where v_B is an adjustable parameter. Parameter v_B effectively decreases the magnitude of the term which represents the attractive interaction between two polymer molecules in a dilute solution. The perturbation term in the equation of state now becomes

$$\begin{aligned} \left(\frac{p}{\rho k_B T} \right)_{\text{pert}} &= - \frac{\rho}{k_B T} \left(x_1^2 r_1^2 a_A + 2x_1 x_2 r_1 r_2^* a_{AB} + x_2^2 r_2^{*2} a_B \right) \\ &= - \frac{\rho}{k_B T} \left(x_1^2 r_1^2 a_A + 2x_1 x_2 r_1 r_2 v_B a_{AB} + x_2^2 r_2^2 v_B^2 a_B \right). \end{aligned} \quad (21)$$

Parameter v_B is introduced only into the perturbation term; the reference state in the equation of state remains unchanged. In the equation of state and Helmholtz energy of the mixture, we only need to replace a_{AB} and a_B by $v_B a_{AB}$ and $v_B^2 a_B$, respectively. We recognize that parameter v_B is a complicated function of composition and polymer molecular weight; v_B approaches unity in the limit of pure polymer. To a reasonable approximation, we expect that v_B is independent of composition for liquid-liquid equilibria in polymer solutions when both liquid phases are dilute (or semidilute) in polymer. Parameter v_B may also vary with solvent quality because polymer molecules interpenetrate each other more significantly in poor solvents. For a given polymer, however, we expect that v_B is a constant in solvents having similar quality.

Comparison with Experiment Using Parameter v_B . Figure 1 compares theoretical coexistence curves with experiment for the system *n*-pentane/polyisobutylene ($M_\eta=72000$; $M_\eta \equiv$ viscosity-average molecular weight)²⁸ exhibiting LCST behavior. With $v_B=1$, the PHSC equation of state predicts a LCST significantly lower than experiment. The theoretical LCST cannot be raised significantly by adjusting κ_{AB} . The theoretical critical composition is also too small compared to experiment. Even with an unreasonably

small $\kappa_{AB}=-0.5$, the calculated LCST is more than 100°C lower than experiment; a negative κ_{AB} represents an energetically favorable intermolecular interaction.

For systems exhibiting LCST only, however, the theoretical LCST is readily raised to the experimental LCST by adjusting the parameter v_B alone; κ_{AB} is set to zero. By introducing parameter v_B , good agreement is obtained with experiment for the theoretical coexistence curve. The results shown in Figure 1 indicate that in dilute polymer solutions, the PHSC equation of state overestimates the equation-of-state effect which gives an unfavorable entropic contribution to the Helmholtz energy.

An important question is whether v_B is a solvent-independent constant for a given polymer. Figure 2 compares theoretical coexistence curves with experiment for several polyisobutylene solutions ($M_\eta=72000$)²⁸ exhibiting LCST behavior. For all systems, $\kappa_{AB}=0.0$ and $v_B=0.797$, except for the system benzene/polyisobutylene ($\kappa_{AB}=0.018$) which is also reported to exhibit UCST behavior near room temperature²⁹. The coexistence curve associated with the UCST of the system benzene/polyisobutylene is not shown in Figure 2. Theory and experiment show semiquantitative agreement; the dependence of LCST on the solvent type is predicted fairly well. Although not shown, the predicted dependence of LCST on the polymer's molecular weight is small for systems shown in Figure 2.

Figure 3 shows Shultz-Flory plots for four *n*-alkane/polyethylene systems³⁰ exhibiting LCST behavior. For all systems, $\kappa_{AB}=0.0$ and $v_B=0.820$. The Shultz-Flory plot is a plot of the reciprocal of critical solution temperatures against $(1/r^{1/2} + 1/2r)$ where r is defined by

$$r \equiv r_2/r_1 \quad (22)$$

Here, r_i is the number of segments per molecule of component i in the PHSC theory. In the Flory-Huggins theory²⁰, where all segments have the same diameter, the Shultz-Flory plot is a straight line given by

$$\frac{1}{T_c} = \frac{1}{\Theta} \left[1 + \frac{1}{\psi} \left(\frac{1}{r^{1/2}} + \frac{1}{2r} \right) \right] \quad (23)$$

where T_c is the critical solution temperature, Θ is the theta temperature, and ψ is Flory's entropy parameter²⁰. The entropy parameter ψ changes the dependence of critical temperatures on the polymer molecular weight but does not affect the theta temperature. Equation (23) shows that the theta temperature is the critical temperature in the limit of infinite polymer molecular weight.

In Shultz-Flory plots, the reciprocal of critical temperature, T_c^{-1} , is plotted. Therefore, the difference between theory and experiment in absolute temperature is larger for smaller T_c^{-1} for a given difference between theoretical and experimental points in Shultz-Flory plots.

In Figure 3, intercepts in the limit $r \rightarrow \infty$ give the calculated theta temperatures reported by Hamada *et al.*³⁰ These authors determined theta temperatures by correlating the measured critical temperatures of various solutions containing different polymer molecular weights to those given by the Shultz-Flory equation, Eq. (23). In n -alkane/polyethylene systems, the LCST rises with increasing molecular weight of n -alkane because the compressibility disparity decreases as the difference in molecular sizes declines, even though the combinatorial entropy of mixing, which favors mutual solubility, decreases with increasing molecular weight of n -alkane. Although theory semiquantitatively predicts the dependence of LCST on solvents, the molecular-weight dependence of LCST is underpredicted. To obtain quantitative agreement of theory with experiment, v_B must be slightly system-dependent.

Figure 4a compares the theoretical coexistence curve with experiment for the system *n*-butyl acetate/polyethylene³¹ exhibiting both an UCST and a LCST ($\kappa_{AB}=0.02650$, $v_B=0.8272$). The Shultz-Flory plot for this system is shown in Figure 4b together with the Shultz-Flory plot for the system *n*-pentyl acetate/polyethylene³¹ ($\kappa_{AB}=0.02281$, $v_B=0.820$). For the latter system, v_B is the same as that used in *n*-alkane/polyethylene systems shown in Figure 3. In the system *n*-butyl acetate/polyethylene, theory overpredicts the LCST about 15°C when κ_{AB} is adjusted to match the UCST with $v_B=0.820$. For high-molecular-weight polyethylene, the system *n*-butyl acetate/polyethylene exhibits an hourglass-type phase diagram with no temperature range where the mixture is miscible in all proportions. Similar to *n*-alkane/polyethylene systems, *n*-alkyl acetate/polyethylene systems become more miscible as the molecular weight of *n*-alkyl acetate rises. For systems shown in Figures 4a and 4b, theory and experiment show good agreement using two adjustable parameters κ_{AB} and v_B .

In all the polystyrene solutions studied in this work, however, theoretical coexistence curves are too narrow compared to experiment. Figure 5 compares theoretical coexistence curves with experiment for the system cyclohexane/polystyrene¹¹ ($\kappa_{AB}=0.02160$, $v_B=0.771$). Theory and experiment show good agreement for the dependence of UCST on the molecular weight of polymer. Theory, however, underpredicts the molecular-weight dependence of LCST.

Figure 6a shows Shultz-Flory plots for cyclohexane/polystyrene^{11,32} ($\kappa_{AB}=0.02160$), methyl cyclohexane/polystyrene¹¹ ($\kappa_{AB}=0.02456$), and cyclopentane/polystyrene¹² ($\kappa_{AB}=0.02038$). These systems exhibit both an UCST and a LCST. For all systems shown in Figure 6, $v_B=0.771$. The intersegmental parameter κ_{AB} was adjusted such that the theoretical UCST agrees with experiment for the highest molecular weight of polymer. Using the same value of v_B , theory gives semiquantitative agreement with experiment.

Figure 6b shows Shultz-Flory plots for several polystyrene solutions which exhibit either an UCST or a LCST ($v_B=0.771$ for all systems). The system *trans*-decalin/polystyrene³³ ($\kappa_{AB}=0.02631$) does not exhibit LCST up to about 360°C. In this system the PHSC equation of state predicts that the theta temperature associated with LCST is about 389°C, consistent with experiment. The critical temperature of *trans*-decalin is reported to be 404°C.³³ In the system *trans*-decalin/polystyrene, the dependence of UCST on the polymer molecular weight is slightly overestimated. Theory gives semiquantitative agreement with experiment for benzene/polystyrene¹² and toluene/polystyrene¹¹, i.e., theory is able to predict that the LCST in the system toluene/polystyrene is higher than that in the system benzene/polystyrene. For the system methyl ethyl ketone/polystyrene¹², however, theory significantly overestimates the LCST; in this system, theory requires v_B larger than 0.771.

For *n*-alkyl acetate/polystyrene¹³ systems, semiquantitative agreement of theory with experiment was not obtained using the same value of v_B . For systems shown in Figure 7, κ_{AB} and v_B were determined simultaneously such that the theoretical UCST and LCST agree with experiment for the highest molecular weight of polymer. Although both κ_{AB} and v_B were adjusted, the underestimation of the dependence of critical temperatures on the molecular weight of polymer is severe. In *n*-alkyl acetate/polystyrene systems, parameter v_B increases as the solvent quality declines. This observation follows from the enhanced interpenetration of polymer molecules in poor solvents. Although not shown, similar behavior was also observed for isoalkyl acetate/polystyrene systems¹³. In solvent/polystyrene systems, it appears that theory and experiment are in poor agreement in polar solvents such as methyl ethyl ketone and alkyl acetates.

Introduction of Entropy Parameter. Figures 3 and 6 to 7 show that theory often underestimates the dependence of critical temperatures on the molecular weight of polymer. Theoretical prediction is not improved by introducing an additional

intersegmental parameter into Eq. (9) to relax the additivity of hard-sphere diameters between unlike segments. Here, we improve the PHSC theory by introducing an entropy parameter into the Helmholtz energy of the mixture in a manner similar to that used by Flory in his equation-of-state theory³⁴⁻³⁷. The correction term introduced by Flory is independent of density³⁴⁻³⁷.

In our equation-of-state theory, the additional term associated with the entropy parameter is also assumed to be independent of density. Therefore, the entropy parameter does not affect the equation of state. While an entropy parameter was used by Flory in his equation-of-state theory³⁴⁻³⁷ as well as in the Flory-Huggins lattice theory²⁰, in equation-of-state theories, there is little discussion in the literature for the effect of an entropy parameter on the predicted molecular-weight dependence of critical solution temperatures of polymer solutions³³.

We introduce an empirical entropy parameter similar to Flory's ψ in the incompressible Flory-Huggins theory. The correction term associated with the entropy parameter in the Helmholtz energy of the mixture should vanish for pure fluids. In Eq. (23), Flory entropy parameter ψ is a useful parameter to correlate experimental data because it does not affect theta temperatures but changes the molecular-weight dependence of critical temperatures.

In the PHSC equation of state, energetic interactions are represented by the perturbation term in Eq. (1). For binary systems, the contribution from the perturbation term to the Helmholtz energy of the mixture is given by

$$\left(\frac{A}{Nk_B T}\right)_{\text{pert}} = -\frac{\rho}{k_B T} \sum_{i=1}^2 \sum_{j=1}^2 x_i x_j r_i r_j a_{ij} \quad (24)$$

In the Helmholtz energy of mixing of the Flory-Huggins theory, the additional term associated with the entropy parameter has the same composition dependence as that in the

term associated with the energy parameter. Therefore, for the PHSC equation of state, the appropriate way to introduce the entropy parameter may be to include the following correction term A^* into the Helmholtz energy of the mixture given by Eq. (5):

$$\frac{A^*}{Nk_B T} = -\frac{2}{3}\pi\sigma_{AB}^3 q_{AB} x_1 x_2 r_1 r_2 \quad (25)$$

where q_{AB} is the PHSC equation-of-state entropy parameter.

However, much better agreement of theory with experiment is obtained if the right hand side of Eq. (25) is multiplied by $r_2^{1/2}$. The proposed entropy correction term is then given by

$$\frac{A^*}{Nk_B T} = -\frac{2}{3}\pi\sigma_{AB}^3 q_{AB} x_1 x_2 r_1 r_2^{3/2} \quad (26)$$

The factor $2/3\pi\sigma_{AB}^3$ was introduced to make q_{AB} of order 0.01 to 0.1. The PHSC equation-of-state entropy parameter q_{AB} defined by Eq. (25) has units of inverse volume.

Equation (26) is added to Eq. (5). Equation (26) is independent of density and therefore does not affect the equation of state, Eq. (1). As shown elsewhere³⁸, the contribution from Eq. (26) vanishes in the theta limit given by Lambert *et al.*¹⁹. The theta limit provides a systematic way to determine theta temperatures of polymer solutions using the PHSC equation of state¹⁹. Similar to the Flory entropy parameter ψ in the incompressible Flory-Huggins theory, the PHSC equation-of-state entropy parameter q_{AB} also does not affect theta temperatures³⁸. Chemical potentials associated with Eq. (26) are given in the Appendix.

A physical interpretation of the entropy parameter, however, is not obvious. This parameter could reflect the possible entropic nature of interactions between solvent and polymer molecules. The Flory entropy parameter, however, can also be interpreted as the

correction to the combinatorial entropy of mixing³⁴⁻³⁷. Similarly, the PHSC equation-of-state entropy parameter may represent a correction to the combinatorial entropy of mixing in the ideal gas limit given by

$$\frac{\Delta_{\text{mix}} S}{Nk_B} = - \sum_{i=1}^m x_i \ln x_i \quad (27)$$

The combinatorial entropy of mixing could depend on various factors (e.g., chain connectivity, chain flexibility, and structure of solvent) which are not included in the Flory-Huggins and PHSC theories.

Using the entropy parameter q_{AB} defined by Eq. (26), theory and experiment show good agreement for the dependence of critical temperatures on the molecular weight of polymer in various systems. Figures 8a and 8b show Shultz-Flory plots for systems *n*-hexane/polyethylene³⁰ and *n*-octane/polyethylene³⁰, respectively. Since these systems show only LCST behavior, κ_{AB} is set to zero. For the theory with $q_{AB}=0$, parameter v_B was determined such that theory and experiment agree for the highest molecular weight of polyethylene used in the data reported by Hamada *et al.*³⁰. The range of molecular weight of polyethylene used by these authors is given in Table III. Without using the entropy parameter, theory underestimates the molecular-weight dependence of critical temperatures. Solid curves in Figures 8a and 8b represent the theory with v_B and q_{AB} ; these parameters were obtained such that theory and experiment agree for the lowest and highest molecular weights of polyethylene.

Figures 9a and 9b show Shultz-Flory plots for systems benzene/polystyrene¹² and methyl ethyl ketone/polystyrene¹², respectively, exhibiting LCST behavior. For the system methyl ethyl ketone/polystyrene, theory is able to represent the observed non-linear behavior in the Shultz-Flory plot.

Figure 10 compares theoretical Shultz-Flory plots with experiment for the system cyclopentane/polystyrene¹² exhibiting both an UCST and a LCST. For the theory with q_{AB} , adjustable parameters were determined such that the LCST and UCST for the highest molecular weight of polystyrene and the UCST for the lowest molecular weight agree with experiment. Theoretical UCST and experiment show good agreement. Theory, however, underestimates the molecular-weight dependence of LCST.

Figures 11a and 11b show Shultz-Flory plots for systems methyl acetate/polystyrene¹³ and isopropyl acetate/polystyrene¹³, respectively. These systems also exhibit noticeable non-linear behavior in Shultz-Flory plots. With entropy parameter q_{AB} , theory and experiment show good agreement for the dependences of both UCST and LCST on the molecular weight of polystyrene.

Figure 12 shows theoretical Shultz-Flory plots for the system ethyl formate/polystyrene³⁹. The molecular weight of polystyrene used in experiment is small ($M_w = 2200 - 37000$). As the molecular weight of polystyrene rises, the system eventually exhibits an hour-glass phase diagram similar to that observed in *n*-butyl acetate/polyethylene³¹ shown in Figure 4b. For polymer solutions, hour-glass phase diagrams are also reported for systems acetone/polystyrene¹⁰ and acetone/cellulose acetate⁹. With entropy parameter q_{AB} , theory and experiment show good agreement.

Finally, we briefly discuss extension of the present model to multicomponent systems. Consider a ternary solvent/solvent/homopolymer system denoted by $A_{r_1}/C_{r_2}/B_{r_3}$ where segments A and C represent segments comprising solvent molecules. The homopolymer molecule, component 3, consists of segments of type B. For ternary systems, three sets of adjustable parameters are required for three possible pairs of components. In principle, these adjustable parameters can be obtained from the three possible binary systems. The PHSC equation of state has been extended to multicomponent systems of homogeneous molecules⁴⁰.

When adjustable parameters are obtained from binary systems, however, it is necessary to use the same value for the parameter v_B in two binary solvent/homopolymer systems: systems A_{r_1}/B_{r_3} and C_{r_2}/B_{r_3} . Since LCST is sensitive to parameter v_B , for the analysis of LCST behavior, it may be necessary to adjust slightly the equation-of-state parameters of one solvent. For systems exhibiting only UCST behavior, equation-of-state parameters of solvents need not be adjusted; UCSTs in binary polymer systems A_{r_1}/B_{r_3} and C_{r_2}/B_{r_3} can be fitted by adjusting intersegmental parameters κ_{AB} and κ_{BC} using the same v_B .

CONCLUSIONS

The perturbed hard-sphere-chain (PHSC) equation of state has been used to calculate liquid-liquid equilibria in binary solvent/homopolymer systems containing polyisobutylene, polyethylene, and polystyrene. Equation-of-state parameters of homopolymers were regressed from the pressure-volume-temperature data of polymer melts. Theory, however, overestimates the equation-of-state effect in solvent/polymer systems.

An empirical adjustable parameter v_B was introduced into the perturbation term to correct the overestimated equation-of-state effect. In the perturbation term, parameter v_B decreases the number of interacting polymer segments. Parameter v_B crudely represents the extent of interpenetration of polymer molecules in dilute and semidilute solutions. Parameter v_B primarily determines the lower critical solution temperature (LCST). The PHSC equation of state also requires intersegmental parameter κ_{AB} which determines the strength of interaction energy between unlike segments A and B. Intersegmental parameter κ_{AB} mainly affects the upper critical solution temperature (UCST).

For a given polymer, semiquantitative agreement of predicted LCST and experiment was obtained by using the constant v_B , except for polystyrene in marginal and poor solvents such as methyl ethyl ketone and *n*-alkyl acetate. Using two adjustable

parameters κ_{AB} and v_B , theoretical coexistence curves and Shultz-Flory plots show good agreement with experiment for *n*-butyl acetate/polystyrene and *n*-pentyl acetate/polystyrene exhibiting both an UCST and a LCST. For cyclohexane/polystyrene and *trans*-decalin/polystyrene, theory and experiment show good agreement for the dependence of UCST on the molecular weight of polystyrene. In solvent/polystyrene systems, however, theoretical coexistence curves are too narrow when compared to experiment.

To obtain quantitative agreement of theory with experiment in various systems, it is necessary that parameter v_B be slightly system-dependent. Parameter v_B increases as the solvent quality decreases because polymer molecules interpenetrate each other more significantly in poor solvents. To obtain the effect of molecular weight on critical temperatures, it is necessary to introduce an entropy parameter q_{AB} that affects the dependence of critical temperatures on the molecular weight of polymer but does not affect theta temperatures. For systems exhibiting only a LCST, parameters v_B and q_{AB} are required to fit the Shultz-Flory plot; the remaining parameter κ_{AB} is set to zero. For systems exhibiting both an UCST and a LCST, theory requires all three adjustable parameters. With adjustable parameters introduced in this paper, PHSC theory gives good agreement with experimental Shultz-Flory plots.

When experimental theta temperatures are available for the system A_{r_1}/B_{r_2} , parameters v_B and κ_{AB} can be obtained from theta temperatures by using the PHSC equation of state in the theta limit described by Lambert *et al.*¹⁹. Entropy parameter q_{AB} is then obtained from the critical temperature of a system A_{r_1}/B_{r_2} for which the molecular weight of polymer is known. The adjustable parameters presented in this paper can also be introduced into the PHSC equation of state for solvent/copolymer systems given by Hino *et al.*¹⁸.

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Appendix. Chemical Potentials Associated with Eq. (26)

The additional chemical potential per molecule of component 1 due to the entropy correction term, Eq. (26), is given by

$$\frac{\mu_1^*}{k_B T} = \left(\frac{\partial A^*/k_B T}{\partial N_1} \right)_{T, V, N_2} = -\frac{2}{3} \pi \sigma_{AB}^3 q_{AB} x_2^2 r_1 r_2^{3/2} . \quad (A.1)$$

Similarly, the additional chemical potential per molecule of component 2 due to the entropy correction term is given by

$$\frac{\mu_2^*}{k_B T} = \left(\frac{\partial A^*/k_B T}{\partial N_2} \right)_{T, V, N_1} = -\frac{2}{3} \pi \sigma_{AB}^3 q_{AB} x_1^2 r_1 r_2^{3/2} . \quad (A.2)$$

Equations (A.1) and (A.2) can be expressed in terms of the segment fraction using

$$x_i = \frac{\phi_i / r_i}{\phi_1 / r_1 + \phi_2 / r_2} \quad (i=1, 2) . \quad (A.3)$$

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TABLE I. PHSC Equation-of-State Parameters of Solvents for the Universal Functions Given by Eqs. (12) and (13)

Solvent	r	σ (Å)	ϵ/k_B (K)
<i>n</i> -pentane	3.149	3.995	226.0
<i>n</i> -hexane	3.446	4.084	235.6
<i>n</i> -octane	5.055	3.850	219.6
benzene	2.727	3.958	291.6
<i>n</i> -heptane	4.255	3.947	225.9
<i>n</i> -butyl acetate	5.413	3.514	216.3
<i>n</i> -pentyl acetate	6.547	3.403	206.6
cyclohexane	2.723	4.215	286.7
methyl cyclohexane	2.968	4.336	283.7
cyclopentane	2.509	4.090	277.3
<i>trans</i> -decalin	3.160	4.657	333.8
benzene	2.727	3.958	291.6
toluene	3.138	4.019	287.0
methyl ethyl ketone	3.344	3.694	255.8
methyl acetate	3.804	3.338	224.8
ethyl acetate	4.509	3.369	213.5
<i>n</i> -propyl acetate	4.989	3.440	213.9
isopropyl acetate	4.779	3.484	210.6
ethyl formate	3.408	3.491	237.2

TABLE II. PHSC Equation-of-State Parameters of Homopolymers for the Universal Functions Given by Eqs. (12) and (13)

Polymer	r/M (mol/g)	σ (Å)	ϵ/k_B (K)
polyisobutylene	0.04963	3.725	331.9
polyethylene	0.05854	3.603	306.0
polystyrene	0.03834	3.899	385.4

M = molecular weight (g/mol)

Table III. Range of Polymer Molecular Weight Used in Experiment

System	Molecular weight range (g/mol)
PE/ <i>n</i> -pentane	$M_w = 4900 - 22760$
PE/ <i>n</i> -hexane	$M_w = 34900 - 442100$
PE/ <i>n</i> -heptane	$M_w = 76800 - 202000$
PE/ <i>n</i> -octane	$M_w = 76800 - 202000$
PE/ <i>n</i> -butyl acetate	$M_\eta = 13600 - 64000$
PE/ <i>n</i> -amyl acetate	$M_\eta = 13600 - 175000$
PS/cyclohexane	$M_w = 37000 - 2700000$
PS/methyl cyclohexane	$M_w = 37000 - 2700000$
PS/cyclopentane	$M_w = 37000 - 2700000$
PS/ <i>trans</i> -decalin	$M_w = 37000 - 2700000$
PS/benzene	$M_w = 37000 - 2700000$
PS/toluene	$M_w = 37000 - 2700000$
PS/methyl ethyl ketone	$M_w = 37000 - 2700000$
PS/ <i>n</i> -alkyl acetate	$M_w = 37000 - 2700000$
PS/isopropyl acetate	$M_w = 10000 - 2700000$
PS/ethyl formate	$M_w = 2200 - 37000$

PE=polyethylene; PS=polystyrene; M_w =weight-average molecular weight; M_η =viscosity-average molecular weight

FIGURE CAPTIONS

Figure 1. Comparison of theoretical coexistence curves with experiment for *n*-pentane/polyisobutylene ($M_\eta=72000$)²⁸ exhibiting LCST behavior. Theory with $v_B=1.0$ significantly underestimates the LCST.

Figure 2. Comparison of theoretical coexistence curves with experiment for several polyisobutylene (PIB) solutions ($M_\eta=72000$)²⁸ exhibiting LCST behavior. In all systems, $\kappa_{AB}=0$ and $v_B=0.797$ except for the system benzene/polyisobutylene ($\kappa_{AB}=0.018$) which is also reported to exhibit an UCST²⁹ near room temperature. The coexistence curve associated with the UCST for the system benzene/polyisobutylene is not shown. The PHSC theory requires the parameter v_B to correct the overestimated equation-of-state effect.

Figure 3. Shultz-Flory plots for *n*-alkane/polyethylene (PE) systems exhibiting LCST behavior ($\kappa_{AB}=0$ and $v_B=0.820$ for all systems)³⁰. Points in the limit $r \rightarrow \infty$ are theta temperatures determined by the Shultz-Flory equation, Eq. (23), reported by Hamada *et al.*³⁰.

Figure 4. (a) Comparison of theoretical coexistence curves with experiment for *n*-butyl acetate/polyethylene (PE) exhibiting both an UCST and a LCST³¹ ($M_\eta=64000$); $\kappa_{AB}=0.02650$, $v_B=0.8272$; (b) Shultz-Flory plots for systems *n*-butyl acetate/polyethylene and *n*-pentyl acetate/polyethylene³¹. For the latter system, $\kappa_{AB}=0.02281$ and $v_B=0.820$.

Figure 5. Comparison of theoretical coexistence curves with experiment for cyclohexane/polystyrene¹¹ ($\kappa_{AB}=0.02160$, $v_B=0.771$), (a) coexistence curves associated with LCST, (b) coexistence curves associated with UCST.

Figure 6. Shultz-Flory plots for (a) cyclohexane/polystyrene (PS)^{11,32} ($\kappa_{AB}=0.02160$), methyl cyclohexane/polystyrene¹¹ ($\kappa_{AB}=0.02456$), and cyclopentane/polystyrene¹² ($\kappa_{AB}=0.02038$) which exhibit both an UCST and a LCST; $v_B=0.771$ for all systems. (b) *trans*-decalin/polystyrene (PS)³³ (UCST), benzene/polystyrene¹² (LCST), toluene/polystyrene¹¹ (LCST), and methyl ethyl ketone/polystyrene¹² (LCST). $\kappa_{AB}=0$ and $v_B=0.771$ for all systems except the system *trans*-decalin/polystyrene for which $\kappa_{AB}=0.02631$.

Figure 7. Shultz-Flory plots for methyl acetate/polystyrene (PS)¹³ ($\kappa_{AB}=0.02324$ and $v_B=0.827$), ethyl acetate/polystyrene¹³ ($\kappa_{AB}=0.01386$ and $v_B=0.813$), and *n*-propyl acetate/polystyrene¹³ ($\kappa_{AB}=0.00751$ and $v_B=0.799$) which exhibit both an UCST and a LCST.

Figure 8. Shultz-Flory plots for *n*-alkane/polyethylene³⁰ exhibiting LCST behavior ($\kappa_{AB}=0$), (a) *n*-hexane/polyethylene; (- - -) $v_B=0.8218$, $q_{AB}=0$; (—) $v_B=0.8234$, $q_{AB}=0.03599 \text{ \AA}^{-3}$, (b) *n*-octane/polyethylene; (- - -) $v_B=0.8153$, $q_{AB}=0$; (—) $v_B=0.8186$, $q_{AB}=0.01985 \text{ \AA}^{-3}$. The entropy parameter q_{AB} is required to obtain quantitative agreement between theory and experiment.

Figure 9. Shultz-Flory plots for polystyrene solutions exhibiting LCST behavior¹² ($\kappa_{AB}=0$), (a) benzene/polystyrene; (- - - -) $v_B=0.7808$, $q_{AB}=0$; (—) $v_B=0.7817$, $q_{AB}=0.09716 \text{ \AA}^{-3}$, (b) methyl ethyl ketone/polystyrene; (- - - -) $v_B=0.8458$, $q_{AB}=0$; (—) $v_B=0.8479$, $q_{AB}=0.1474 \text{ \AA}^{-3}$.

Figure 10. Shultz-Flory plots for cyclopentane/polystyrene¹² exhibiting both an UCST and a LCST; (- - - -) $\kappa_{AB}=0.01988$, $v_B=0.7796$, $q_{AB}=0$; (—) $\kappa_{AB}=0.01993$, $v_B=0.780$, $q_{AB}=0.02791 \text{ \AA}^{-3}$.

Figure 11. Shultz-Flory plots for polystyrene solutions exhibiting both an UCST and a LCST¹³, (a) methyl acetate/polystyrene; (- - - -) $\kappa_{AB}=0.02324$, $v_B=0.8270$, $q_{AB}=0$; (—) $\kappa_{AB}=0.02364$, $v_B=0.8282$, $q_{AB}=0.09185 \text{ \AA}^{-3}$, (b) isopropyl acetate/polystyrene; $\kappa_{AB}=0.01305$, $v_B=0.8037$, $q_{AB}=0$; (—) $\kappa_{AB}=0.01332$, $v_B=0.8049$, $q_{AB}=0.04792 \text{ \AA}^{-3}$.

Figure 12. Shultz-Flory plots for ethyl formate/polystyrene³⁹ exhibiting both an UCST and a LCST; (- - - -) $\kappa_{AB}=0.02267$, $v_B=0.8185$, $q_{AB}=0$; (—) $\kappa_{AB}=0.02513$, $v_B=0.8270$, $q_{AB}=0.0759 \text{ \AA}^{-3}$.

Figure 1

Figure 2

Figure 3

Figure 4

Figure 5

Figure 6

Figure 7

Figure 8

Figure 9

Figure 10

Figure 11

Figure 12

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