

# Solute-Induced Effects on the Structure and Thermodynamics of Infinitely Dilute Mixtures

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*A general molecular-based formalism developed rigorously establishes microscopic bases of the supercritical solubility enhancement in terms of well-defined molecular correlation function integrals by unambiguously splitting the mixture's properties into short-(finite) and long-range (diverging) contributions. Consequently, the short-range nature of the solute's and solvent's residual chemical potentials is proved and the change of the solvent's local environment around an infinitely dilute solute and its finite contribution to solute mechanical partial molar properties are interpreted in terms of the short-range solute-solvent and solvent-solvent direct correlation function integrals. The solute-induced effect on the system's microstructure and thermodynamics approaches zero as the mixture approaches ideality or the solute becomes an ideal gas particle. At the solvent's critical conditions, the solute-induced effect on the solute's partial molar properties shows no compressibility-driven singularity, though along the critical isotherm it can exhibit a finite extremum or a change of curvature near critical density, depending on the type and strength of solute-solvent interactions. The utility of the proposed solvation formalism is illustrated using statistical mechanical integral equation calculations for three simple models of infinitely dilute near-critical mixtures: pyrene-CO<sub>2</sub>, di-tert-butyl nitroxide-ethane, and Ne-Xe.*

## Introduction

The behavior of infinitely dilute solutes in near-critical solvents is currently the focus of active research (Johnston and Penninger, 1989; Bruno and Ely, 1991; Bright and McNally, 1992; Kiran and Brennecke, 1993). This is brought about by the unique characteristics offered by near-critical fluids to achieve specific solvation properties by simply tuning the system's state conditions (McHugh and Krukonis, 1986). Although supercritical fluids are successfully applied as solvents in a wide variety of separation processes and chemical reactions, a complete molecular-based understanding of the mechanism underlying the supercritical solubility enhancement is still lacking (Bruno and Ely, 1991).

Most theoretical studies on supercritical solubility enhancement have focused on relating the solute mechanical partial molar properties at infinite dilution, for example, volume and enthalpy, to the mixture's microstructure at conditions close

to the solvent's critical point. A microscopic view has consequently emerged and evolved (popularly referred to as *solvent clustering* (Kim and Johnston, 1987a), *local density augmentation/depletion* (Brennecke et al., 1990b), *densification/cavitation* (Wu et al., 1992), and *molecular charisma* (Eckert and Knutson, 1993)) in which the near-critical local solvent's environment (microstructure) around the infinitely dilute solute appears to be dramatically different from that around the solvent molecule. This view has been supported, up to certain extent, by experimental (Kim and Johnston, 1987a; Kim and Johnston, 1987b; Kajimoto et al., 1988; Brennecke et al., 1990b; Knutson et al., 1992; Sun et al., 1992; Zagrobelny and Bright, 1992; Carlier and Randolph, 1993; Eckert and Knutson, 1993), theoretical (Cochran et al., 1990; Wu et al., 1990; Jonah and Cochran, 1993; Pfund and Cochran, 1993; Chialvo, 1993a), and simulation (Petsche and Debenedetti, 1989; Cummings et al., 1991; Chialvo and Debenedetti, 1992; Cochran et al., 1992; Knutson et al., 1992; O'Brien et al., 1993) evidence and has been frequently associated with the divergence of the solute

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partial molar volume (Kim and Johnston, 1987a; Brennecke et al., 1990b; Zagrobelny and Bright, 1992).

Although solute-induced local effects (the solvent's local density changes around the dilute solute) and solvent's criticality are not mutually exclusive, they involve two different length scales. While the solute-induced local effect on the system's microstructure is a density perturbation—the result of replacing a solvent particle by a solute particle—occurring within a few molecular diameters around the solute molecule, its effect propagates a distance given by the solvent's correlation length which diverges at the solvent's critical point. Controversy and continued debate have originated concerning the lack of precision on what is meant by either local or short-ranged effect, and consequently, by significant changes in the system's microstructure (Brennecke et al., 1990a; Economou and Donohue, 1990; McGuigan and Monson, 1990). In particular, on the basis of an integral equation study, McGuigan and Monson (1990) concluded that the physical effects associated with the divergence of the solute partial molar volume at infinite dilution are due to the development of long-range correlations in the solvent and not to drastic changes in the local structure about the solute. Economou and Donohue (1990) showed that although the large negative partial molar volumes of solutes near a solvent critical point are due predominantly to long-range mean field effects, short-range phenomena do exist and can have an effect on both solubility and partial molar volume. However, one question still remains unanswered: Can we separate the solute-induced local effect on the system's microstructure from the solvent's criticality in a unambiguous statistical mechanical formalism?

Attempts have been made to answer that question (Knutson et al., 1992; Muñoz and Chimowitz, 1992; Sun et al., 1992; Carlier and Randolph, 1993; O'Brien et al., 1993; Tom and Debenedetti, 1993) with limited success. One problem has been the lack of an appropriate definition of solvent's local density augmentation. For example, the definition introduced by Kim and Johnston (1987b) has the unfortunate property of predicting the wrong asymptotic behavior for two important limiting conditions—when the solute particle behaves either as a solvent or as an ideal gas particle. They defined the solvent's local density augmentation in terms of the solute-solvent total correlation function integral  $G_{12}^\infty$  as follows:

$$\rho_{12}(R) - \rho = \frac{4\pi\rho \int_0^R [g_{12}^\infty(r) - 1]r^2 dr}{4\pi \int_0^R r^2 dr} \quad (1)$$

$$\equiv \frac{G_{12}^\infty}{V_{12}(R)}$$

by choosing a value of  $R$  such that (Mansoori and Ely, 1985)

$$4\pi\rho \int_R^\infty [g_{12}^\infty(r) - 1]r^2 dr = 0 \quad (2)$$

where  $\rho_{12}(R)$  is the average solvent's density in the solute's solvation shell of radius  $R$ .

Another troubling aspect of Eq. 1 is that the requirement given by Eq. 2 does not hold for any near-critical mixture. In

fact, Eq. 2 cannot be satisfied by dilute near critical mixtures because their pair distribution functions— $g_{11}^\infty(r)$ ,  $g_{12}^\infty(r)$ , and  $g_{22}^\infty(r)$ —develop long tails which approach asymptotically to one either from above or below (Chialvo and Debenedetti, 1992; Chialvo, 1993a). Consequently, the lefthand side of Eq. 2 diverges to plus or minus infinity depending on whether the mixture is attractive (nonvolatile solute) or repulsive (volatile solute), respectively (Debenedetti and Mohamed, 1989; Levelt Sengers, 1991a,b). The problems with Eqs. 1–2 imply that the conclusion reached by Johnston and collaborators (Kim and Johnston, 1986; Johnston and Haynes, 1987; Kim and Johnston, 1987b; Johnston et al., 1989a) about the linearity between the solvent's local density change and its isothermal compressibility is invalid, that is, the solvent's local density cannot be highest at the solvent critical point contrary to what has been frequently suggested in literature (Brennecke and Eckert, 1989; Flarsheim et al., 1989; Brennecke et al., 1990b; Shaw et al., 1991; Combes et al., 1992; Roberts et al., 1992; Betts et al., 1992a,b). Note that there may be some merit to using Eq. 1 to interpret experimental spectroscopic data when  $R$  is identified with the range of the spectroscopic probe (Johnston, 1993).

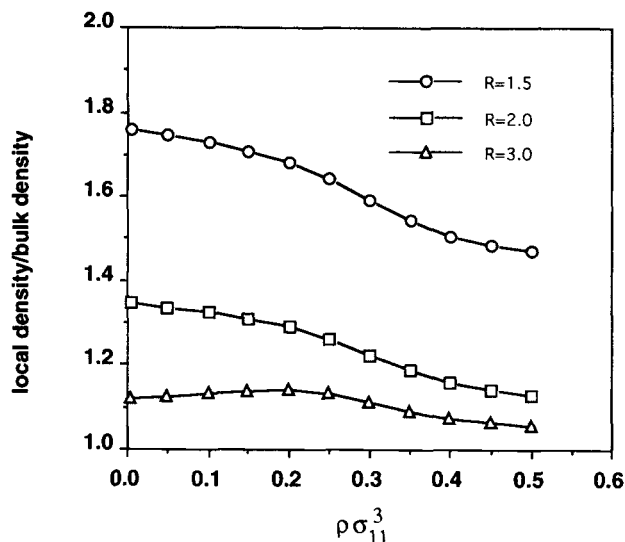
Recently reported molecular based calculations of the solvent's local density change are based on a slightly different expression (Knutson et al., 1992; O'Brien et al., 1993; Tom and Debenedetti, 1993),

$$\rho_{12}(R) - \rho = \frac{4\pi\rho \int_0^R g_{12}^\infty(r)r^2 dr}{4\pi \int_{r_c}^R r^2 dr} - \rho$$

$$= \frac{3\rho}{(R^3 - r_c^3)} \int_{r_c}^R [g_{12}^\infty(r) - 1]r^2 dr \quad (3)$$

where  $r_c$  is the radius of the solute soft core, that is, the distance at which  $g_{12}^\infty(r)$  becomes nonzero. From our point of view this definition of the solvent's local density suffers from two problematic properties. First, Eq. 3 predicts a solute-induced local effect on the solvent's local density even for ideal solutions (that is, pure solvent) and ideal gas solutes. For example, when the solute molecule becomes identical to a solvent molecule, that is,  $g_{12}^\infty(r) = g_{11}^\infty(r)$  but  $\rho_{12}(R) - \rho \neq 0$ , contrary to the physical meaning of a solute-induced local effect. This is clearly seen in Figure 1 where we plot the density dependence of the local to bulk density ratio ( $\rho_{12}(R)/\rho$ ) for pure CO<sub>2</sub> at  $T_r = 1.02$ . Secondly, the radius  $R$  of the solvation shell, where the solute-induced local effect takes place, is arbitrarily chosen. While the second property might be less important provided we keep consistency in the comparison, we consider the first property more problematic because physically solvent *local density augmentation* represents the change of the solvent *local* density due to solute solvation.

The second obstacle, the lack of a clear definition for the short- and the long-range contributions to the solute-induced solvent's buildup (or depletion) around the infinitely dilute solute, has hindered attempts to deduce a fundamental connection between the *changes* of the solvent's local environment around the dilute solute (solvation) and the behavior of the macroscopic properties of the system. In fact, the solvent's



**Figure 1. Density dependence of local to bulk density ratio of supercritical Lennard-Jones CO<sub>2</sub> at  $T_r = T/T_c = 1.02$  from integral equation calculations according to Eq. 1.**

Curves represent three solvation shells with radius  $R = 1.5\sigma_{AA}$ ,  $R = 2.0\sigma_{AA}$ , and  $R = 3.0\sigma_{AA}$ .

buildup/depletion inside the solute's solvation shell of radius  $R$  in Eq. 3 originates from both short-range direct interactions (solute-solvent direct correlations) and long-range indirect interactions (solute-solvent indirect correlations) even though the calculation involves a finite-size solvation shell. Consequently, the solvent's local density calculated by Eq. 3 includes direct and indirect interactions, that is, Eq. 3 does not provide a clear-cut distinction between the short-range (solvation) and the long-range (critical) contributions to the solvent's density change in the solvation shell.

In this article we study the solvation of an infinitely dilute solute in a near-critical solvent. We derive new expressions for the calculation of the infinite dilution solute's and pure solvent's chemical potentials in terms of the solute-solvent and solvent-solvent direct correlation function integrals. Since the direct correlation functions are short-range quantities, we are also able to connect rigorously the behavior of the solvent's local environment around the dilute solute with the system's macroscopic properties—the solvation thermodynamics—and consequently, to introduce an unambiguous definition of solute-induced local effect upon the structure and the thermodynamic properties of infinitely dilute near-critical fluid mixtures. This definition of solute-induced local effect satisfies some natural constraints such as giving the correct result in the ideal solution and the solute's ideal gas limiting conditions. We argue and prove that the solvent's local density change around an infinitely dilute solute—the solvation process—is a short-range phenomenon, and therefore not connected to the solvent's criticality even though it defines the sign of the divergence of the solute's partial molar properties.

In this article we first derive the solvation thermodynamics of infinitely dilute solutes in near-critical solvents in terms of direct correlation function integrals. We introduce a definition of solute-induced local density effect and connect it to the density dependence of the ratio of solute to solvent fugacity

coefficients and the solubility enhancement factor  $E$ . The new development is illustrated by using the Ornstein-Zernike integral equations (Ornstein and Zernike, 1914) in the Percus-Yevick (1958) approximation for three attractive and repulsive Lennard-Jones binary mixtures which have been used as simplified models for three prototypical supercritical fluid mixtures. Finally, we discuss the shortcomings of some earlier theoretical developments on solvent local density augmentation.

## Fundamentals

### Solute-induced local density effects

The short-range nature of the solute's chemical potential at infinite dilution was recently studied using integral equation calculations in two closely related articles (Muñoz and Chmowitz, 1992; Tom and Debenedetti, 1993). These authors analyzed the spatial dependence of the infinite dilution solute's chemical potential and concluded that this quantity should be short-range because more than 99% of the contribution to the property comes from the first two-three solvation shells around the solute, even at the solvent's critical point.

Here we take a more rigorous approach (in that neither integral equation approximations nor numerical solutions are used or an explicit size for the solvation shells is invoked) to show that the chemical potentials of the infinitely dilute solute and the pure solvent are short-range quantities. This also allows us to analyze the solvation process that takes place when a solvent particle is replaced with a solute (even for the case where the solute particle differs from the solvent particle by the name only, that is, for an ideal solution), in terms of well defined short-range quantities which are fundamentally connected to the system's macroscopic properties.

To begin, we write the solute residual chemical potential at infinite dilution as follows (Modell and Reid, 1983),

$$\begin{aligned} \mu_2^{\infty}(T, P) &= \beta^{-1} \ln \phi_2^{\infty} \\ &= -\beta^{-1} \left[ \int_{\infty}^{V(P)} \left[ \beta \left( \frac{\partial P}{\partial N_2} \right)_{V, T, N_1}^{\infty} - V^{-1} \right] dV + \ln \left( \frac{\beta P}{\rho} \right) \right] \\ &= -\beta^{-1} \left[ \int_0^{\rho(P)} \left( 1 - \frac{\beta \bar{v}_2^{\infty}}{\kappa} \right) \frac{d\rho}{\rho} + \ln \left( \frac{\beta P}{\rho} \right) \right] \end{aligned} \quad (4)$$

where  $\phi_2$  is the solute's fugacity coefficient, superscripts  $r$  and  $\infty$  denote residual and infinite dilution quantities at the indicated state conditions, respectively,  $k$  is the Boltzmann constant,  $\beta^{-1} = kT$ ,  $T$  is the absolute temperature, and  $\kappa$  is the isothermal compressibility. Here we have invoked the following identity (Debenedetti and Mohamed, 1989),

$$\left( \frac{\partial P}{\partial N_2} \right)_{V, T, N_1}^{\infty} = \frac{\rho \bar{v}_2^{\infty}}{N\kappa} \quad (5)$$

Then, by recalling that (O'Connell, 1972; Eckert et al., 1986; Chialvo, 1993a):

$$\frac{\beta \bar{v}_2^{\infty}}{\kappa} = 1 - C_{12}^{\infty} \quad (6)$$

and substituting it in Eq. 4 we obtain:

$$\mu_2^{\infty}(T, P) = -\beta^{-1} \left[ \int_0^{\rho(P)} C_{12}^{\infty} \frac{d\rho}{\rho} + \ln \left( \frac{\beta P}{\rho} \right) \right] \quad (7)$$

where  $C_{ij}$  is the direct correlation function integral (O'Connell, 1971, 1990)

$$C_{ij} = \rho \int c_{ij} d\mathbf{r} = \rho \hat{c}_{ij}(\mathbf{0}) \quad (8)$$

and  $\hat{c}_{ij}(\mathbf{k})$  is the Fourier transform of the direct  $ij$ -pair correlation function.

Similarly, the chemical potential of the pure solvent can be written as:

$$\begin{aligned} \mu_1^{\circ}(T, P) &= -\beta^{-1} \left[ \int_0^{\rho(P)} \left( 1 - \frac{\beta}{\rho\kappa} \right) \frac{d\rho}{\rho} + \ln \left( \frac{\beta P}{\rho} \right) \right] \\ &= -\beta^{-1} \left[ \int_0^{\rho(P)} C_{11}^{\circ} \frac{d\rho}{\rho} + \ln \left( \frac{\beta P}{\rho} \right) \right] \end{aligned} \quad (9)$$

where the superscript  $^{\circ}$  denotes a pure component property. Therefore, from Eqs. 7 and 9 it follows that (Chialvo, 1991)

$$\begin{aligned} \mu_2^{\infty}(T, P) - \mu_1^{\circ}(T, P) &= \beta^{-1} \int_0^{\rho(P)} (C_{11}^{\circ} - C_{12}^{\infty}) \frac{d\rho}{\rho} \\ &= \beta^{-1} \ln [H_2(T, P)/f_1^{\circ}(T, P)] \end{aligned} \quad (10)$$

where  $H_2$  and  $f_1^{\circ}$  are the Henry constant of component 2 and the fugacity of pure component 1, respectively. Because Eqs. 7–9 involve direct correlation function integrals which remain finite even at the solvent's critical point (Levelt Sengers, 1991), the chemical potentials and their difference, Eq. 10, become short-range quantities. Some properties of direct correlation functions both near and away from the solvent critical point are discussed in Appendix E.

Note that Eq. 10 represents the change of free energy in the solvation process that takes place when a solvent particle is switched to a solute one, and so it is directly connected to the solute's solubility enhancement,  $E \approx 1/\phi_2^{\infty}$ , as we will show later. Therefore, it might be revealing to derive the expressions for the short- and long-range contributions to the residual partial molar properties of a solute at infinite dilution in a near-critical solvent because it will allow us to discriminate the solvation process from the critical phenomenon. To do so we start with the rigorous fluctuation formalism of Kirkwood and Buff (1951) and O'Connell (1971, 1990). Specifically, we relate the solute partial molar volume at infinite dilution  $\bar{v}_2^{\infty}$  to the solvent-solvent and solute-solvent total correlation function integrals  $G_{11}^{\circ}$  and  $G_{12}^{\infty}$ , as follows:

$$\bar{v}_2^{\infty} = \rho^{-1} + G_{11}^{\circ} - G_{12}^{\infty} \quad (11)$$

where  $\rho$  is the system's density, and the superscripts  $^{\circ}$  and  $\infty$  denote pure component and infinite dilution properties, respectively. Now, by invoking the definition of total  $g_{12}(r)$  and direct  $c_{12}(r)$  correlation functions (McQuarrie, 1976), we define the indirect correlation function integral as:

$$I_{ij} \equiv \int (g_{ij} - c_{ij} - 1) d\mathbf{r} = G_{ij} - \rho^{-1} C_{ij} \quad (12)$$

where  $G_{ij}$  is the total correlation function integral (Kirkwood and Buff, 1951),

$$G_{ij} = \int (g_{ij} - 1) d\mathbf{r} = \hat{h}_{ij}(\mathbf{0}) \quad (13)$$

$C_{ij}$  is given by Eq. 8, and  $\hat{h}_{ij}(\mathbf{k})$  is the Fourier transform of the total  $ij$ -pair correlation function. Thus, the solute partial molar volume at infinite dilution can be recast as (see Appendix A):

$$\begin{aligned} \bar{v}_2^{\infty} &= \rho^{-1} + G_{11}^{\circ} - G_{12}^{\infty} \\ &= \rho^{-1} (1 + C_{11}^{\circ} - C_{12}^{\infty}) + (I_{11}^{\circ} - I_{12}^{\infty}) \\ &= \underbrace{\rho^{-1} (1 + C_{11}^{\circ} - C_{12}^{\infty})}_{\bar{v}_2^{\infty}(SR)} + \underbrace{\kappa C_{11}^{\circ} (C_{11}^{\circ} - C_{12}^{\infty}) \beta^{-1}}_{\bar{v}_2^{\infty}(LR)} \end{aligned} \quad (14)$$

where  $SR$  and  $LR$  denote short- and long-range contributions to the properties based on the fact that the direct correlation function integrals  $C_{ij}$  remain finite whereas  $\kappa$  diverges at the solvent's critical point (Levelt Sengers, 1991). Note that this splitting between short- and long-range contributions to  $\bar{v}_2^{\infty}$  will allow us to define not only the region where the solvent's local density effect occurs, but also its precise contribution to  $\bar{v}_2^{\infty}$ . Note also that, because  $C_{11}^{\circ}$  and  $C_{12}^{\infty}$  must be finite (O'Connell, 1990; Levelt Sengers, 1991), Eq. 12 ascribes the divergence of  $G_{ij}$  to  $I_{ij}$ , that is:

$$I_{11}^{\circ} - I_{12}^{\infty} = \kappa C_{11}^{\circ} (C_{11}^{\circ} - C_{12}^{\infty}) \beta^{-1} \quad (15)$$

Alternatively, we can express  $\bar{v}_2^{\infty}(SR)$  and  $\bar{v}_2^{\infty}(LR)$  in terms of macroscopic properties. By recalling that (Levelt Sengers, 1991):

$$\left( \frac{\partial P}{\partial x_2} \right)_{v, T}^{\infty} = \frac{\rho}{\beta} (C_{11}^{\circ} - C_{12}^{\infty}) \quad (16)$$

we have, from Eq. 14, that

$$\bar{v}_2^{\infty}(SR) = \left[ 1 + \left( \frac{\partial P}{\partial x_2} \right)_{v, T}^{\infty} \beta \rho^{-1} \right] \rho^{-1} \quad (17)$$

and

$$\bar{v}_2^{\infty}(LR) = \left( \frac{\kappa}{\rho} \right) \left( 1 - \frac{\beta}{\rho\kappa} \right) \left( \frac{\partial P}{\partial x_2} \right)_{v, T}^{\infty} \quad (18)$$

Therefore, by recalling Eqs. 10 and 16 the solvent's local density change—solute-induced local effect—due to the introduction of an infinite dilute solute in an otherwise pure solvent becomes:

$$[\bar{v}_2^{\infty}(SR) - v_1^{\circ}]_{v, T} = \frac{\beta}{\rho^2} \left( \frac{\partial P}{\partial x_2} \right)_{v, T}^{\infty} \quad (19)$$

so that Eq. 10 also reads:

$$\mu_2^{\infty}(T, P) - \mu_1^{\infty}(T, P) = \beta^{-1} \int_0^{\rho(P)} [\bar{v}_2^{\infty}(SR) - v_1^o] d\rho \quad (20)$$

The corresponding expressions for the enthalpy and the entropy are given by:

$$\begin{aligned} [\bar{h}_2^{\infty}(SR) - h_1^{ro}]_{T, P} = & - \int_0^{\rho(P)} \left( \frac{\partial C_{12}^{\infty}}{\partial \beta} - \frac{\partial C_{11}^o}{\partial \beta} \right) \frac{d\rho}{\rho} \\ & - \left( \frac{\partial P}{\partial \beta} \right) \beta \rho^{-1} (C_{11}^o - C_{12}^{\infty}) \quad (21) \end{aligned}$$

and

$$\begin{aligned} [\bar{s}_2^{\infty}(SR) - s_1^{ro}]_{T, P} = & k \int_0^{\rho(P)} (C_{12}^{\infty} - C_{11}^o) \frac{d\rho}{\rho} \\ & - T^{-1} \int_0^{\rho(P)} \left( \frac{\partial C_{12}^{\infty}}{\partial \beta} - \frac{\partial C_{11}^o}{\partial \beta} \right) \frac{d\rho}{\rho} \\ & - \left( \frac{\partial P}{\partial \beta} \right) (kT^2 \rho)^{-1} (C_{11}^o - C_{12}^{\infty}) \quad (22) \end{aligned}$$

and are derived in the Appendix B. Note that from Eqs. 10, 21, and 22 we also have:

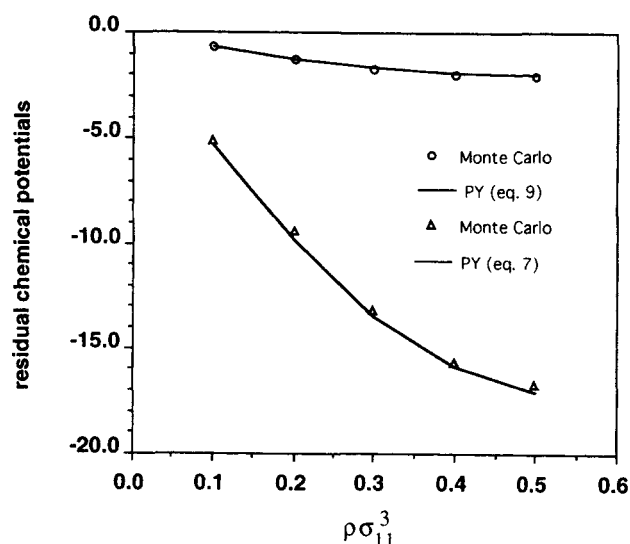
$$\begin{aligned} \Delta G_{\text{solvation}} = & [\bar{h}_2^{\infty}(SR) - h_1^{ro}]_{T, P} - T[\bar{s}_2^{\infty}(SR) - s_1^{ro}]_{T, P} \\ = & \mu_2^{\infty}(T, P) - \mu_1^{\infty}(T, P) = \mu_2^{\infty}(T, \rho) - \mu_1^{\infty}(T, \rho) \quad (23) \end{aligned}$$

where the asterisks indicate that the residual properties are defined at constant density and temperature (as opposed to pressure and temperature). This expression also indicates that we can define the entire solvation process without even worrying about long-range solute-solvent and solvent-solvent correlations around the solvent's critical point.

### Integral equation calculations

In this section we present results of the solvation thermodynamics for three near-critical Lennard-Jones binary mixtures. Here we use the Ornstein-Zernike integral equations in the Percus-Yevick approximation to determine the pair correlation functions, their integrals, and the thermodynamic properties according to the approach proposed by McGuigan and Monson (1990). This approach is an attractive alternative to molecular based simulation, specially for dilute near-critical mixtures for which total correlation functions are long-range. The accurate determination of these correlation functions is extremely expensive in terms of current standards of supercomputing resources (Cummings et al., 1991; Chialvo and Debenedetti, 1992).

For the limited set of thermodynamic properties studied by them, McGuigan and Monson were able to calculate the thermodynamic properties directly without integration over the density (McGuigan and Monson, 1990). For example, they did not calculate either chemical potentials (Eqs. 7 and 9) or sol-

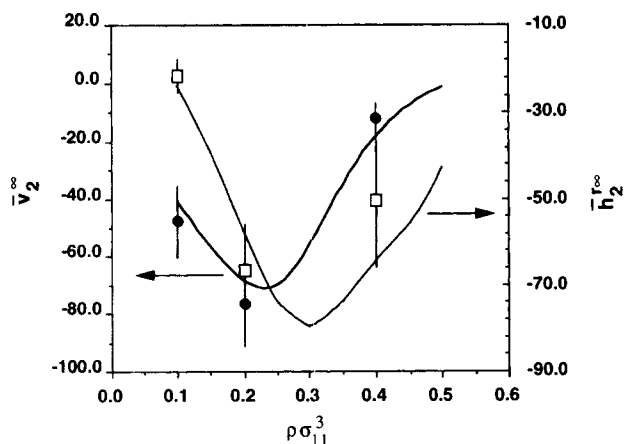


**Figure 2. Density dependence of residual chemical potentials of solvent  $\mu_1^{\infty}(T, \rho)$  and infinitely dilute solute  $\mu_2^{\infty}(T, \rho)$  for Lennard-Jones mixtures at  $kT/\epsilon_{AA} = 1.5$  with  $\epsilon_{AB}/\epsilon_{AA} = 1.5$  and  $\sigma_{AB}/\sigma_{AA} = 1.518$  (AA = solvent-solvent, AB = solute-solvent).**

Circles and triangles are solvent's and solute's chemical potentials from test particle Monte Carlo simulations, respectively. Lines are corresponding PY predictions according to Eqs. 7 and 9. All quantities are reduced in terms of solvent's Lennard-Jones parameters.

ute's partial molar enthalpy (Eq. B6). In order to check the accuracy of our numerical integration over density, we first perform several calculations and compare with simulation results. In Figure 2 we compare the density dependence of the chemical potentials of the solvent and the infinitely dilute solute for Lennard-Jones binary mixtures from simulation (Shing et al., 1988) and integral equation calculations. The PY results for the chemical potentials are in very good agreement with test's particle calculations. Note that the chemical potentials in Figure 2 are the residual values at the prevailing density instead of pressure, that is, they are given by the first terms of Eq. 7— $\mu_2^{\infty}(T, \rho)$ —and Eq. 9— $\mu_1^{\infty}(T, \rho)$ . With respect to the solute's partial molar volume and enthalpy at infinite dilution, according to Figure 3, the agreement is as good as we can expect considering that the error bars in the simulation results are greater as a result of the hybrid method of calculation used (Shing and Chung, 1989).

In what follows we analyze the solute-induced local effects on the microstructure and the thermodynamic properties of three Lennard-Jones near-critical mixtures which have been studied previously by molecular dynamics simulation as simple models for the following systems: the infinitely dilute pyrene in near-critical carbon dioxide (Chialvo and Debenedetti, 1992; Knutson et al., 1992), the infinitely dilute di-*ter*-butylnitroxide (DTBN) in near-critical ethane (O'Brien et al., 1993), and the infinitely dilute neon in near-critical xenon (Petsche and Debenedetti, 1989; Chialvo and Debenedetti, 1992). According to the classification of Debenedetti and Mohamed (1989), these mixtures are usually referred to as attractive and repulsive systems, which in macroscopic terms means either a nonvolatile  $[(\partial P/\partial x_2)_{T, P}^{\infty} < 0]$  or a volatile solute  $[(\partial P/\partial x_2)_{T, P}^{\infty} > 0]$ , respectively (Levelt Sengers, 1991). For the sake of comparison



**Figure 3.** Density dependence of solute's partial molar volume and residual partial molar enthalpy at infinite dilution for Lennard-Jones mixtures at  $kT/\epsilon_{AA} = 1.5$  with  $\epsilon_{AB}/\epsilon_{AA} = 1.5$  and  $\sigma_{AB}/\sigma_{AA} = 1.518$  (AA = solvent-solvent and AB = solute-solvent).

Comparison between Monte Carlo simulations (symbols) and PY predictions (lines) according to Eqs. 11 and B5, respectively. All quantities are reduced in terms of solvent's Lennard-Jones parameters.

we have studied the density dependence ( $0.05 \leq \rho\sigma_1^3 \leq 0.5$ ) of the microscopic and macroscopic properties of these three systems at the same  $T_r = T/T_c = 1.02$ .

### Attractive systems

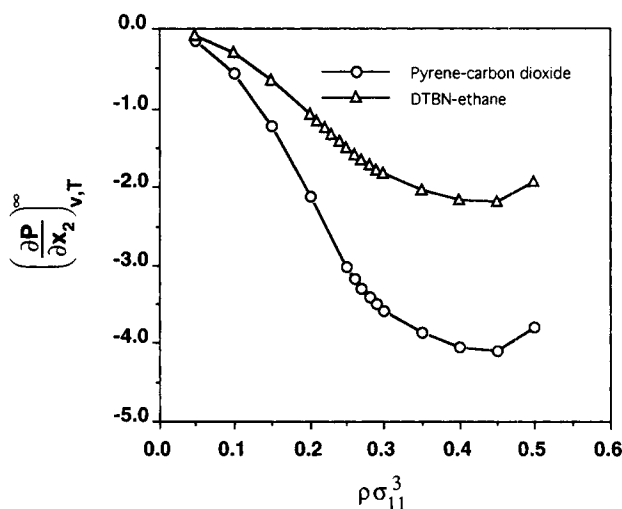
Here we study the solvation of infinitely dilute pyrene and DTBN in  $\text{CO}_2$  and ethane, respectively, modeled as Lennard-Jones mixtures of spheres with potential parameters given in Tables 1 and 2. Note that while the Lennard-Jones parameters for the pyrene- $\text{CO}_2$  interactions are given by the Lorentz-Berthelot combining rules, the corresponding parameters for the DTBN-ethane interactions are given by the Berthelot combining rule alone, that is, both unlike pair potential parameters are given by the geometric mean.

Results in Figures 4 and 5 confirm unambiguously that both mixtures involve attractive solute-solvent interactions, that is,  $(\partial P/\partial x_2)_{v,T}^\infty < 0$  and  $C_{12}^\infty > 1$ , the pyrene- $\text{CO}_2$  system being more attractive than the DTBN-ethane one as we would expect according to the relative sizes of the corresponding Lennard-Jones parameters. This is also clearly reflected in the sign (negative) of the corresponding solute's partial molar volumes (Figure 6), solute's residual partial molar enthalpy (Figure 7), and solute's residual chemical potentials (Figure 8).

In Figures 9 and 10 we compare the density dependence for

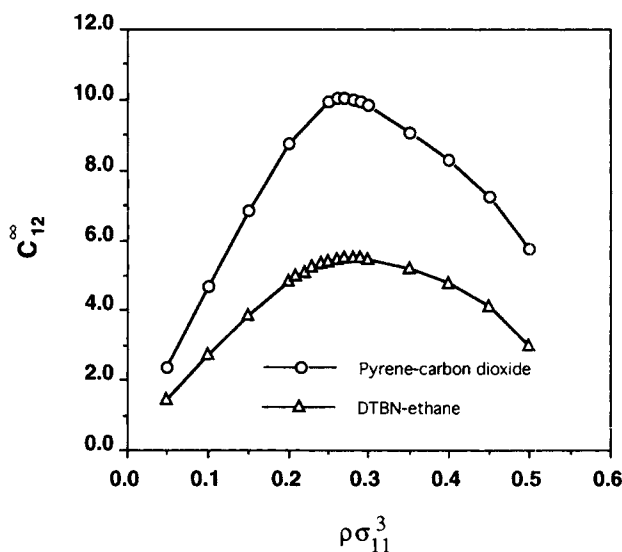
**Table 2. Lennard-Jones Parameters for the Model System DTBN-Ethane**

DTBN(2)- $\text{C}_2\text{H}_6(1)$	$\sigma_{ij}$ (Å)	$\epsilon_{ij}/k$ (K)
Solvent-solvent	5.22	194.39
Solute-solvent	6.89	291.01
Solute-solute	9.09	435.63



**Figure 4.** Comparison between density dependences of  $(\partial P/\partial x_2)_{v,T}^\infty$  for attractive Lennard-Jones pyrene(2)- $\text{CO}_2(1)$  and DTBN(2)-ethane(1) systems at  $T_r = T/T_c = 1.02$  from PY calculations.

All quantities are reduced in terms of solvent's Lennard-Jones parameters.

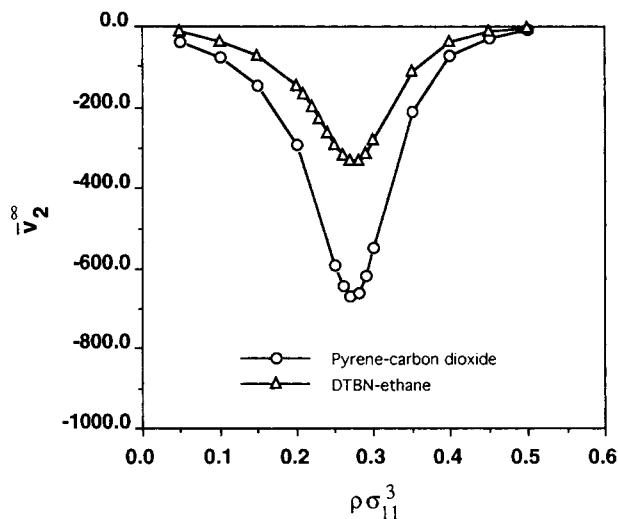


**Figure 5.** Comparison between density dependences of  $C_{12}^\infty$  for attractive Lennard-Jones pyrene(2)- $\text{CO}_2(1)$  and DTBN(2)-ethane(1) systems at  $T_r = T/T_c = 1.02$  from PY calculations.

All quantities are reduced in terms of solvent's Lennard-Jones parameters.

**Table 1. Lennard-Jones Parameters for the Model System Pyrene- $\text{CO}_2$**

Pyrene(2)- $\text{CO}_2(1)$	$\sigma_{ij}$ (Å)	$\epsilon_{ij}/k$ (K)
Solvent-solvent	3.794	225.3
Solute-solvent	5.467	386.4
Solute-solute	7.140	662.8

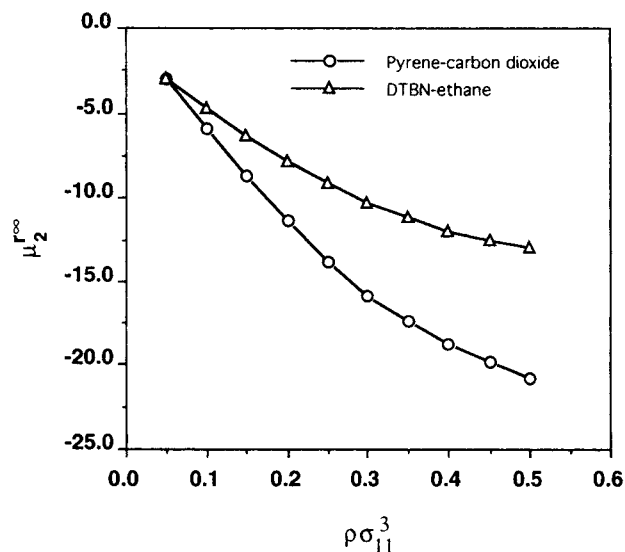


**Figure 6.** Comparison between density dependences of  $\bar{v}_2^\infty$  for attractive Lennard-Jones pyrene(2)-CO<sub>2</sub>(1) and DTBN(2)-ethane(1) systems at  $T_r = T/T_c = 1.02$  from PY calculations.

All quantities are reduced in terms of solvent's Lennard-Jones parameters.

the short-range contribution to the solute's partial molar volume  $\bar{v}_2^\infty(SR)$  and residual enthalpy  $\bar{h}_2^\infty(SR)$ , respectively. For both mixtures the density dependence of  $\bar{v}_2^\infty(SR)$  shows a minimum at  $\rho\sigma_1^3 < \rho_c\sigma_1^3 = 0.28$ ,  $\bar{v}_2^\infty(SR)$  being more negative for the pyrene-CO<sub>2</sub> system. However, the density dependencies of  $\bar{h}_2^\infty(SR)$ , the solute-induced local effect on the solvent's local density [ $\bar{v}_2^\infty(SR) - v_1^o$ ]<sub>T,P</sub> (Figure 11) and residual enthalpy [ $\bar{h}_2^\infty(SR) - h_1^o$ ]<sub>T,P</sub> (Figure 12) show only a change of curvature around  $\rho\sigma_1^3 < \rho_c\sigma_1^3 = 0.28$ .

Note also that even though  $\mu_2^\infty$  presents a moderate density



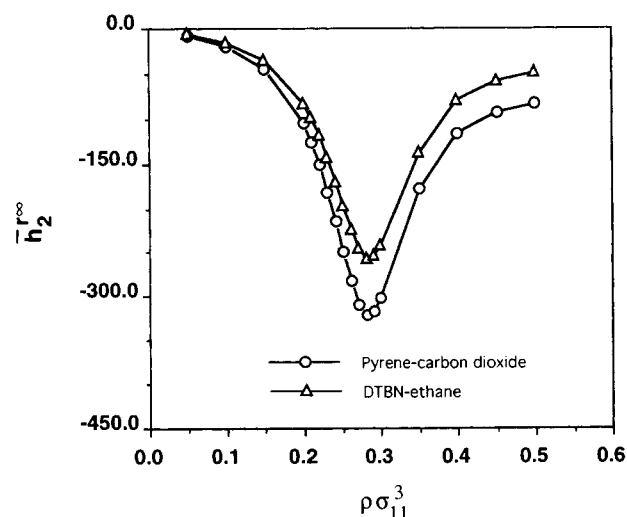
**Figure 8.** Comparison between density dependences of  $\mu_2^\infty$  for attractive Lennard-Jones pyrene(2)-CO<sub>2</sub>(1) and DTBN(2)-ethane(1) systems at  $T_r = T/T_c = 1.02$  from PY calculations.

All quantities are reduced in terms of solvent's Lennard-Jones parameters.

dependence (it changes by a factor of 2–3 for  $0.05 \leq \rho\sigma_1^3 \leq 0.5$ ),  $\phi_2^\infty$  (Figure 13) shows extreme sensitivity to density, exhibiting a 3–6 orders of magnitude change in the same density range.

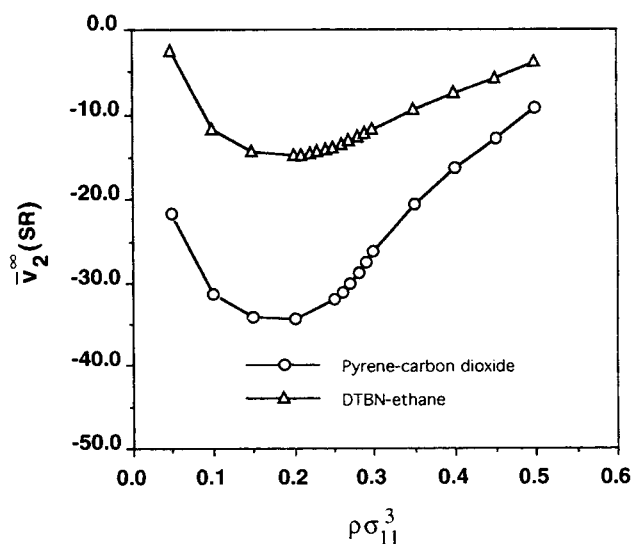
### Repulsive system

Here we study the solvation of infinitely dilute neon in xenon with Lennard-Jones parameters given in Table 3. The solute-



**Figure 7.** Comparison between density dependences of  $\bar{h}_2^\infty$  for attractive Lennard-Jones pyrene(2)-CO<sub>2</sub>(1) and DTBN(2)-ethane(1) systems at  $T_r = T/T_c = 1.02$  from PY calculations.

All quantities are reduced in terms of solvent's Lennard-Jones parameters.



**Figure 9.** Comparison between density dependences of  $\bar{v}_2^\infty(SR)$  for attractive Lennard-Jones pyrene(2)-CO<sub>2</sub>(1) and DTBN(2)-ethane(1) systems at  $T_r = T/T_c = 1.02$  from PY calculations.

All quantities are reduced in terms of solvent's Lennard-Jones parameters.

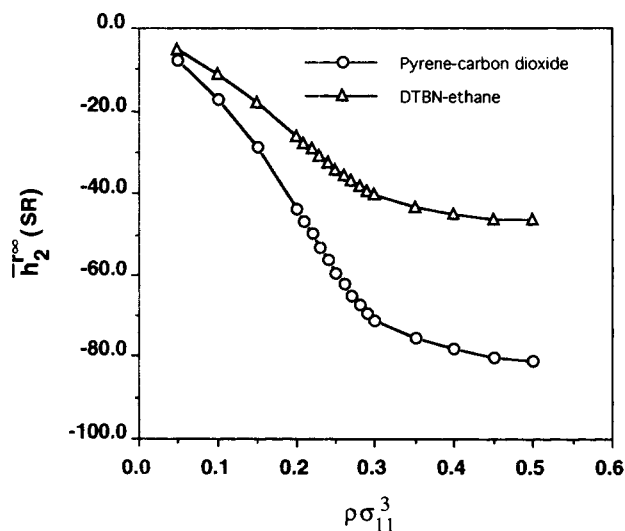
**Table 3. Lennard-Jones Parameters for the System Ne-Xe**

Neon(2)-Xenon(1)	$\sigma_{ij}$ (Å)	$\epsilon_{ij}/k$ (K)
Solvent-solvent	4.047	231.0
Solute-solvent	3.433	87.0
Solute-solute	2.820	32.8

solvent Lennard-Jones parameters are given by the Lorentz-Berthelot combining rules.

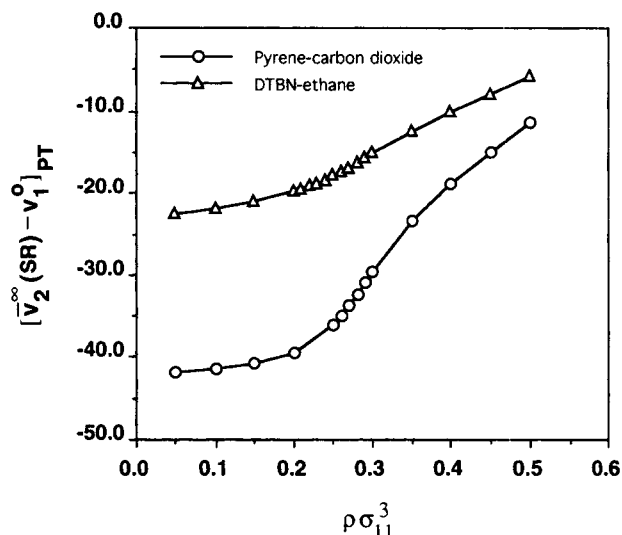
In Figure 14 we corroborate the repulsive nature of this mixture, that is,  $(\partial P/\partial x_2)_{v,T}^\infty > 0$  and  $C_{12}^\infty < 0$ . Additional evidence of that behavior is given by the sign (positive) of the corresponding solute's partial molar volume (Figure 15), residual partial molar enthalpy (Figure 16), and residual chemical potential (Figure 17).

The density dependences of  $(\partial P/\partial x_2)_{v,T}^\infty$  and  $C_{12}^\infty$  for the repulsive mixture in contrast to the corresponding behavior of the attractive mixtures do not show any extrema. Similar behavior is observed in the density dependence for the short-range contribution to the solute's partial molar volume  $\bar{v}_2^\infty(SR)$  and enthalpy  $\bar{h}_2^\infty(SR)$ , as well as for the solute-induced local effects on the solvent's local density  $[\bar{v}_2^\infty(SR) - v_1^0]_{T,P}$  and enthalpy  $[\bar{h}_2^\infty(SR) - h_1^0]_{T,P}$  (Figure 18). The absence of an extremum in the density dependence of  $(\partial P/\partial x_2)_{v,T}^\infty$  and  $C_{12}^\infty$  could not necessarily be a general rule for repulsive systems. The rationale is the following. Since  $C_{11}^\infty$  shows a maximum at the solvent's critical point ( $C_{11}^\infty = 1$  when  $\kappa \rightarrow \infty$ ), then  $C_{12}^\infty$  for an ideal solution will also show a maximum because for an ideal solution we have  $C_{12}^\infty = C_{11}^\infty$ . An ideal solution is one in which the solute's and solvent's potential parameters are identical and the "mixture" is at the border between attractive and weakly-attractive in the sense of Debenedetti and Mohamed's (1989) classification. As the solute-solvent asymmetry grows,



**Figure 10. Comparison between density dependences of  $\bar{h}_2^\infty(SR)$  for attractive Lennard-Jones pyrene(2)-CO<sub>2</sub>(1) and DTBN(2)-ethane(1) systems at  $T_r = T/T_c = 1.02$  from PY calculations.**

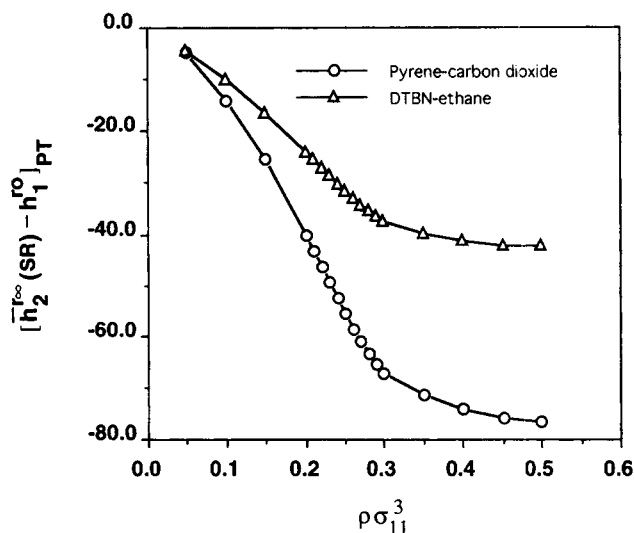
All quantities are reduced in terms of solvent's Lennard-Jones parameters.



**Figure 11. Comparison between density dependences of  $[\bar{v}_2^\infty(SR) - v_1^0]_{T,P}$  for attractive Lennard-Jones pyrene(2)-CO<sub>2</sub>(1) and DTBN(2)-ethane(1) systems at  $T_r = T/T_c = 1.02$  from PY calculations.**

All quantities are reduced in terms of solvent's Lennard-Jones parameters.

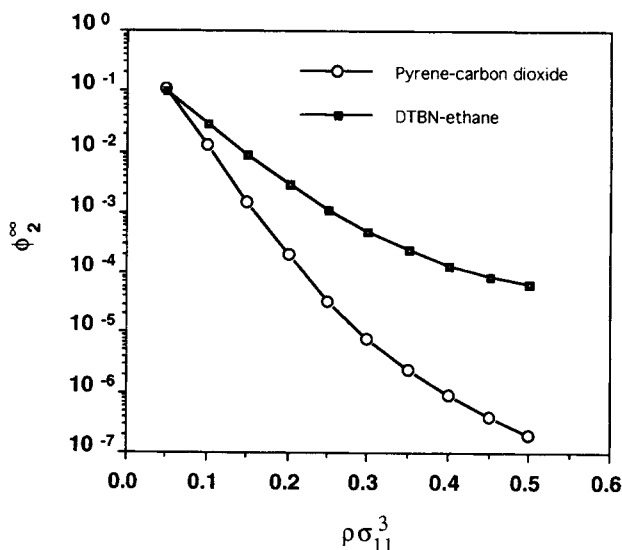
the density at which  $C_{12}^\infty$  shows a maximum changes as shown in Figure 19 for three very special types of Lennard-Jones mixtures;  $(\sigma_2/\sigma_1) = 1$ ,  $(\epsilon_2/\epsilon_1) = 1$ , and  $(\epsilon_2/\epsilon_1) = (\sigma_2/\sigma_1)$  under Lorentz-Berthelot combining rules. For the case of repulsive mixtures  $C_{12}^\infty$  can show a minimum around the solvent's critical point according to the prediction of Eqs. D5-D8, though we were not able to confirm it by PY calculations.



**Figure 12. Comparison between density dependences of  $[\bar{h}_2^\infty(SR) - h_1^0]_{T,P}$  for attractive Lennard-Jones pyrene(2)-CO<sub>2</sub>(1) and DTBN(2)-ethane(1) systems at  $T_r = T/T_c = 1.02$  from PY calculations.**

All quantities are reduced in terms of solvent's Lennard-Jones parameters.





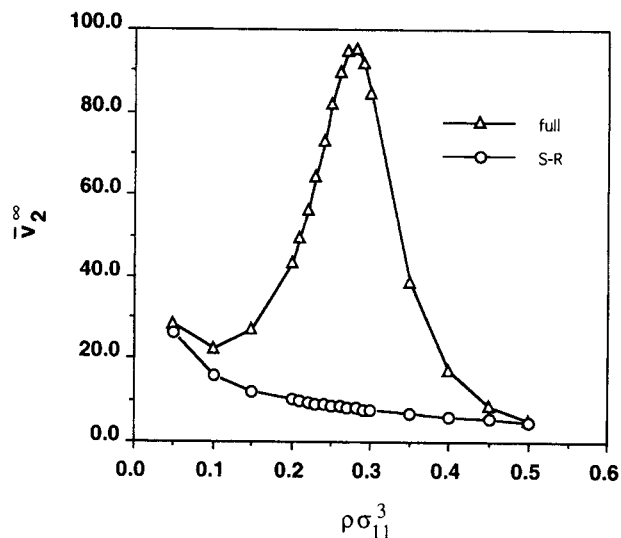
**Figure 13.** Comparison between density dependences of  $\phi_2^\infty$  for attractive Lennard-Jones pyrene(2)-CO<sub>2</sub>(1) and DTBN(2)-ethane(1) systems at  $T_r = T/T_c = 1.02$  from PY calculations.

All quantities are reduced in terms of solvent's Lennard-Jones parameters.

Note also that, in contrast to the observed extreme sensitivity of  $\phi_2^\infty$  to density in attractive mixtures, this repulsive system presents a moderate density dependence (Figure 17)— $\mu_2^\infty$  and  $\phi_2^\infty$  change by a factor of 5 in the interval  $0.05 \leq \rho\sigma_1^3 \leq 0.5$ .

## Discussion and Conclusions

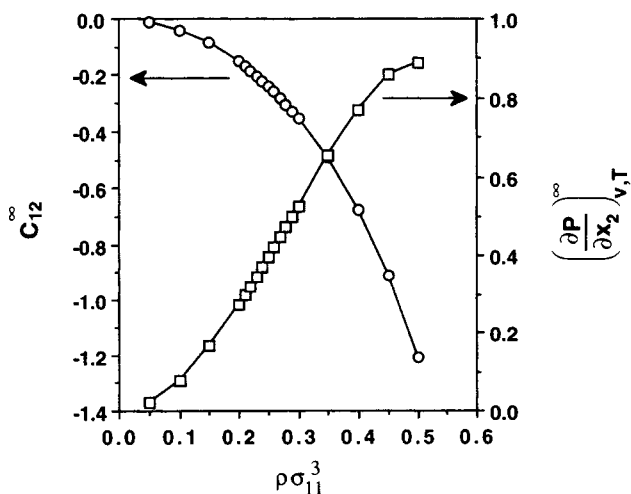
In this article we developed a general and rigorous molecular-based formalism to establish the microscopic bases of the supercritical solubility enhancement/depletion in terms of molecular direct correlation function integrals. The strength of



**Figure 15.** Density dependences of  $\bar{v}_2^\infty$  and  $\bar{v}_2^\infty(SR)$  for repulsive Lennard-Jones Ne(2)-Xe(1) system at  $T_r = T/T_c = 1.02$  from PY calculations.

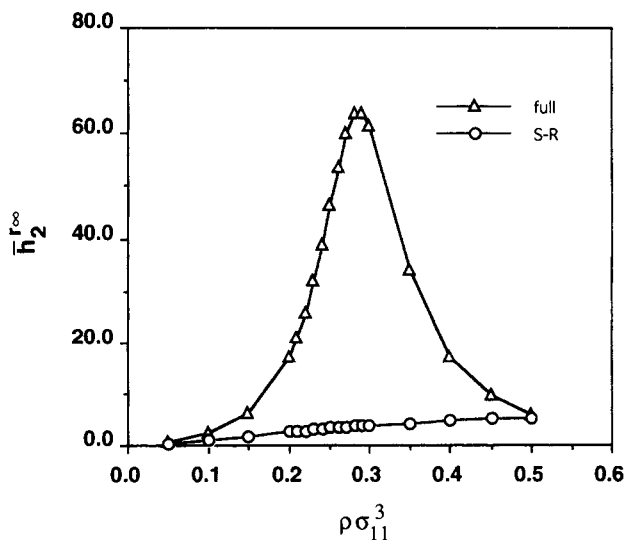
All quantities are reduced in terms of solvent's Lennard-Jones parameters.

this approach is the unambiguous separation between direct and indirect molecular correlations functions according to the Ornstein-Zernike equation, a concept that does not rely on any explicit choice for the size of the solute's solvation shell. Therefore, the formalism provides not only a natural splitting between short-(finite) and long-range (diverging) contributions to the mixture's properties, but also a proof of the short-range nature of the solute's and solvent's reduced chemical potentials, as well as for the change of the solvent's local environment around an infinitely dilute solute (solute-induced effect) and



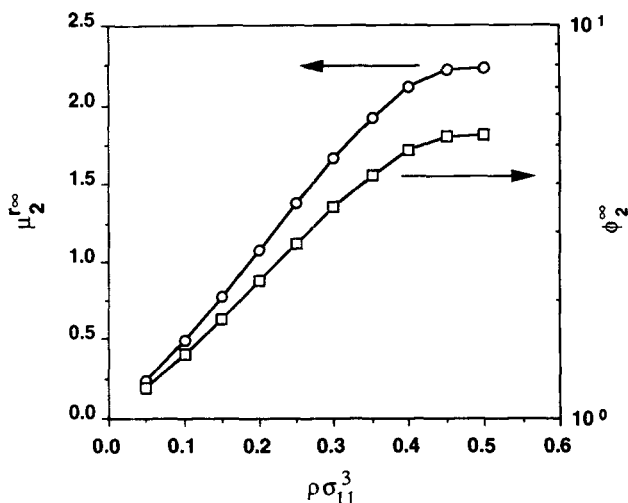
**Figure 14.** Density dependence of  $(\partial P / \partial x_2)_{v,T}^\infty$  and  $C_{12}^\infty$  for repulsive Lennard-Jones Ne(2)-Xe(1) system at  $T_r = T/T_c = 1.02$  from PY calculations.

All quantities are reduced in terms of solvent's Lennard-Jones parameters.



**Figure 16.** Density dependences of  $\bar{h}_2^\infty$  and  $\bar{h}_2^\infty(SR)$  for repulsive Lennard-Jones Ne(2)-Xe(1) system at  $T_r = T/T_c = 1.02$  from PY calculations.

All quantities are reduced in terms of solvent's Lennard-Jones parameters.



**Figure 17.** Density dependence of  $\mu_2^{\infty}$  and  $\phi_2^{\infty}$  for repulsive Lennard-Jones Ne(2)-Xe(1) system at  $T_r = T/T_c = 1.02$  from PY calculations.

All quantities are reduced in terms of solvent's Lennard-Jones parameters.

its finite contribution to the solute mechanical partial molar properties.

In addition, from Eqs. 10, 16, and 19 we find that the solute-induced local effect can be recast as:

$$\frac{\beta}{\rho^2} \left( \frac{\partial P}{\partial x_2} \right)_{v, T} = \left[ \frac{\partial \ln[H_2(T, P)/f_1^o(T, P)]}{\partial \rho} \right]_{T, x}$$

$$= [\partial \ln[\phi_2^{\infty}(T, P)/\phi_1^o(T, P)]/\partial \rho]_{T, x} \quad (24)$$

where  $\phi_1^o$  is the fugacity coefficient of the pure solvent. Equation 24 is a revealing expression because it indicates the direct

connection between the solute-induced local effect on the system's microstructure and the solute's infinite dilution to pure solvent fugacity coefficients—the key player in the solubility enhancement/depletion of dilute solutes in near-critical solvents. In fact, we can make such a connection more evident by considering the case of an incompressible pure nonvolatile phase in equilibrium with a near-critical solvent. For such a case the solubility equation reads (Modell and Reid, 1983):

$$P\phi_2x_2 = f_2^s \approx \phi_2^{\text{sat}} P_2^{\text{sat}} \exp[\beta v_2^s (P - P_2^{\text{sat}})] \quad (25)$$

and the solubility enhancement factor is (Paulaitis et al., 1983):

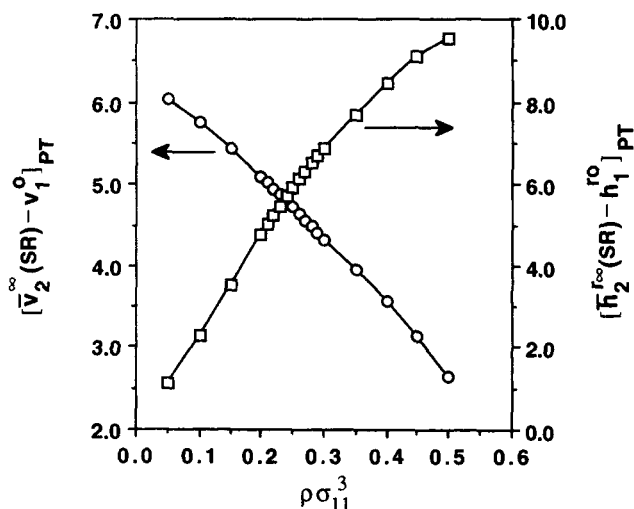
$$E \equiv (x_2/x_2^{\text{ideal gas}}) = (\phi_2^{\text{sat}}/\phi_2) \exp[\beta v_2^s (P - P_2^{\text{sat}})] \quad (26)$$

with  $x_2^{\text{ideal gas}} = P_2^{\text{sat}}/P$ , where  $P_2^{\text{sat}}$ ,  $v_2^s$ , and  $\phi_2^{\text{sat}}$  are the vapor pressure, molar volume, and fugacity coefficient of the pure solute in the condensed phase at the prevailing state conditions, respectively. After some algebra the enhancement factor can be finally recast as follows (see Appendix C):

$$E \approx \phi_2^{\infty}(T, P)^{-1} = \phi_1^o(T, P)^{-1} \exp \left[ - \int_0^{\rho(P)} \frac{\beta}{\rho^2} \left( \frac{\partial P}{\partial x_2} \right)_{v, T} d\rho \right]$$

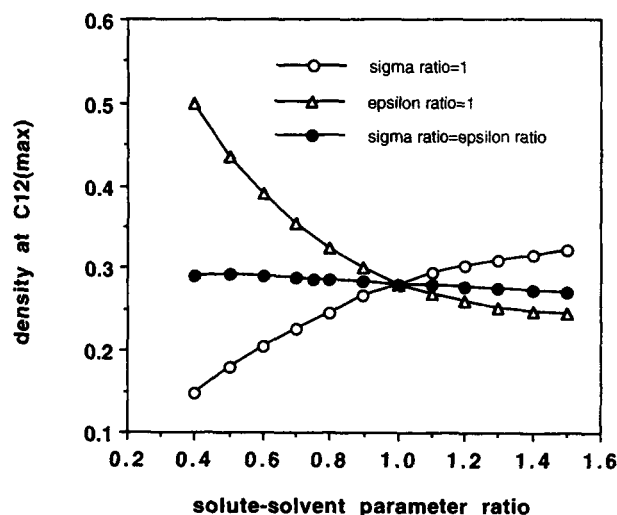
$$= \left( 1 - \rho^{-1} \int_0^{\rho(P)} C_{11}^o d\rho \right) \exp \left( \int_0^{\rho(P)} C_{12}^{\infty} \frac{d\rho}{\rho} \right) \quad (27)$$

an expression that indicates the fundamental link between the solubility enhancement/depletion (decrease/increase in  $\phi_2^{\infty}(T, P)$ ) and the strength of the solute-solvent and solvent-solvent direct correlation functions (microstructure). Note also that Eq. 27 involves only short-range quantities, therefore the increase in the solubility enhancement for attractive mixtures cannot be ascribed to the corresponding long-range increase in  $\Gamma = \rho G_{12}^{\infty}$  as some have proposed (Lee et al., 1991). Note, however, that in the near-critical supercritical region, small



**Figure 18.** Density dependence of  $[\bar{v}_2^{\infty}(\text{SR}) - v_1^o]_{T, P}$  and  $[\bar{h}_2^{\infty}(\text{SR}) - h_1^o]_{T, P}$  for repulsive Lennard-Jones Ne(2)-Xe(1) system at  $T_r = T/T_c = 1.02$  from PY calculations.

All quantities are reduced in terms of solvent's Lennard-Jones parameters.



**Figure 19.** Location of maximum in density dependence of  $C_{12}^{\infty}$  for three types of Lennard-Jones mixtures at  $T_r = T/T_c = 1.0$  from PY calculations.

changes in the system pressure result in large changes in the solvent density (and thus the limits of integration in Eq. 27, including the exponentiated term). Hence, Eq. 27 illustrates mathematically one of the advantages of near-critical conditions: the solvation properties of the solvent can be modified significantly (and thus "tuned") through small changes in pressure.

The interpretation of the solute-induced effect on the solvent's local properties given by Eqs. 19–22 follows automatically from the rigorous statistical mechanical formalism of Kirkwood and Buff (1951). Consequently, it results in the correct limiting values of the solute-induced effect for both ideal gas solutes and ideal solutions. These two limiting conditions are not satisfied by Eqs. 1 and 3, and therefore, we understand that they may not capture properly the physics behind the observed solvent's local density augmentation. In fact, our understanding is that the electron paramagnetic resonance (Carlier and Randolph, 1993) and the fluorescent (Brennecke et al., 1990b; Knutson et al., 1992) spectroscopic devices detect changes of signals connected to the perturbation of the solvent's local density due to the presence of the solute. Hence, a more appropriate expression for the calculation of the solvent's local density augmentation/depletion—even though  $R$  is still arbitrarily chosen—should read:

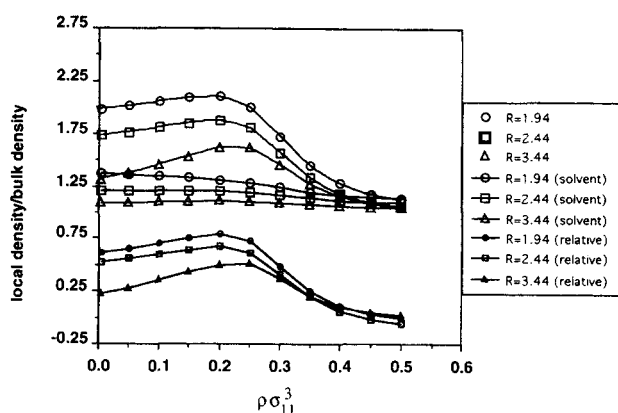
$$\rho_{12}(R) - \rho_{11}(R) = \frac{3\rho \int_{r_o}^R [g_{12}^{\infty}(r) - g_{11}^o(r)] r^2 dr}{(R^3 - r_o^3)} \quad (28)$$

where  $\rho_{11}(R)$  is the average solvent's density in the solvent's solvation shell with a radius  $R$ , and  $r_o$  is the radius at which the difference  $g_{12}^{\infty}(r) - g_{11}^o(r)$  becomes nonzero.

In Figure 20 we plot  $(\rho_{12}(R) - \rho_{11}(R))/\rho$ , the normalized values of the lefthand side of Eq. 27 predicted by the integral equations in the PY approximation for the pyrene(2)-CO<sub>2</sub>(1) system at  $T_r = 1.02$ . Even though  $(\rho_{11}(R)/\rho)$  contributes substantially to the total solvent's local to bulk density ratio, it does not change the position of the maximum in the density dependence of  $(\rho_{12}(R) - \rho_{11}(R))/\rho$ . Interestingly, the location of the maximum in the local density augmentation predicted by either Eq. 3 or 28 appears to coincide with that at which  $C_{12}^{\infty}$  and  $\bar{v}_2^{\infty}(SR)$  show extrema (see Figures 5 and 9).

The derived solvation formalism also indicates that the near-critical solubility enhancement/depletion of dilute solutes cannot be ascribed to a long-range (compressibility-driven) solvent's local density augmentation/depletion around the solute but to the short-range (local) solute-induced effect on the microstructure of the solvent (solvation) due to the pronounced solute-solvent molecular asymmetry. In fact, the relative (to solvent-solvent) size of the solute-solvent RDF's (radial distribution function) first peak is an indication of the substantial solvent's local density augmentation/depletion resulting from the marked solute-solvent asymmetry. This is readily understood by recalling that the first peak of the RDF corresponds to the attractive potential well, and that at low density  $g_{ij}(r, \rho \rightarrow 0) \equiv \exp(-\beta u_{ij}(r))$ . Thus, for any Lennard-Jones system at low density we must expect that (McQuarrie, 1976):

$$\lim_{\rho \rightarrow 0} \left[ \frac{g_{ij}(r/\sigma_{ij} = 2^{1/6})}{g_{ii}(r/\sigma_{ii} = 2^{1/6})} \right] = \exp[-\beta(\epsilon_{ii} - \epsilon_{ij})] \quad (29)$$



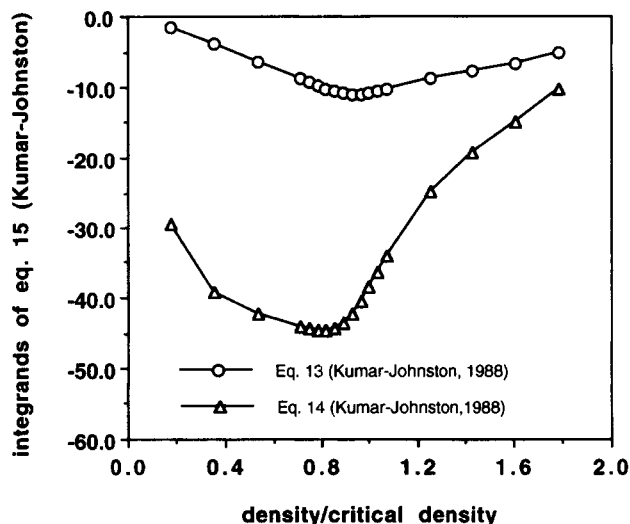
**Figure 20. Comparison between density dependence of local to bulk density ratio for attractive Lennard-Jones pyrene(2)-CO<sub>2</sub>(1) system at  $T_r = T/T_c = 1.02$  from PY calculations.**

Three sets of curves correspond to total, solvent, and relative contributions to solvent's local density augmentation for three solvation shells.

For example, the solute-solvent to solvent-solvent RDF ratios for pyrene(2)-CO<sub>2</sub>(1) and Ne(2)-Xe(1) at  $T_r = 1.02$  are 1.7 and 0.63 at zero density using Eq. 28, while the corresponding PY-values at  $T_r = 1.02$  and  $\rho_r = 1.0$  are 1.6 and 0.67, respectively. Therefore, the change in the solvent's local environment around the dilute solute cannot be interpreted either as a solvent condensation (Kim et al., 1985) or collapse (Brennecke and Eckert, 1989), but as the rearrangement of the solvent's microstructure around the dilute solute (that is, a solvation phenomenon). In addition, the observed weak isothermal density dependence for the solute's chemical potential  $\mu_2^{\infty}(\rho)$ , and simultaneously, the strong isothermal density dependence for the solute's fugacity coefficient  $\phi_2^{\infty}(\rho)$  are just the result of the exponential dependence of  $\phi_2^{\infty}(\rho)$  with the integral over the local microstructure (Appendix C).

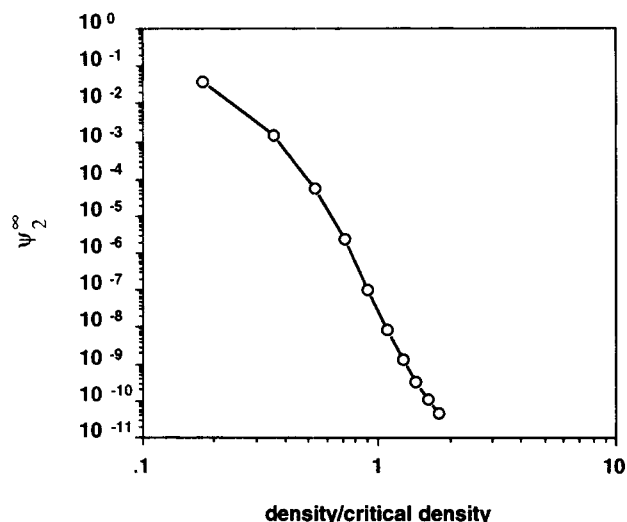
$$\phi_2^{\infty}(T, P) = \frac{\exp\left(-\int_0^{\rho(P)} C_{12}^{\infty} \frac{d\rho}{\rho}\right)}{\left(1 - \rho^{-1} \int_0^{\rho(P)} C_{11}^o d\rho\right)} \quad (30)$$

Finally, we use the formalism to guide the interpretation and modeling of experimental data of dilute near-critical systems (Chialvo, 1993a). For example, the expressions  $(\beta \bar{v}_2^{\infty}/\kappa)$  and  $(\beta \bar{v}_2^{\infty}/\rho\kappa)$ , or the related quantity  $(\partial P/\partial N_2)_{T, N_1}^{\infty}$ , are usually the target for modeling since they remain finite even at the solvent's critical point (Kim et al., 1985; Eckert et al., 1986; Kumar and Johnston, 1988). Recently, Kumar and Johnston (1988) proposed two alternative expressions for  $(\beta \bar{v}_2^{\infty}/\kappa)$  and  $(\beta \bar{v}_2^{\infty}/\rho\kappa)$  along the critical isotherm and in the vicinity of the critical isochor, based on the classical Taylor series expansion of the pressure around the solvent's critical point (Levelt Sengers, 1991). They assumed that either  $(\beta \bar{v}_2^{\infty}/\kappa)$  and  $(\beta \bar{v}_2^{\infty}/\rho\kappa)$  could be taken as density independent, an assumption that was indirectly supported by the prediction of a quasi-linear density dependence for the function  $\Psi_2^{\infty} = (P\beta/\rho)\phi_2^{\infty}$  (in log-log coordinates) using the Peng-Robinson EOS.



**Figure 21.** Density dependence of  $(\beta \bar{v}_2^0/\kappa)$  and  $(\beta \bar{v}_2^0/\rho\kappa)$  for attractive Lennard-Jones pyrene(2)-CO<sub>2</sub>(1) system at  $T_r = T/T_c = 1.0$  from PY calculations.

Our results of Figure 21 suggest that the assumption made by Kumar and Johnston does not hold in the vicinity of the solvent critical point, that is, neither  $(\beta \bar{v}_2^0/\kappa)$  nor  $(\beta \bar{v}_2^0/\rho\kappa)$  or  $(\partial P/\partial N_2)_{T, N_1}$  can be assumed to be density independent along the critical isotherm and in the vicinity of the solvent's critical point. In fact, it can be shown (see Appendix D) that the conditions invoked by Kumar and Johnston to assume density independency for either  $(\beta \bar{v}_2^0/\kappa)$  or  $(\beta \bar{v}_2^0/\rho\kappa)$  (see their Eqs. 13 and 14) are actually the necessary conditions for extrema in those functions. Moreover, the fact that the function  $\ln \Psi_2^\infty$  shows a quasi-linear dependence with the logarithm of the system's density around the solvent's critical point does not necessarily imply that either  $(\beta \bar{v}_2^0/\kappa)$  or  $(\beta \bar{v}_2^0/\rho\kappa)$  must be density independent (though the inverse is valid). Note also



**Figure 22.** Density dependence of  $\ln \Psi_2^\infty$  for the attractive Lennard-Jones pyrene(2)-CO<sub>2</sub>(1) system at  $T_r = T/T_c = 1.0$  from PY calculations.

that the mentioned linearity has not been derived but observed through EOS calculations using some ad hoc mixing rules (usually a vdW1-type) which are not compatible with the microstructure of these near-critical mixtures (Chialvo, 1993a). In fact, even a simple system like a Lennard-Jones mixture of spheres along the solvent's critical isotherm shows  $(\beta \bar{v}_2^0/\kappa)$  and  $(\beta \bar{v}_2^0/\rho\kappa)$  with strong density dependencies around the solvent's critical point (Figure 21). In contrast,  $\ln \Psi_2^\infty$  presents a quasi-linear dependence with  $\ln(\rho/\rho_c)$  as shown in Figure 22.

## Acknowledgment

It is a pleasure to thank Prof. Peter Monson for making available the Fortran code used in our PY integral equation calculations. This work was supported by the Division of Chemical Sciences, Office of Basic Energy Sciences, U.S. Department of Energy. The reported calculations were performed on Cray Y-MP/832 and C-90 machines located at the Pittsburgh Supercomputing Center (CPWSCB) through grant CBT910039P.

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## Appendix A: Derivation of Eq. 15

Starting from Eq. 14 and recalling Eq. 6 we have that:

$$(I_{11}^o - I_{12}^o) = \frac{\kappa}{\beta} (1 - C_{12}^o) - \rho^{-1} (1 + C_{11}^o - C_{12}^o) \quad (A1)$$

which can be recast as follows:

$$(I_{11}^o - I_{12}^o) = \frac{\kappa C_{11}^o}{\beta} (C_{11}^o - C_{12}^o) \quad (A2)$$

by invoking the compressibility expression:

$$\frac{\kappa}{\beta} = (1 - C_{11}^o)^{-1} \rho^{-1} \quad (A3)$$

## Appendix B: Derivation of Eqs. 21-22

The residual solute partial molar enthalpy  $\bar{h}_2^r(T, P)$  is straightforwardly derived from Eq. 7. To do so we recall that (Modell and Reid, 1983):

$$\bar{h}_2^r = (\partial \ln \phi_2^o / \partial \beta)_P \quad (B1)$$

and (Modell and Reid, 1983):

$$\left( \frac{\partial \ln \phi_2^o}{\partial \beta} \right)_P = \left( \frac{\partial \ln \phi_2^o}{\partial \beta} \right)_\rho - \left( \frac{\partial P}{\partial \beta} \right)_\rho \left( \frac{\partial \ln \phi_2^o}{\partial P} \right)_\beta \quad (B2)$$

From Eqs. 4-7 we have:

$$\left( \frac{\partial \ln \phi_2^o}{\partial \beta} \right)_\rho = - \int_0^{\rho(P)} \left( \frac{\partial C_{12}^o}{\partial \beta} \right) \frac{d\rho}{\rho} - \left( \frac{\partial \ln (\beta P \rho^{-1})}{\partial \beta} \right) \quad (B3)$$

with

$$\begin{aligned} \left( \frac{\partial \ln \phi_2^o}{\partial P} \right)_\beta &= \beta \bar{v}_2^o - P^{-1} \\ &= \kappa (1 - C_{12}^o) - P^{-1} \end{aligned} \quad (B4)$$

Thus, from Eqs. 7 and B2-B4 we have:

$$\bar{h}_2^r(T, P) = - \int_0^{\rho(P)} \left( \frac{\partial C_{12}^o}{\partial \beta} \right) \frac{d\rho}{\rho} - \beta^{-1} - \beta \left( \frac{\partial P}{\partial \beta} \right)_\rho \bar{v}_2^o \quad (B5)$$

and, after invoking Eq. 14, Eq. B5 becomes:

$$\begin{aligned} \bar{h}_2^r(T, P) &= - \beta^{-1} - \underbrace{\int_0^{\rho(P)} \left( \frac{\partial C_{12}^o}{\partial \beta} \right) \frac{d\rho}{\rho} - \left( \frac{\partial P}{\partial \beta} \right)_\rho \beta \rho^{-1} (1 + C_{11}^o - C_{12}^o)}_{\bar{h}_2^r(SR)} \\ &\quad - \underbrace{\left( \frac{\partial P}{\partial \beta} \right)_\rho \kappa C_{11}^o (C_{11}^o - C_{12}^o)}_{\bar{h}_2^r(LR)} \quad (B6) \end{aligned}$$

Likewise, the solvent's residual molar enthalpy becomes:

$$h_1^r(T, P) = - \int_0^{\rho(P)} \left( \frac{\partial C_{11}^o}{\partial \beta} \right) \frac{d\rho}{\rho} - \beta^{-1} - \left( \frac{\beta}{\rho} \right) \left( \frac{\partial P}{\partial \beta} \right)_\rho \quad (B7)$$

and the solute-induced local enthalpy effect is:

$$\begin{aligned} [\bar{h}_2^r(SR) - h_1^r]_{T, P} &= - \int_0^{\rho(P)} \left( \frac{\partial C_{12}^o}{\partial \beta} - \frac{\partial C_{11}^o}{\partial \beta} \right) \frac{d\rho}{\rho} - \left( \frac{\partial P}{\partial \beta} \right)_\rho \beta \rho^{-1} (C_{11}^o - C_{12}^o) \\ &= - \int_0^{\rho(P)} \left( \frac{\partial C_{12}^o}{\partial \beta} - \frac{\partial C_{11}^o}{\partial \beta} \right) \frac{d\rho}{\rho} - \left( \frac{\beta}{\rho} \right)^2 \left( \frac{\partial P}{\partial \beta} \right)_\rho \left( \frac{\partial P}{\partial x_2} \right)_{v, T}^\infty \end{aligned} \quad (B8)$$

which is Eq. 21.

Finally, the residual solute partial molar entropy is obtained from Eqs. B5 and 7:

$$\begin{aligned} \bar{s}_2^r(T, P) &= [\bar{h}_2^r(T, P) - \mu_2^r(T, P)] T^{-1} \\ &= k \left[ \underbrace{\int_0^{\rho(P)} C_{12}^o \frac{d\rho}{\rho} + \ln \left( \frac{\beta P}{\rho} \right) - 1}_{\bar{s}_2^r(SR)} - T^{-1} \int_0^{\rho(P)} \left( \frac{\partial C_{12}^o}{\partial \beta} \right) \frac{d\rho}{\rho} - \left( \frac{\partial P}{\partial \beta} \right)_\rho (k T^2 \rho)^{-1} (1 + C_{11}^o - C_{12}^o) \right. \\ &\quad \left. - \underbrace{\left( \frac{\partial P}{\partial \beta} \right)_\rho \kappa C_{11}^o (C_{11}^o - C_{12}^o) T^{-1}}_{\bar{s}_2^r(LR)} \right] \quad (B9) \end{aligned}$$

Similarly, from Eqs. 9 and B7 the solvent's residual molar entropy becomes:

$$s_1^o(T, P) = k \left[ \int_0^{\rho(P)} C_{11}^o \frac{d\rho}{\rho} + \ln \left( \frac{\beta P}{\rho} \right) - 1 \right] - T^{-1} \int_0^{\rho(P)} \left( \frac{\partial C_{11}^o}{\partial \beta} \right) \frac{d\rho}{\rho} - \left( \frac{\partial P}{\partial \beta} \right)_{\rho} (kT^2 \rho)^{-1} \quad (\text{B10})$$

so that the solute-induced local entropic effect is:

$$\begin{aligned} [\bar{s}_2^o(SR) - s_1^o]_{T, P} &= k \int_0^{\rho(P)} (C_{12}^o - C_{11}^o) \frac{d\rho}{\rho} \\ &- T^{-1} \int_0^{\rho(P)} \left( \frac{\partial C_{12}^o}{\partial \beta} - \frac{\partial C_{11}^o}{\partial \beta} \right) \frac{d\rho}{\rho} - \left( \frac{\partial P}{\partial \beta} \right)_{\rho} (kT^2 \rho)^{-1} (C_{11}^o - C_{12}^o) \\ &= k \int_0^{\rho(P)} (C_{12}^o - C_{11}^o) \frac{d\rho}{\rho} \\ &- T^{-1} \int_0^{\rho(P)} \left( \frac{\partial C_{12}^o}{\partial \beta} - \frac{\partial C_{11}^o}{\partial \beta} \right) \frac{d\rho}{\rho} - \left( \frac{\partial P}{\partial \beta} \right)_{\rho} (kT^{1.5} \rho)^{-2} \left( \frac{\partial P}{\partial x_2} \right)_{v, T}^{\infty} \end{aligned} \quad (\text{B11})$$

which is Eq. 22.

## Appendix C: Derivation of Eq. 27

Equation 26 can be greatly simplified by noting first that  $\phi_2^{\text{sat}} \exp[\beta v_2^s (P - P_2^{\text{sat}})]$  is a quantity of order one while  $\phi_2$  changes several orders of magnitude in the region of interest, and secondly, that for dilute mixtures we have (Debenedetti and Kumar, 1986):

$$\begin{aligned} \phi_2(T, P, x_2) &\cong \phi_2^o(T, P) \exp(K_{12} x_2) \\ &= \phi_2^o(T, P) \exp(x_2/x_2^{LS}) \end{aligned} \quad (\text{C1})$$

where the superscript *LS* indicates limit of stability, and (Chialvo, 1993a)

$$\begin{aligned} K_{12} &= - \left( \frac{\partial \ln \phi_2}{\partial x_1} \right)_{T, P}^{\infty} \\ &= \rho (G_{11}^o + G_{22}^o - 2G_{12}^o) \\ &= (C_{11}^o + C_{22}^o - 2C_{12}^o) + \rho \kappa \beta^{-1} (C_{11}^o - C_{12}^o)^2 \end{aligned} \quad (\text{C2})$$

Therefore, from Eq. C1 we have that  $1 > (\phi_2/\phi_2^o) > e^{-1}$  (Debenedetti and Kumar, 1986) so that by invoking Eqs. 10 and 16 we have:

$$\begin{aligned} E \approx \phi_2^o(T, P)^{-1} &= \phi_1^o(T, P)^{-1} \exp \left[ - \int_0^{\rho(P)} \frac{\beta}{\rho^2} \left( \frac{\partial P}{\partial x_2} \right)_{v, T}^{\infty} d\rho \right] \\ &= \left( \frac{\rho}{\beta P} \right) \exp \left( \int_0^{\rho(P)} C_{12}^o \frac{d\rho}{\rho} \right) \end{aligned} \quad (\text{C3})$$

In addition, by recalling the microscopic interpretation of the isothermal compressibility we can write (O'Connell, 1981):

$$P = \left( \frac{\rho}{\beta} \right) \left( 1 - \rho^{-1} \int_0^{\rho} C_{11}^o d\rho \right) \quad (\text{C4})$$

and finally, from Eqs. C3 and C4:

$$\begin{aligned} E &\approx \phi_2^o(T, P)^{-1} \\ &= \left( 1 - \rho^{-1} \int_0^{\rho(P)} C_{11}^o d\rho \right) \exp \left( \int_0^{\rho(P)} C_{12}^o \frac{d\rho}{\rho} \right) \end{aligned} \quad (\text{C5})$$

## Appendix D

From the expansion of the classical molar Helmholtz free energy  $A(v, T, x)$  follows (Levelt Sengers, 1991):

$$\begin{aligned} f_1(v, T_c) &\equiv \frac{\beta_c \bar{v}_2^{\infty}}{\kappa} \\ &\cong 0.5 \beta_c (v_c + \delta v)^2 A_{4c}^s \delta v^2 - \beta_c v [A_{1c}^s + A_{2cx}^s \delta v + O(\delta v^2)] \end{aligned} \quad (\text{D1})$$

where  $\delta v = (v - v_c)$ ,  $A_s \equiv (\partial A / \partial s)$  and the (sub) superscript *c* denotes solvent's critical conditions. Consequently  $f_1(v, T_c)$  might show an extremum at  $v_1$ , that is, in the neighborhood of the solvent's critical volume if:

$$\left( \frac{\partial f_1}{\partial v} \right)_{\beta} = -\beta_c [A_{1c}^s + A_{2cx}^s (v_1 - v_c)] - \beta_c v_1 A_{2cx}^s = 0 \quad (\text{D2})$$

that is:

$$v_1 = 0.5 (v_c - A_{1c}^s / A_{2cx}^s) \quad (\text{D3})$$

where we keep only first-order terms in  $v$  or  $\delta v$ . Then:

$$\left( \frac{\partial^2 f_1}{\partial v^2} \right)_{\beta} = -\beta_c A_{2cx}^s \neq 0 \quad (\text{D4})$$

Recalling that the coefficients of the Taylor expansion are  $A = -(A_{1c}^s / P_c)$  and  $C = (v_c A_{2cx}^s / P_c)$  (Kumar and Johnston, 1988), we have that as  $(-A_{1c}^s / A_{2cx}^s)$  approaches  $v_c$ , the difference  $(A - C)$  approaches zero (see Eq. 13) of Kumar and Johnston (1988).

Likewise, we can write the following expansion:

$$\begin{aligned} f_2(v, T_c) &\equiv \frac{\beta_c \bar{v}_2^{\infty}}{\rho \kappa} \\ &\cong 0.5 \beta_c (v_c + \delta v)^3 A_{4c}^s \delta v^2 - \beta_c v^2 [A_{1c}^s + A_{2cx}^s \delta v + O(\delta v^2)] \end{aligned} \quad (\text{D5})$$

so that the conditions for an extremum at  $v_2$  in the vicinity of  $v_c$  are:

$$\left(\frac{\partial f_2}{\partial v}\right)_\beta = -2\beta_c v(A_{ux}^c + A_{2ux}^c \delta v) - \beta_c v^2 A_{2ux}^c = 0 \quad (D6)$$

that is:

$$v_2 = (2/3)(v_c - A_{ux}^c/A_{2ux}^c) \quad (D7)$$

and then:

$$\left(\frac{\partial^2 f_2}{\partial v^2}\right)_\beta = -3\beta_c A_{2ux}^c \quad (D8)$$

Note that as  $(-2A_{ux}^c/A_{2ux}^c)$  approaches  $v_c$ , the difference  $(A-2C)$  approaches zero (see Eq. 14) of Kumar and Johnston (1988).

In general  $A_{ux}^c$  and  $A_{2ux}^c$  have different signs:  $A_{ux}^c > 0$  and  $A_{2ux}^c < 0$  for nonvolatile solutes whereas  $A_{ux}^c < 0$  and  $A_{2ux}^c > 0$  for volatile solutes (Rozen, 1969; Fernandez-Prini et al., 1992). Therefore, for attractive mixtures, that is,  $A_{ux}^c > 0$ ,  $f_1(v, T_c)$  and  $f_2(v, T_c)$  might show a minimum at  $v_1$  and  $v_2$  in the vicinity of  $v_c$  when  $(-A_{ux}^c/A_{2ux}^c) \approx v_c$  and  $(-2A_{ux}^c/A_{2ux}^c) \approx v_c$ , respectively. Obviously, both conditions cannot be satisfied simultaneously at the solvent's critical point, that is,  $v_1 = v_2 = v_c$ , because from Eqs. D3 and D7 we must have:

$$v_1 = 0.75v_2 \quad (D9)$$

From Figure 21 we have  $\rho_1 = 1/v_1 \approx 0.26$  and  $\rho_2 = 1/v_2 \approx 0.23$  so that  $(v_1/v_2) \approx 0.88$  ( $\approx 17\%$  greater than that predicted by Eq. D9), which might indicate that a better prediction can be achieved by including higher order terms in Eqs. D1-D9.

In summary, if we assume that either  $A-C \approx 0$  or  $A-2C \approx 0$  along the critical isotherm we cannot expect density independency for either  $(\beta \bar{v}_2^\infty/\kappa)$  or  $(\beta \bar{v}_2^\infty/\rho\kappa)$ —even though  $\ln \Psi_2^\infty = \beta \mu_2^{*\infty}(\rho, T)$  might show a quasi-linear dependence with  $\ln(\rho/\rho_c)$ —because at such conditions both functions for attractive systems ( $A_{ux}^c > 0$  and  $A_{2ux}^c < 0$ ) show a minimum in the vicinity of the solvent's critical density.

## Appendix E: Asymptotic Properties of the Direct Correlation Function

In this appendix, we present some results concerning the exact asymptotic behavior of the direct correlation function. For the sake of notational simplicity, we will present the results for the pure solvent (no solute) case only. For mixtures, similar relationships will hold, since all the total correlation functions in a mixture have a common correlation length (defined below).

As the critical point of a pure fluid is approached, the total correlation function becomes long-range. In fact, in the vicinity of the critical point we can write:

$$h(R) \approx \frac{\exp(-R/\xi)}{r^{1+\eta}} \quad (E1)$$

where  $\xi$  is the correlation length (a measure of the range over which molecules are correlated) and  $\eta$  is a critical exponent. Since  $\xi$  diverges ( $\xi \rightarrow \infty$ ) at the critical point (characterized by the critical temperature  $T_c$  and critical density  $\rho_c$ ):

$$h(r) \rightarrow \frac{1}{r^{1+\eta}} \quad (E2)$$

Thus, the total correlation function becomes long-range and, in particular,  $\int h(r)dr \rightarrow \infty$ . However, from the Ornstein-Zernike equation it is evident that at the critical point  $\int c(r)dr$  is finite, and in fact  $\int c(r)dr \rightarrow 1/\rho_c$ , so that in particular  $c(r)$  is rigorously finite ranged at the critical point. It should be noted, however, that just because the direct correlation function is a short-range function does not mean it is in some way insensitive to the approach to the critical point. In fact,  $\int c(r)dr$  has its maximum value at the critical point and its asymptotic form changes as the critical point is approached. Groeneveld and Stell (1977) showed that the asymptotic form of the direct correlation function away from the critical point is given by:

$$c(r) = -\frac{u(r)}{kT} + A_2 h^2(r) + A_{22} \frac{h^2(r)}{r^2} + A_3 h^3(r) + \dots \text{ as } r \rightarrow \infty \quad (E3)$$

where  $A_2$ ,  $A_{22}$ , and  $A_3$  are state dependent coefficients,  $u(r)$  is the intermolecular potential,  $k$  is Boltzmann's constant,  $T$  is the temperature, and the ellipsis indicates that the higher-order terms are dominated by the terms shown. Given the exponential damping of the total correlation function away from the critical point indicated in Eq. E1, the leading term in this asymptotic expansion is:

$$c(r) \rightarrow -\frac{u(r)}{kT} \text{ as } r \rightarrow \infty \quad (E4)$$

At the critical point, the asymptotic form of the direct correlation function changes because the coefficient  $A_2 \rightarrow 0$  and because the long-range nature of the total correlation function changes the ordering of the higher-order terms in Eq. E4. The result is (Stell, 1977):

$$c(r) \rightarrow -\frac{u(r)}{kT} + D h^\delta(r) \text{ as } r \rightarrow \infty \text{ at } T_c, \rho_c \quad (E5)$$

where  $D$  is a constant and  $\delta$  is a critical exponent (equal to 4.8 experimentally and to 3 in classical theories such as engineering equations of state).

The main conclusion from the results presented here is that, rigorously,  $c(r)$  is finite-ranged at all points in the phase diagram since  $\int c(r)dr < \infty$  everywhere (though higher moments of  $c(r)$  will in general not be finite at the critical point). Hence, defining a quantity in terms of direct correlation functions is a demonstration of the finite range of that property. This does not mean, however, that such a property is insensitive to the approach to the critical point. As is clear from the analysis of this appendix, the direct correlation function changes as the critical point is approached so that properties expressed in terms of direct correlation functions will exhibit near critical effects (though in general of a less singular nature than those defined in terms of the total correlation functions). Moreover, a very accurate model based on the formalism described in this article (for example, one which predicted nonclassical behavior in thermodynamic properties) would need to take these changes into account.

Manuscript received May 11, 1993, and revision received Oct. 8, 1993.