

# Solvation Thermodynamics of Gas Solubility at Sub- and Near-Critical Conditions

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*The recently developed formalism for describing the solute-induced effect in dilute near-critical mixtures is extended to fluids composed of anisotropic molecules through the statistical mechanical interpretation of the derivative  $(\partial P/\partial x_2)_{T,p}^\infty$  whose critical value is the Krichevskii parameter.*

*Rigorous expressions for Henry's constant and the solute distribution factor along the orthobaric curve are derived in terms of the volumetric and entropic solute-induced local effects, and the quasi-linear behavior of their orthobaric density dependence away from the solvent's critical point is rationalized.*

*The formalism is illustrated with integral equation calculations of the orthobaric density dependence of several solvation thermodynamic quantities for an infinitely dilute volatile solute in near-critical solutions of hard-sphere Yukawa fluids.*

## Introduction

The Krichevskii parameter, the derivative  $(\partial P/\partial x_2)_{T,p}^\infty$  at the solvent's critical condition, plays an important role in the solvation thermodynamics of dilute mixtures at near-critical conditions by determining the asymptotic behavior of the vapor-liquid distribution factor (Japas and Levelt Sengers, 1989), Henry's constant (Japas and Levelt Sengers, 1989; Harvey et al., 1990), the solubility enhancement (Levelt Sengers, 1991b; Chialvo and Cummings, 1994), and the initial departure of the critical line from the critical point of the pure solvent (Chang et al., 1984). If valid for orthobaric regions away from the solvent's critical point, these asymptotic expressions become useful linear relationships for correlation purposes because they involve only the solvent's thermodynamic properties and the initial slope of the critical line that depends on the solute-solvent molecular asymmetry (Japas and Levelt Sengers, 1989).

For the case of Henry's constant  $H_{2,1}(T)$  and the infinite dilution distribution factor  $K^\infty(T)$  along the coexistence curve, Japas and Levelt Sengers (1989) derived the following expressions:

$$T \ln K^\infty = \left( \frac{2}{k\rho_c^2} \right) \left( \frac{\partial P}{\partial x_2} \right)_{T_c, \rho_c}^\infty (\rho^l - \rho_c) \quad (1)$$

and

$$T \ln (H_{2,1}/f_1^0) = A + \left( \frac{1}{k\rho_c^2} \right) \left( \frac{\partial P}{\partial x_2} \right)_{T_c, \rho_c}^\infty (\rho^l - \rho_c), \quad (2)$$

where the constant  $A \equiv T_c \ln [H_{2,1}(T_c)/f_1^0(T_c)]$  (Harvey and Levelt Sengers, 1990) and  $\rho^l$  is the orthobaric liquid density with a critical value  $\rho_c$ . Even though these expressions were expected to be closely obeyed by real systems only in the neighborhood of the solvent's critical point, where the orthobaric path obeys the asymptotic expression  $(v - v_c) = \pm |T - T_c|^{\beta-1}$ , these authors found that the linearity appeared to hold over a rather large orthobaric density range. However, the observed slopes are not in good agreement with the expected asymptotic values (Harvey et al., 1990), those from the  $T \ln K^\infty$  vs.  $(\rho^l - \rho_c)$  plots (Eq. 1) being closer than those from  $T \ln (H_{2,1}/f_1^0)$  vs.  $(\rho^l - \rho_c)$  plots (Eq. 2). Later, Wilhelm (1992) suggested that  $T \ln L^\infty$  vs.  $(\rho^l - \rho_c)$ , where  $L^\infty =$

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$(\rho'/\rho^\nu)_o/K^\infty$  is the Ostwald coefficient, rather than  $T \ln K^\infty$  vs.  $(\rho' - \rho_c)$ , might result in a better linear relationship over a wider range of orthobaric densities.

Here we argue that a statistical mechanical approach to sub- and near-critical solvation phenomena may offer insight into the mechanism behind the observed linearity. For example, we have recently shown from a molecular viewpoint that  $(\partial P/\partial x_2)_{T,\rho}^\infty$  measures the isothermal–isochoric finite pressure change induced by the rearrangement of the solvent structure around an infinitely dilute solute, a process driven by the difference of chemical potentials between the dilute solute and the nearly pure solvent (solute–solvent molecular asymmetry) (Chialvo and Cummings, 1994, 1995). In our previous article (Chialvo and Cummings, 1994) we developed a molecular-based formalism to establish the statistical mechanical basis of supercritical solvation in terms of well-defined molecular correlation function integrals. The formalism was centered on the statistical mechanical separation between direct and indirect correlation functions, through the Ornstein–Zernike (OZ) equation for spherically symmetric molecules (Ornstein and Zernike, 1914), and applied to defining the solvation (finite) and compressibility-driven (diverging) contributions to the thermodynamic properties in terms of finite solute–solvent and solvent–solvent direct correlation function integrals (DCFIs). Such a separation made it possible to derive the solvation thermodynamics in terms of the difference between the solute–solvent and the solvent–solvent DCFIs, giving a rigorous statistical mechanical interpretation to the derivative  $(\partial P/\partial x_2)_{T,\rho}^\infty$ , the supercritical solubility enhancement, and the solute synergism in mixed-solute systems (Chialvo and Cummings, 1993; Chialvo, 1993a,b).

The strength of this approach resides in the unambiguous separation between direct and indirect molecular correlation functions according to the isotropic OZ equation, a concept that does not rely on any explicit choice for the size of the solute's solvation shell. Yet, the separation between solvation and compressibility-driven contributions can be done without invoking direct correlation function integrals, a feature that will make the formalism more powerful than the current version in that it will apply to any mixture regardless of the molecular asymmetry involved.

In this article we generalize our solvation formalism to fluid mixtures composed of anisotropic molecules, by deriving the volumetric, enthalpic, entropic, and heat capacity finite solute-induced local effects in terms of the finite derivative  $(\partial P/\partial x_2)_{T,\rho}^\infty$ . Then, we obtain statistical mechanical expressions for Henry's constant and the solute distribution factor along the orthobaric curve, in terms of the volumetric and entropic solute-induced local effects, and discuss a statistical mechanical interpretation of the observed linearity and slope for the orthobaric density dependence of Henry's constant and the distribution factor at near-critical conditions. Finally, we illustrate the formalism with integral equation calculations of the orthobaric density dependence of several solvation thermodynamic quantities for an infinitely dilute volatile solute in near-critical solutions of the hard core Yukawa fluid.

## Fundamentals

The solvation of a solute molecule in a pure solvent can be portrayed as the process of formation of an infinitely dilute

*nonideal solution* starting from the corresponding pure solvent that can be considered (from the viewpoint of its residual properties) as an *ideal solution*. This “thought” experiment is the realization of Kirkwood's coupling parameter charging (see Chialvo, 1993a, for details), in which a solvent molecule (labeled solute, i.e., solute–solvent interactions = solvent–solvent interactions) is converted to the final solute molecule in solution. This hypothetical process involves an isothermal–isobaric coupling work given by the difference of residual (at constant temperature and either constant pressure or volume) chemical potentials between the infinitely dilute solute and the pure solvent (Chialvo and Cummings, 1994) (see Appendix A for the multicomponent counterpart),

$$\mu_2^\infty(T, P) - \mu_1^0(T, P) = \mu_2^\infty[T, \rho(P)] - \mu_1^0[T, \rho(P)] \\ = \int_0^{\rho(P)} \left( \frac{\partial P}{\partial x_2} \right)_{T,\rho}^\infty \frac{d\rho}{\rho^2} \quad (3)$$

and

$$\ln [H_2(T, P)/f_1^0(T, P)] = \beta \int_0^{\rho(P)} \left( \frac{\partial P}{\partial x_2} \right)_{T,\rho}^\infty \frac{d\rho}{\rho^2}, \quad (4)$$

where  $H_2$  and  $f_1^0$  are Henry's constant of solute and the fugacity of the pure solvent, respectively, and  $\beta = 1/kT$ . Note that this definition of Henry's constant pertains to one-phase system, that is,  $H_2(T, P)$  (Japas and Levelt Sengers, 1989). Equation 4 relates the change of Gibbs free energy in the solvation process of a solute 2 at infinite dilution with the behavior of  $(\partial P/\partial x_2)_{T,\rho}^\infty$ , a quantity that characterizes the solvent's local density perturbation (microstructural rearrangement) around the infinitely dilute solute molecule relative to the solvent's local density around any solvent molecule in the ideal solution (pure solvent) (Chialvo and Cummings, 1995).

In what follows we focus specifically on infinitely dilute binary mixtures to make contact with the recently derived formalism based on direct correlation functions integrals (Chialvo and Cummings, 1994). From the exact fluctuation formalism of Kirkwood–Buff (KB) (Kirkwood and Buff, 1951) we have for a binary mixture (see Appendix B for the multicomponent counterpart)

$$\left( \frac{\partial P}{\partial x_2} \right)_{T,\rho}^\infty = \frac{kT\rho^2[x_1(G_{11} - G_{12}) + x_2(G_{12} - G_{22})]}{1 + \rho x_1 G_{11} + \rho x_2 G_{22} + \rho^2 x_1 x_2 (G_{11} G_{22} - G_{12}^2)}, \quad (5)$$

where  $G_{ij}$  denotes the KB total correlation function integral (TCFI) defined as (Kirkwood and Buff, 1951),

$$G_{ij} = \int h_{ij} d\mathbf{r} = \hat{h}_{ij}(\mathbf{0}) \quad (6)$$

with  $\hat{h}_{ij}(\mathbf{k})$ , the Fourier transform of the total  $ij$ -pair correlation function  $h_{ij}(\mathbf{r}) \equiv [g_{ij}(\mathbf{r}) - 1]$ , and  $g_{ij}(\mathbf{r}) = \langle g_{ij}(r_{ij}, \omega_i, \omega_j) \rangle_{\omega_i, \omega_j}$ , the spatial (unweighted angle average) center-to-center  $ij$ -pair distribution function. A discussion of the relationship between the OZ equations for  $g_{ij}(\mathbf{r}) =$

$\langle g_{ij}(r_{ij}, \omega_i, \omega_j) \rangle_{\omega_i, \omega_j}$  and for  $g_{ij}(r)$  is given in Appendix C. At infinite dilution Eq. 5 becomes

$$\left( \frac{\partial P}{\partial x_2} \right)_{T, \rho}^{\infty} = \frac{kT \rho^2 (G_{11}^0 - G_{12}^{\infty})}{1 + \rho G_{11}^0}, \quad (7)$$

where the superscripts 0 and  $\infty$  denote pure component and infinite dilution properties, respectively. Note that the pair distribution function  $g_{ij}(r) = \langle g_{ij}(r_{ij}, \omega_i, \omega_j) \rangle_{\omega_i, \omega_j}$  for near-critical systems can be described in terms of two length scales, the *range of correlation*  $\xi$ , which diverges at the solvent's critical point, and the *effective range of direct interactions*  $r_o(T)$ , which remains finite (Fisher, 1964) so that,

$$g_{ij}(r) = g_{ij}^{\text{SR}}(r) + g_{ij}^{\text{LR}}(r) \quad (8)$$

with

$$g_{ij}^{\text{SR}}(r) \approx O[\exp(-r/r_o)] \quad \text{as } r \rightarrow \infty$$

$$g_{ij}^{\text{LR}}(r) \rightarrow 1 + \frac{D_{ij} \exp(-r/\xi)}{r^{1+\eta}} [1 + Q_{ij}(r/\xi)], \quad (9)$$

where SR and LR denote short and long range,  $\xi$  is the solvent's correlation length,  $\eta$  is a critical exponent [whose best estimation is  $\eta = 0.03$  (Levelt Sengers, 1991a)], and  $D_{ij}$  is a prefactor that depends on  $r_o$ ,  $\rho$ ,  $T$ , and  $\eta$ . The  $Q_{ij}(x)$  are functions with the properties that  $Q_{ij}(x) \rightarrow 0$  as  $x \rightarrow 1$  and  $Q_{ij}(x)$  do not grow exponentially fast as  $x \rightarrow \infty$ . Note that because all  $g_{ij}^{\text{LR}}(r)$ 's in the near-critical mixture decay with a common correlation length  $\xi$ , which is that of the solvent in the case of infinitely dilute solutes (Levelt Sengers, 1991a), in Eq. 9 we express the short- and long-range contributions to the total correlation functions in terms of the solvent parameters. For OZ systems defined by  $\eta = 0$ ,  $r_o^2$  is the second moment of the solvent direct correlation function, and consequently the *range of direct interactions* is also the range of the corresponding pair intermolecular potentials (Stell, 1977). OZ systems are generalizations of mean field theories of the critical point in that the critical exponents  $\gamma$  and  $\delta$  are not constrained to their mean field values of 1 and 3, respectively. One example of an OZ system, the mean spherical approximation, yields spherical model exponents ( $\gamma = 2$ ,  $\delta = 5$ ). OZ systems are defined by the relationship  $\eta = 0$ , which simplifies the analysis of the critical point. The classical, or mean field theory, of critical point is thus a special case of an OZ system (Stell, 1977).

Now, from Eq. 8 we can write,

$$G_{ij}^{\infty} = G_{ij}^{\infty}(\text{SR}) + F[G_{ij}^{\infty}(\text{SR})]I_{ij}(\xi) \quad (10)$$

where,

$$I_{ij}(\xi) = \hat{D}_{ij,o} \xi^{2-\eta} \quad (11)$$

$\hat{D}_{ij,o}$  is a slowly varying function of  $T$  [which depends on  $Q_{ij}(x)$ ] and  $F[G_{ij}^{\infty}(\text{SR})]$  is a finite prefactor that depends on the short-range behavior of  $g_{ij}(r)$  and whose precise algebraic form is of no concern here. As the solvent approaches

its critical point, the solvent compressibility  $\kappa$  goes as  $\kappa \sim \xi^2 \rightarrow \infty$ , and  $I_{ij}(\xi)$  diverges. Consequently,

$$\left[ \frac{G_{ij}^{\infty}}{G_{ii}^{\infty}} \right]_{T_c, \rho_c} = \lim_{\xi \rightarrow \infty} \frac{F[G_{ij}^{\infty}(\text{SR})] + \frac{G_{ij}^{\infty}(\text{SR})}{I_{ij}(\xi)}}{F[G_{ii}^{\infty}(\text{SR})] + \frac{G_{ii}^{\infty}(\text{SR})}{I_{ij}(\xi)}} = \left( \frac{F[G_{ij}^{\infty}(\text{SR})]}{F[G_{ii}^{\infty}(\text{SR})]} \right)_{T_c, \rho_c}, \quad (12)$$

which is finite, and

$$\left[ \frac{G_{ij}^{\infty}}{G_{11}^0} \right]_{T_c, \rho_c} = \lim_{\xi \rightarrow \infty} \frac{F[G_{ij}^{\infty}(\text{SR})] + \frac{G_{ij}^{\infty}(\text{SR})}{I_{ij}(\xi)}}{F[G_{11}^0(\text{SR})] + \frac{G_{11}^0(\text{SR})}{I_{ij}(\xi)}} = \left( \frac{F[G_{ij}^{\infty}(\text{SR})]}{F[G_{11}^0(\text{SR})]} \right)_{T_c, \rho_c}, \quad (13)$$

which is finite since  $F[\dots]$  remains finite. Therefore, at the solvent's critical point Eq. 7 becomes,

$$\left( \frac{\partial P}{\partial x_2} \right)_{T_c, \rho_c}^{\infty} = kT_c \rho_c \left( 1 - \frac{G_{12}^{\infty}}{G_{11}^0} \right)_{T_c, \rho_c} = kT_c \rho_c \left( 1 - \frac{F[G_{12}^{\infty}(\text{SR})]}{F[G_{11}^0(\text{SR})]} \right)_{T_c, \rho_c}, \quad (14)$$

which is the Krichevskii parameter (Levelt Sengers, 1991a). For systems composed of spherically symmetric molecules, Eqs. 11–12 become equal to the corresponding ratios of DC-FIs (as shown in Appendix D) and the Krichevskii parameter reduces to

$$\left( \frac{\partial P}{\partial x_2} \right)_{T_c, \rho_c}^{\infty} = kT_c \rho_c \left[ 1 - \left( \frac{C_{12}^{\infty}}{C_{11}^0} \right)_{T_c, \rho_c} \right], \quad (15)$$

where  $(C_{11}^0)_{T_c, \rho_c} = 1$ .

Equations 7–15 and the more intuitive statistical mechanical quantity  $N_{ex}^{\infty}$ ,

$$N_{ex}^{\infty} = \rho(G_{12}^{\infty} - G_{11}^0) = -\kappa \left( \frac{\partial P}{\partial x_2} \right)_{T, \rho}^{\infty}, \quad (16)$$

which represents the excess number of solvent molecules around the infinitely dilute solute relative to that number around any solvent molecule (the ideal solution), suggest that the size and sign of  $(\partial P / \partial x_2)_{T, \rho}^{\infty}$  at near critical conditions are given by the magnitude of the finite local solvent's density perturbation around the solute molecule (Cummings et al., 1994; Chialvo and Cummings, 1995). Note that if the solute is just another solvent molecule at any state conditions and

composition (an ideal solution or pure solvent), then  $N_{ex}^\infty$ ,  $G_{11}^0 - G_{12}^\infty$ , and  $(\partial P/\partial x_2)_{T,\rho}^\infty$  are all zero, and consequently, there is no solute-induced local effect and the Krichevskii parameter is also zero (Note that the Krichevskii parameter can also be zero in a totally different situation, i.e., at a critical azeotrope (Fernandez-Prini and Japas, 1992)).

Therefore, we can draw a connection between the structural perturbation of the solvent, the derivative  $(\partial P/\partial x_2)_{T,\rho}^\infty$ , the quantity  $N_{ex}^\infty$ , and the volumetric solute-induced local effect (Chialvo and Cummings, 1994) by invoking the following identity,

$$\begin{aligned} (\beta/\rho^2)(\partial P/\partial x_2)_{T,\rho}^\infty &= \left(\frac{\beta}{\rho^2}\right)\left(\frac{N_{ex}^\infty}{\kappa}\right) \\ &= (\bar{v}_2^\infty - \bar{v}_1^0)(\kappa^{IG}/\kappa), \end{aligned} \quad (17)$$

where  $\kappa^{IG} = \beta/\rho$  is the ideal gas compressibility and  $\bar{v}_1^0 = \rho^{-1}$ , and then, by recasting the righthand side of Eq. 17 as a difference of solute partial molar volumes between that of the real infinitely dilute system and that of its ideal solution counterpart (pure solvent):

$$(\bar{v}_2^\infty - \bar{v}_1^0)(\kappa^{IG}/\kappa) = \bar{v}_2^\infty(\text{SR}) - \bar{v}_1^0. \quad (18)$$

Thus, Eq. 18 defines the volumetric solute-induced local effect as the excess/defect of the solvation contribution to the solute partial molar volume over that of the solute in the ideal solution (equal to the pure solvent's partial molar volume). In that sense, Eq. 18 also defines  $\bar{v}_2^\infty(\text{SR})$ , where SR emphasizes the fact that this property represents the solvation contribution to  $\bar{v}_2^\infty$ , that is, the contribution due to the structural perturbation of the solvent around the solute. Immediately, from Eqs. 16–18 and  $\bar{v}_2^\infty = \bar{v}_2^\infty(\text{SR}) + \bar{v}_2^\infty(\text{LR})$  we have

$$\begin{aligned} \bar{v}_2^\infty(\text{SR}) &= \rho^{-1} + \rho^{-1}\kappa^{IG}\left(\frac{\partial P}{\partial x_2}\right)_{T,\rho}^\infty \\ &= \bar{v}_1^0 + (\kappa^{IG}/\kappa)(G_{11}^0 - G_{12}^\infty) \end{aligned} \quad (19)$$

is the solvation contribution, and

$$\begin{aligned} \bar{v}_2^\infty(\text{LR}) &= \rho^{-1}\left(\frac{\partial P}{\partial x_2}\right)_{T,\rho}^\infty \kappa^r \\ &= (\kappa^r/\kappa)(G_{11}^0 - G_{12}^\infty) \end{aligned} \quad (20)$$

is the compressibility-driven contribution with  $\kappa^r = \kappa - \kappa^{IG}$ . Note that Eqs. 19 and 20 are the TCFT's counterparts of the two terms in Eq. 14 of Chialvo and Cummings (1994), respectively, even though the latter were derived through a rather different approach based on the isotropic OZ equation.

The enthalpic and entropic solute-induced local effects are straightforwardly obtained following an analogous strategy as described in Appendix B of Chialvo and Cummings (1994). The resulting expressions are

$$\begin{aligned} [\bar{h}_2^\infty(\text{SR}) - h_1^{r0}]_{T,\rho} &= \int_0^\rho \frac{(G_{11}^0 - G_{12}^\infty)}{\rho\kappa} d\rho \\ &+ \beta \int_0^\rho \left(\frac{\partial[(G_{11}^0 - G_{12}^\infty)/\kappa]}{\partial\beta}\right)_{\rho,x} \frac{d\rho}{\rho} \\ &- \beta\left(\frac{\kappa^{IG}}{\kappa}\right)\left(\frac{\partial P}{\partial\beta}\right)_\rho (G_{11}^0 - G_{12}^\infty) \end{aligned} \quad (21)$$

and

$$\begin{aligned} [\bar{s}_2^\infty(\text{SR}) - s_1^{r0}]_{T,\rho} &= -k\beta^2\left(\frac{\kappa^{IG}}{\kappa}\right)\left(\frac{\partial P}{\partial\beta}\right)_\rho (G_{11}^0 - G_{12}^\infty) \\ &+ k\beta^2 \int_0^\rho \left(\frac{\partial[(G_{11}^0 - G_{12}^\infty)/\kappa]}{\partial\beta}\right)_{\rho,x} \frac{d\rho}{\rho}, \end{aligned} \quad (22)$$

which are the counterparts of Eqs. 21 and 22 of Chialvo and Cummings (1994) in terms of the finite quantity  $(G_{11}^0 - G_{12}^\infty)\kappa^{-1}$  and its temperature derivative. Moreover, from Eq. 21 the solute-induced local effect on the constant pressure heat capacity becomes

$$\begin{aligned} [\bar{c}_{p2}^\infty(\text{SR}) - c_{p1}^{r0}]_{T,\rho} &= \left(\frac{k\beta^4}{\rho}\right)\left[\left(\frac{\partial[(G_{11}^0 - G_{12}^\infty)/\kappa]}{\partial\beta}\right)_{\rho,x}\left(\frac{\partial P}{\partial\beta}\right)_\rho^\infty\right. \\ &+ \left.\frac{(G_{11}^0 - G_{12}^\infty)}{\kappa}\left(\frac{\partial^2 P}{\partial\beta^2}\right)_{\rho,x}^\infty\right] + k\beta^3\left[2\frac{(G_{11}^0 - G_{12}^\infty)}{\rho\kappa}\left(\frac{\partial P}{\partial\beta}\right)_\rho^\infty\right. \\ &- \left.\int_0^\rho \left(\frac{\partial^2[(G_{11}^0 - G_{12}^\infty)/\kappa]}{\partial\beta^2}\right)_{\rho,x} \frac{d\rho}{\rho}\right] \\ &- 2k\beta^2 \int_0^\rho \left(\frac{\partial[(G_{11}^0 - G_{12}^\infty)/\kappa]}{\partial\beta}\right)_{\rho,x} \frac{d\rho}{\rho}. \end{aligned} \quad (23)$$

Similarly, the solute-induced local effect on the residual (at constants  $T$  and  $\rho$ ) internal energy and entropy read

$$\begin{aligned} [\bar{u}_2^\infty(\text{SR}) - u_1^{r0}]_{T,\rho} &= \int_0^\rho \frac{(G_{11}^0 - G_{12}^\infty)}{\rho\kappa} d\rho \\ &+ \beta \int_0^\rho \left(\frac{\partial[(G_{11}^0 - G_{12}^\infty)/\kappa]}{\partial\beta}\right)_{\rho,x} \frac{d\rho}{\rho} \end{aligned} \quad (24)$$

and

$$[\bar{s}_2^\infty(\text{SR}) - s_1^{r0}]_{T,\rho} = k\beta^2 \int_0^\rho \left(\frac{\partial[(G_{11}^0 - G_{12}^\infty)/\kappa]}{\partial\beta}\right)_{\rho,x} \frac{d\rho}{\rho} \quad (25)$$

so that the solute-induced local effect on the constant volume heat capacity becomes

$$\left[ \bar{c}_{v_2}^{r\infty}(\text{SR}) - c_{v_1}^{r0} \right]_{T,\rho} = -k\beta^3 \int_0^\rho \left( \frac{\partial^2 [(G_{11}^0 - G_{12}^\infty)/\kappa]}{\partial \beta^2} \right)_{\rho,x} \frac{d\rho}{\rho} \\ - 2k\beta^2 \int_0^\rho \left( \frac{\partial [(G_{11}^0 - G_{12}^\infty)/\kappa]}{\partial \beta} \right)_{\rho,x} \frac{d\rho}{\rho}. \quad (26)$$

Finally, from Eqs. 21 and 22 or 24 and 25, the change of Gibbs free energy for the solvation process of an infinitely dilute solute in a pure solvent becomes

$$\Delta G_{\text{solvation}} = [\bar{h}_2^{r\infty}(\text{SR}) - h_1^{r0}]_{T,P} - T[\bar{s}_2^{r\infty}(\text{SR}) - s_1^{r0}]_{T,P} \\ = [\bar{u}_2^{r\infty}(\text{SR}) - u_1^{r0}]_{T,\rho} - T[\bar{s}_2^{r\infty}(\text{SR}) - s_1^{r0}]_{T,\rho}, \quad (27)$$

where the subscripts  $(T,P)$  and  $(T,\rho)$  denote the variables kept constant in the definition of the residual quantities. Equation 27 indicates that the solvation may be entirely characterized by the finite perturbation of the solvent structure due to the presence of the solute, that is, compressibility-driven effects play no role in this process. Note also that even though the isochoric heat capacity exhibits a weak singularity around the solvent's critical point with a critical exponent  $\alpha$  (Levelt Sengers, 1991a), Eq. 26 indicates that its solvation contribution to the isochoric heat capacity remains finite even at the solvent's critical point.

## Statistical Mechanical Interpretation of Gas Solvation

Although we have defined the solute-induced local effects in one-phase systems, our analysis also applies to solvation phenomena involving two phases in equilibrium such as the solubility of gases in liquids. Here we derive the statistical mechanical expressions for the temperature dependence of Henry's constant  $H_{2,1}(T)$  and the solute's distribution factor  $K^\infty(T)$  along the solvent's coexistence line, in terms of the solute-induced local effects and discuss an interpretation for the observed linearity and slope for the orthobaric density dependence of these coefficients at sub- and near-critical conditions.

For that purpose we invoke the thermodynamic expressions for  $\ln H_{2,1}(T)$  and  $\ln K^\infty(T)$  derived by Japas and Levelt Sengers (1989), that is,

$$\ln K^\infty(T) = \lim_{x_2 \rightarrow 0} \ln(y_2/x_2) \\ = \beta(a_x^{r\infty} - a_y^{r\infty}) \quad (28)$$

and,

$$\ln[H_{2,1}(T)/f_1^0(T)] = \beta a_x^{r\infty} \quad (29)$$

with the derivative  $a_\alpha^{r\infty} = (\partial a^r / \partial \alpha)_{T,\rho}^\infty$  given by (Appendix E),

$$a_\alpha^{r\infty} = \int_0^\rho \frac{(G_{11}^0 - G_{12}^\infty)_{\sigma(\alpha)}}{\rho \kappa} d\rho, \quad \alpha = x, y \\ \text{and } \sigma(\alpha) = l, v, \quad (30)$$

where  $x_2$  and  $y_2$  denote the solute mole fractions in the liquid and vapor phases, respectively,  $a^r = A^r/N$  is the residual Helmholtz free energy per molecule, and superscript  $\infty$  indicates infinite dilution.

Equations 28 and 30 depict the fundamental link between the solute's distribution factor  $K^\infty(T)$  and the difference of solute-solvent and solvent-solvent interaction strength between the two phases in equilibrium—difference of nonidealities between the phases in vapor-liquid equilibrium. This connection becomes more evident by analyzing the temperature dependence of the integrals in Eq. 28 along the saturation line:

$$\left( \frac{da_x^{r\infty}}{dT} \right)_\sigma = \left( \frac{\partial a_x^{r\infty}}{\partial T} \right)_{\rho^l} + \left( \frac{\partial a_x^{r\infty}}{\partial \rho} \right)_T \left( \frac{d\rho^l}{dT} \right)_\sigma \quad (31)$$

and

$$\left( \frac{da_y^{r\infty}}{dT} \right)_\sigma = \left( \frac{\partial a_y^{r\infty}}{\partial T} \right)_{\rho^v} + \left( \frac{\partial a_y^{r\infty}}{\partial \rho} \right)_T \left( \frac{d\rho^v}{dT} \right)_\sigma, \quad (32)$$

where indices  $l$ ,  $v$ , and  $\sigma$  indicate liquid, vapor, and saturation conditions, respectively. The two partial derivatives of  $a_\alpha^{r\infty}$  involved in Eqs. 31 and 32 can be straightforwardly written as

$$\left( \frac{\partial a_\alpha^{r\infty}}{\partial \rho} \right)_T = \rho^{-2} \left( \frac{\partial P}{\partial \alpha_2} \right)_{T,\rho}^\infty, \quad \alpha = x, y \quad (33)$$

and (Japas and Levelt Sengers, 1989)

$$\left( \frac{\partial a_\alpha^{r\infty}}{\partial T} \right)_\rho = - \left( \frac{\partial s^r}{\partial \alpha_2} \right)_{T,\rho}^\infty, \quad \alpha = x, y, \quad (34)$$

where  $s^r(T,\rho)$  is the residual entropy per molecule.

Interestingly, while the righthand side of Eq. 33 is  $\beta^{-1}$  times the volumetric solute-induced local effect (Chialvo and Cummings, 1994):

$$\rho^{-2} \left( \frac{\partial P}{\partial \alpha_2} \right)_{T,\rho}^\infty = \beta^{-1} [\bar{v}_2^\infty(\text{SR}) - v_1^0]_{T,\rho}^{\sigma(\alpha)}, \\ \alpha = x, y \quad \text{and} \quad \sigma(\alpha) = l, v \quad (35)$$

the righthand side of Eq. 34 is the entropic solute-induced local effect (see Appendix E):

$$\left( \frac{\partial s^r}{\partial \alpha_2} \right)_{T,\rho}^\infty = [\bar{s}_2^{r\infty}(\text{SR}) - s_1^{r0}]_{T,\rho}^{\sigma(\alpha)}, \\ \alpha = x, y \quad \text{and} \quad \sigma(\alpha) = l, v \quad (36)$$

and  $\sigma(\alpha) = l, v$  indicates that the properties are taken at the orthobaric conditions of the corresponding phases in equilibrium. Thus, according to Eqs. 28, 33, and 34,  $T \ln K^\infty(T)$  can be written in the following alternative forms:

$$T \ln K^\infty(T) = -k^{-1} \int_{T_c}^T \left[ \left( \frac{\partial s^r}{\partial x_2} \right)_{T, \rho^l}^\infty - \left( \frac{\partial s^r}{\partial y_2} \right)_{T, \rho^v}^\infty \right] dT \\ + k^{-1} \left[ \int_{\rho_c}^{\rho^l} \left( \frac{\partial P}{\partial x_2} \right)_{T, \rho^l}^\infty \frac{d\rho}{\rho^2} - \int_{\rho_c}^{\rho^v} \left( \frac{\partial P}{\partial y_2} \right)_{T, \rho^v}^\infty \frac{d\rho}{\rho^2} \right] \quad (37)$$

or

$$T \ln K^\infty(T) = -k^{-1} \int_{T_c}^T [(\bar{s}_2^{r\infty}(\text{SR}) - s_1^{r0})_{T, \rho^l} \\ - (\bar{s}_2^{r\infty}(\text{SR}) - s_1^{r0})_{T, \rho^v}] dT + \int_{\rho_c}^{\rho^l} T_\sigma (\bar{v}_2^\infty(\text{SR}) - v_1^0)_{T, \rho^l} d\rho^l \\ - \int_{\rho_c}^{\rho^v} T_\sigma (\bar{v}_2^\infty(\text{SR}) - v_1^0)_{T, \rho^v} d\rho^v, \quad (38)$$

where  $K^\infty(T_c) = 1$ . According to the statistical mechanical interpretation of the integrands of Eq. 38,  $T \ln K^\infty(T)$  is a *measure of the difference of solute-induced local effects between the two phases in vapor-liquid equilibrium*.

Analogously, from Eqs. 29 and 30  $T \ln (H_{2,1}/f_1^0)$  can be expressed as follows:

$$T \ln [H_{2,1}(T)/f_1^0(T)] = T_c \ln [H_{2,1}(T_c)/f_1^0(T_c)] \\ - k^{-1} \left[ \int_{T_c}^T \left( \frac{\partial s^r}{\partial x_2} \right)_{T, \rho^l}^\infty dT - \int_{\rho_c}^{\rho^l} \left( \frac{\partial P}{\partial x_2} \right)_{T, \rho^l}^\infty \frac{d\rho}{\rho^2} \right] \quad (39)$$

or according to Eqs. 35 and 36,

$$T \ln [H_{2,1}(T)/f_1^0(T)] = T_c \ln [H_{2,1}(T_c)/f_1^0(T_c)] \\ - k^{-1} \int_{T_c}^T (\bar{s}_2^{r\infty}(\text{SR}) - s_1^{r0})_{T, \rho^l} dT \\ + \int_{\rho_c}^{\rho^l} T_\sigma (\bar{v}_2^\infty(\text{SR}) - v_1^0)_{T, \rho^l} d\rho^l, \quad (40)$$

which indicates that  $T \ln (H_{2,1}/f_1^0)$  is a *measure of the solute-induced local effects on the properties of the condensed phase along the orthobaric curve*.

Now, with the use of these statistical mechanical expressions we seek an interpretation for the linearity (or lack thereof) in the  $T \ln (H_{2,1}/f_1^0)$  vs.  $(\rho^l - \rho_c)$  and  $T \ln K^\infty(T)$  vs.  $(\rho^l - \rho_c)$  plots, specially for  $\rho^l \gg \rho_c$ , that is, beyond the asymptotic region  $(v - v_c) = \pm |T - T_c|^{\beta-1}$ . Note first that the expressions for  $T \ln K^\infty(T)$  and  $T \ln (H_{2,1}/f_1^0)$  depend on integrands with the following limiting behavior:

$$\left( \frac{\partial P}{\partial x_2} \right)_{T, \rho^l}^\infty \rightarrow \left( \frac{\partial P}{\partial y_2} \right)_{T, \rho^v}^\infty \rightarrow \left( \frac{\partial P}{\partial x_2} \right)_{T_c, \rho_c}^\infty, \\ \rho^l \rightarrow \rho^v \rightarrow \rho_c \quad (41)$$

and

$$\left( \frac{\partial s^r}{\partial x_2} \right)_{T, \rho^l}^\infty \rightarrow \left( \frac{\partial s^r}{\partial y_2} \right)_{T, \rho^v}^\infty \rightarrow \left( \frac{\partial s^r}{\partial x_2} \right)_{T_c, \rho_c}^\infty, \\ \rho^l \rightarrow \rho^v \rightarrow \rho_c \quad (42)$$

so that in the vicinity of the solvent's critical point we can assume (Japas and Levelt Sengers, 1989)

$$\left( \frac{\partial P}{\partial x_2} \right)_{T, \rho^l}^\infty \approx \left( \frac{\partial P}{\partial y_2} \right)_{T, \rho^v}^\infty \approx \left( \frac{\partial P}{\partial x_2} \right)_{T_c, \rho_c}^\infty, \quad (43)$$

and

$$\left( \frac{\partial s^r}{\partial x_2} \right)_{T, \rho^l}^\infty \approx \left( \frac{\partial s^r}{\partial y_2} \right)_{T, \rho^v}^\infty \approx \left( \frac{\partial s^r}{\partial x_2} \right)_{T_c, \rho_c}^\infty. \quad (44)$$

Therefore, by invoking Eqs. 41-44 in Eq. 37 and recalling that  $\rho^{-2} d\rho = -dv$  with  $(v^l - v_c) \approx -(v^v - v_c)$  around  $T = T_c$  we recover the asymptotic expression (1). However, if  $(\partial s^r/\partial \alpha_2)_{T, \rho}^\infty$  and  $\rho^{-2}(\partial P/\partial \alpha_2)_{T, \rho}^\infty$  show some sort of symmetric orthobaric density dependence around the solvent's critical point, we may still have that

$$\overline{\rho^{-2}(\partial P/\partial \alpha_2)_{T, \rho}^\infty} = \frac{1}{2\Delta} \int_{\rho_c - \Delta}^{\rho_c + \Delta} (\partial P/\partial \alpha_2)_{T, \rho}^\infty \frac{d\rho}{\rho^2} \\ \approx \rho_c^{-2} (\partial P/\partial x_2)_{T_c, \rho_c}^\infty \quad (45)$$

and

$$\overline{(\partial s^r/\partial \alpha_2)_{T, \rho}^\infty} = \frac{1}{2\Delta} \int_{\rho_c - \Delta}^{\rho_c + \Delta} (\partial s^r/\partial \alpha_2)_{T, \rho}^\infty d\rho \\ \approx (\partial s^r/\partial x_2)_{T_c, \rho_c}^\infty, \quad (46)$$

where the overbar denotes the mean value of the integrand in the density range  $[\rho_c - \Delta, \rho_c + \Delta]$ . For instance, any orthobaric density dependence of the form

$$\Gamma(\rho) = \chi(\rho - \rho_c)^{2n+1} + \vartheta_c \rho, \quad n = 1, 2, 3, \dots \quad (47)$$

with  $\vartheta_c$  being the critical value of either  $(\partial s^r/\partial \alpha_2)_{T, \rho}^\infty$  or  $\rho^{-2}(\partial P/\partial \alpha_2)_{T, \rho}^\infty$ , and  $\chi$  being an arbitrary constant (not necessarily zero), will result in  $\bar{\vartheta} = \vartheta_c$ , that is, the mean of the function equals the function at the critical point. Consequently, even away from the critical point we may have that

$$\overline{\rho^{-2} \left( \frac{\partial P}{\partial x_2} \right)_{T, \rho^l}^\infty} \approx \overline{\rho^{-2} \left( \frac{\partial P}{\partial y_2} \right)_{T, \rho^v}^\infty} \approx \rho_c^{-2} \left( \frac{\partial P}{\partial x_2} \right)_{T_c, \rho_c}^\infty \quad (48)$$

and

$$\overline{\left( \frac{\partial s^r}{\partial x_2} \right)_{T, \rho^l}^\infty} \approx \overline{\left( \frac{\partial s^r}{\partial y_2} \right)_{T, \rho^v}^\infty} \approx \left( \frac{\partial s^r}{\partial x_2} \right)_{T_c, \rho_c}^\infty. \quad (49)$$

Therefore, by invoking Eqs. 48 and 49 in Eq. 37 we can expect for the plot  $T \ln K^\infty(T)$  vs.  $(\rho^l - \rho_c)$  to exhibit a close agreement with the asymptotic behavior described by Eq. 1, even at conditions away from the solvent's critical point, that is,  $\rho^l \gg \rho_c$ . Our analysis suggests that real systems may obey Eq. 1 at orthobaric densities outside the asymptotic region,  $(v - v_c) = \pm |T - T_c|^\beta$ , provided the volumetric and entropic solute-induced local effects in both phases are respectively similar in magnitude.

Likewise, by recalling Eqs. 43 and 44, Eq. 39 can be written as

$$T \ln [H_{2,1}(T)/f_1^0(T)] \cong T_c \ln [H_{2,1}(T_c)/f_1^0(T_c)] - k^{-1} \left( \frac{\partial s^r}{\partial x_2} \right)_{T_c, \rho_c}^\infty (T - T_c) + \rho_c^{-2} \left( \frac{\partial P}{\partial x_2} \right)_{T_c, \rho_c}^\infty (\rho^l - \rho_c), \quad (50)$$

which will be valid only in the narrow density range where the conditions 43 and 44 are satisfied. If this range is within the asymptotic region  $(v - v_c) = \pm |T - T_c|^\beta$ , then the second term of Eq. 50 prevails over the first and we recover the asymptotic expression 2. However, at orthobaric conditions away from the solvent's critical point, that is,  $\rho^l \gg \rho_c$ , Eqs. 43 and 44 are not necessarily good approximations, and consequently Eq. 50 may not be obeyed. Furthermore, because  $T \ln (H_{2,1}/f_1^0)$  depends not on the difference of solute-induced local effects between the phases in equilibrium, but entirely on the solute-induced local effects in the condensed phase, there is neither a cancellation of entropic nor an averaging of volumetric solute-induced local effect as in the case of  $T \ln K^\infty$  vs.  $(\rho^l - \rho_c)$ . Therefore, even though  $T \ln (k_H/f_1^s)$  vs.  $(\rho^l - \rho_c)$  may show a linear dependence due to some compensation between the entropic and volumetric solute-induced local effects, the regressed slopes are not expected to agree with the asymptotic values predicted by Eq. 2 (see next section). In fact, the experimental evidence indicates that the regressed slopes are typically greater than the predicted asymptotic values (Harvey et al., 1990).

## Integral Equation Calculations

In this section we illustrate the use of our statistical mechanical expressions, Eqs. 38 and 40, by considering the thermodynamic behavior of an infinitely dilute solution of Ne along the coexistence curve of the solvent, Xe, and extract some important information about the orthobaric density dependence of  $(\partial P/\partial x_2)_{T, \rho}^\infty$  in the vicinity of and away from the solvent's critical point. Although our expressions have been derived for molecules of arbitrary symmetry, we illustrate their application here to model a simple fluid mixture because in this case we can obtain results analytically, thereby ensuring consistency between thermodynamics and structural critical points (as described below). The system is modeled as a two-component hard core Yukawa fluid (HCYF), for which the intermolecular potential  $\phi_{ij}(r)$  is

$$\phi_{ij}(r) = \begin{cases} \infty & \text{if } r < \sigma_{ij} \\ \omega_{ij}(r) & \text{if } r > \sigma_{ij} \end{cases} \quad (51)$$

where  $\sigma_{ij}$  is hard-sphere diameter for the  $ij$ -interaction, and

$$\omega_{ij}(r) = -\frac{\epsilon_{ij}\sigma_{ij}}{r} \exp[-\alpha_{ij}(r - \sigma_{ij})]. \quad (52)$$

Although real fluids do not follow this behavior, they can be qualitatively described by this simple model. In particular, the parameters  $\sigma_{ij}$  and  $\epsilon_{ij}$  can be identified with the corresponding size and energy Lennard-Jones (LJ) parameters, and the unlike interactions follow the Lorentz-Berthelot combining rules. By using a suitable choice for these parameters one can recover the phase diagram of the LJ system by a simple HCYF (Rudisill and Cummings, 1989). Following Henderson et al. (1978) we choose  $\alpha_{ij}\sigma_{ij} = 1.8$  for all  $ij$ -pairs.

The rationale behind this choice is twofold: despite its simplicity this model shows a vapor-liquid phase transition and, within the mean spherical approximation (MSA) closure, this model offers an analytical solution to the OZ equation (Ornstein and Zernike, 1914). The MSA is known to be quite reliable in predicting thermodynamic properties of Yukawa fluids (Henderson et al., 1978; Arrieta et al., 1991). In particular, the phase envelope for the LJ fluid can be described by the MSA for the corresponding HCYF (Kalyuzhnyi and Cummings, 1995). According to the analysis of the previous sections, the integral equation calculations must be carried out using a theory that is able to provide a consistent description of both the structure and the thermodynamics in the vicinity of the solvent's critical point. By consistency we mean that the critical point of the liquid-vapor coexisting curve, obtained from the condition of equal chemical potentials and pressure in both phases, should coincide with the critical point of the spinodal line defined by the condition  $\beta(\partial P/\partial \rho)_T = 1 - \rho \hat{c}(0) = 0$ . This consistency is absent from previous integral equation studies of supercritical fluid mixtures.

To achieve this consistency we have chosen to use the generalized MSA (GMSA), which for the present two-component system reads

$$\begin{cases} c_{ij}(r) = -\beta \omega_{ij}(r) + r^{-1} \sum_{n=1}^N A_{ij}^{(n)} \exp(-z_{ij}^{(n)} r) & \text{if } r > \sigma_{ij} \\ h_{ij}(r) = -1 & \text{if } r < \sigma_{ij}, \end{cases} \quad (53)$$

where the Yukawa terms are introduced to correct the regular MSA for thermodynamic self-consistency. If the contact values of the radial distribution functions  $g_{ij}(r)$  and the isothermal compressibility are known, then the method of Høye and Stell (1977) can be used to determine the Yukawa coefficients in Eq. 53, which will enforce thermodynamic consistency.

In the present study we consider an infinitely dilute solution, which means that the correction is only done for the solvent-solvent correlation, and, for simplicity, we truncate the summation of Yukawa terms at  $N = 2$ , with  $\sigma_{11}z_{11}^{(1)} = 9$  and  $\sigma_{11}z_{11}^{(2)} = 16$ . The parameters  $A_{ij}^{(n)}$  ( $n = 1, 2$ ) follow from the solution of the constraints imposed on the contact values of the pair correlation functions and the isothermal compressibility, that is, the condition of thermodynamic consistency. One way to do this is by means of an equation of state derived via the MSA energy route (Høye and Stell, 1977), which yields quite accurate thermodynamics. However, again

for the sake of simplicity, here we have used the thermodynamic results from a perturbation theory presented elsewhere (Henderson et al., 1978). In order to satisfy the ideal solution condition, that is, for which solute–solute, solute–solvent, and solvent–solvent potential parameters and consequently the corresponding chemical potential are equal, in our previous publication (Chialvo et al., 1995) we assumed the convenient though arbitrary condition for the Yukawa parameters,

$$\sigma_{ij}z_{ij}^{(n)} = \sigma_{11}z_{11}^{(n)}$$

$$A_{ij}^{(n)} = \frac{\epsilon_{ij}\sigma_{ij}}{\epsilon_{11}\sigma_{11}}A_{11}^{(n)}. \quad (54)$$

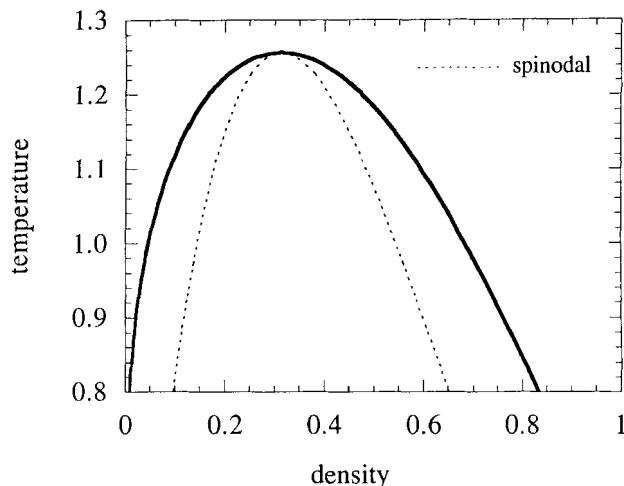
However, for large solute–solvent molecular asymmetry as is usually found in gas solvation, the GMSA closure for solute–solvent correlations does not guarantee accurate results. Therefore, in the present case we assume the regular MSA closure for the solute–solvent correlations, since it is known to yield reasonable accurate thermodynamics (Ebner et al., 1976; Henderson et al., 1978; Arrieta et al., 1991). Our choice is supported by the fact that here we are studying systems with large solute–solvent asymmetries.

In order to calculate the chemical potential along the liquid branch of the phase envelope we need to perform an integration, Eq. 3, across the two-phase region. Since our GMSA does not give real solutions in this region, we perform the integration by means of the method proposed by Ebner et al. (1976). In these studies a similar integration is performed by interpolating the values of the direct correlation functions corresponding to the orthobaric conditions. Since the solution of the GMSA is available in the entire range of temperature and density, except for a rather small region between the spinodal lines, this interpolation is sufficiently accurate for our purposes.

The solution of the GMSA with the Yukawa coefficients as defined in Eq. 54 is obtained by the Baxter factorization method (Baxter, 1970). The general scheme of the solution is similar to that presented elsewhere (Høye et al., 1976; Høye and Blum, 1977). In the present case the analytical solution results in a set of nonlinear algebraical equations for the Yukawa parameters  $A_{11}^{(n)}$  together with the parameters related to the Baxter factorization functions. We solve this set of equations by an iterative approach as described by Kalyuzhnyi and Holovko (1993). In summary, this formalism gives a self-consistent description of both thermodynamics and microstructure for the model in the entire region of state conditions of interest.

In Figure 1 we show the vapor–liquid coexistence curve for the pure solvent, described as a hard-core Yukawa fluid. Note that the binodal and spinodal curves meet at the critical conditions, that is,  $kT_c/\epsilon_{11} = 1.2561$  and  $\rho_c\sigma_{11}^3 = 0.3129$  where  $\sigma_{11}$  and  $\epsilon_{11}$  are the solvent's size and energy parameters. In what follows we study an infinitely dilute solute 2 in a solvent 1 characterized by a ratio of size parameters  $(\sigma_{22}/\sigma_{11}) = 0.697$  and a ratio of energy parameters  $(\epsilon_{22}/\epsilon_{11}) = 0.142$ . This asymmetry corresponds to the system Ne(2)–Xe(1) if described as L-J spheres (Chialvo and Cummings, 1994).

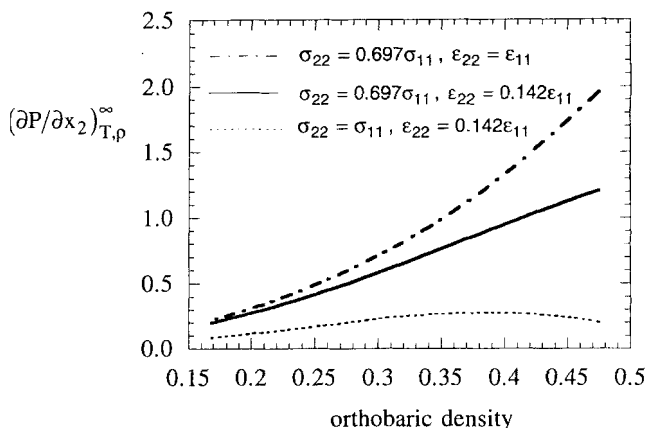
The orthobaric density dependence of  $(\partial P/\partial x_2)_{T,\rho}^\infty$  for this infinitely dilute mixture is shown in Figure 2. In order to un-



**Figure 1.** Phase envelope of a hard-sphere Yukawa fluid with  $\alpha_{11}\sigma_{11} = 1.8$  as predicted by the integral equation calculations.

Temperature and density are reduced as  $(kT/\epsilon_{11})$  and  $(\rho\sigma_{11}^3)$ , respectively.

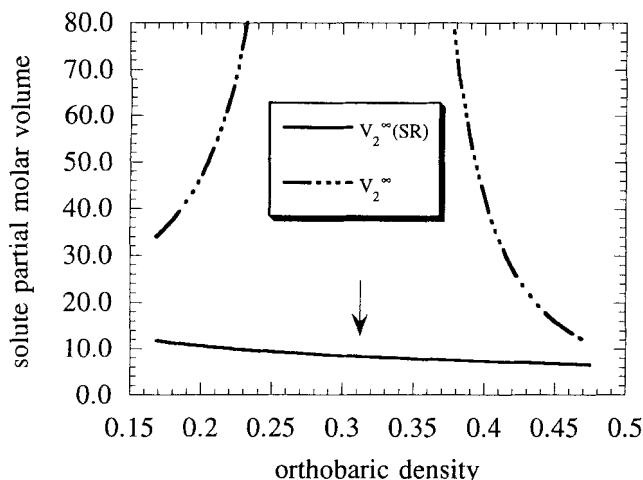
derstand how the two asymmetries contribute to the nonideality, we compare the original system  $(\sigma_{22}/\sigma_{11}) = 0.697$  and  $(\epsilon_{22}/\epsilon_{11}) = 0.142$  with two special cases; one in which  $\sigma_{22} = \sigma_{11}$  and  $\epsilon_{22} = 0.142\epsilon_{11}$ , and the other in which  $\sigma_{22} = 0.697\sigma_{11}$  and  $\epsilon_{22} = \epsilon_{11}$ . According to the results of Figure 2 the change on the solute's size and energy parameters,  $\sigma_{22}$ , and  $\epsilon_{22}$ , shows opposite effects on the orthobaric density dependence of  $(\partial P/\partial x_2)_{T,\rho}^\infty$ . Compensation between nonidealities originated from energy and size asymmetries has been already observed for model systems (Shukla et al., 1988; Chialvo and Debenedetti, 1991) and, in this case, it may explain the observed quasilinearity on the orthobaric density dependence of  $(\partial P/\partial x_2)_{T,\rho}^\infty$ . For the system of interest,  $(\sigma_{22}/\sigma_{11}) = 0.697$  and  $(\epsilon_{22}/\epsilon_{11}) = 0.142$ , Krichevskii's parameter  $(\partial P/\partial x_2)_{T_c,\rho_c}^\infty = 0.6246\epsilon_{11}/\sigma_{11}^3$ .



**Figure 2.** Comparison of the orthobaric density dependence of  $(\partial P/\partial x_2)_{T,\rho}^\infty$  for three repulsive infinitely dilute hard-sphere Yukawa fluid mixtures with  $\alpha_{11}\sigma_{11} = 1.8$ .

The coefficients indicate the relative sizes of  $\sigma_{22}$  and  $\epsilon_{22}$  with respect to the solvent's parameters. Pressure and density reduced as  $(P\sigma_{11}^3/\epsilon_{11})$  and  $(\rho\sigma_{11}^3)$ , respectively.

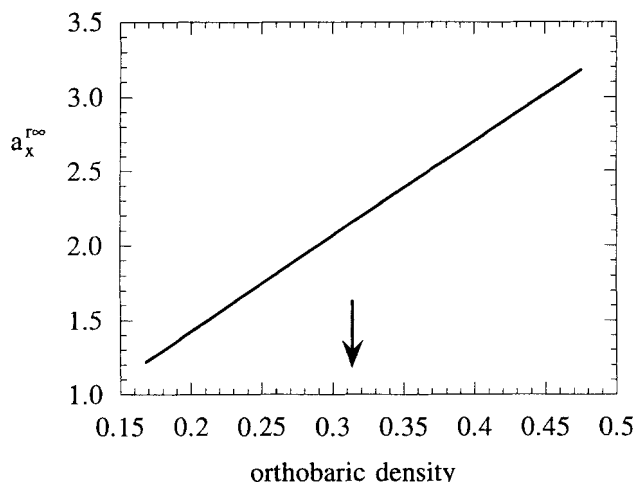




**Figure 3.** Orthobaric density dependence of the infinite dilute solute partial molar volume  $\bar{v}_2^{\infty}$  for the infinitely dilute hard-sphere Yukawa system with  $\alpha_{11}\sigma_{11}=1.8$ ,  $(\sigma_{22}/\sigma_{11})=0.697$ , and  $(\epsilon_{22}/\epsilon_{11})=0.142$ .

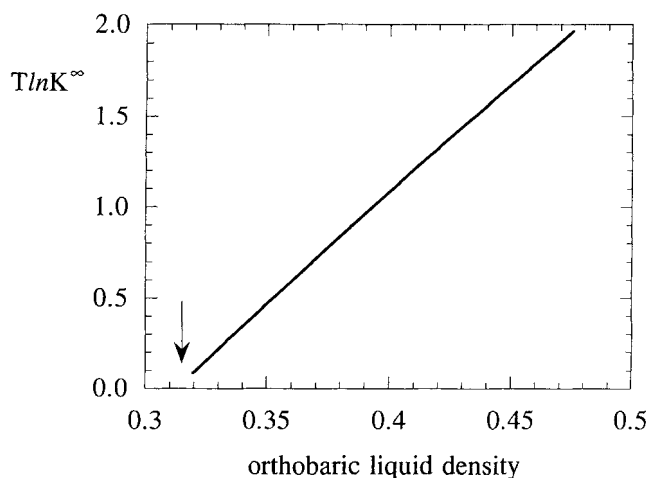
Comparison between the total (SR+LR) and the short-range (SR) contributions. Arrow indicates the location of the solvent's critical density. Molar volume and density reduced as  $(\bar{v}_2^{\infty}/\sigma_{11}^3)$  and  $(\rho\sigma_{11}^3)$ , respectively.

In Figure 3 we show the comparison between the behavior of the infinitely dilute solute partial molar volume,  $\bar{v}_2^{\infty}$ , and its corresponding short-range (SR) contribution,  $\bar{v}_2^{\infty}(\text{SR})$ , along the coexistence curve of pure solvent as predicted by the integral equation calculations. These properties are positive, the solute-solvent asymmetry gives rise to a volatile solute characterized macroscopically by  $(\partial P/\partial x_2)_{T,\rho}^{\infty} > 0$  (Figure 2), and microscopically by a relative depletion of the local density of solvent around the solute with respect to that around any



**Figure 4.** Orthobaric density dependence of  $a_x^{\infty} = (\partial a^{\infty}/\partial x_2)_{T,\rho}^{\infty}$  (Eq. 30) for the infinitely dilute hard-sphere Yukawa system with  $\alpha_{11}\sigma_{11}=1.8$ ,  $(\sigma_{22}/\sigma_{11})=0.697$ , and  $(\epsilon_{22}/\epsilon_{11})=0.142$ .

Arrow indicates the location of the solvent's critical density. Composition derivative of the residual molar free energy and density reduced as  $(a_x^{\infty}/\epsilon_{11})$  and  $(\rho\sigma_{11}^3)$ , respectively.

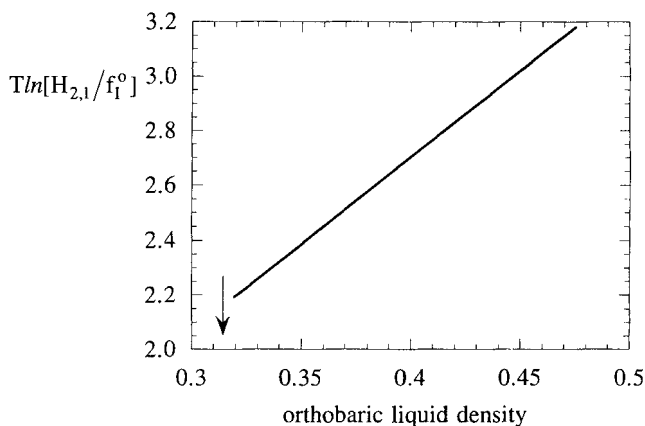


**Figure 5.** Orthobaric density dependence of  $T \ln(H_{2,1}/f_1^0)$  for the infinitely dilute hard-sphere Yukawa system with  $\alpha_{11}\sigma_{11}=1.8$ ,  $(\sigma_{22}/\sigma_{11})=0.697$ , and  $(\epsilon_{22}/\epsilon_{11})=0.142$ .

Arrow indicates the location of the solvent's critical density. Temperature and density are reduced as  $(kT/\epsilon_{11})$  and  $(\rho\sigma_{11}^3)$ , respectively.

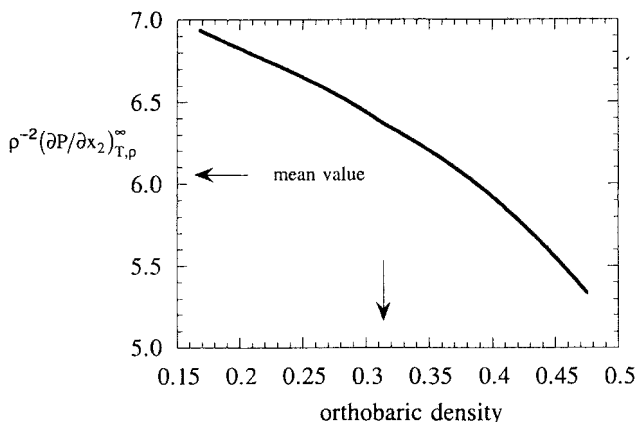
solvent molecule. Note that while  $\bar{v}_2^{\infty}$  shows the typical compressibility-driven divergency at the solvent's critical point,  $\bar{v}_2^{\infty}(\text{SR})$  behaves smoothly along the coexistence curve.

In Figure 4 we display the predicted orthobaric density dependence of  $a_x^{\infty} = \int_0^1 [(G_{11}^0 - G_{12}^{\infty})/\rho\kappa] d\rho$ , Eq. 30. Note that this property shows an almost linear behavior along the entire density domain, a prelude of similar behavior for the related solvation quantities. For example, in Figures 5 and 6 we present the corresponding behavior for Henry's constant and solute distribution factor along the liquid branch of the coexistence curve. The slopes of the  $T \ln K^{\infty}$  vs.  $\rho^l$  and  $T \ln(H_{2,1}/f_1^0)$  vs.  $\rho^l$  representations are  $12.092\epsilon_{11}\sigma_{11}^3/k$  and  $6.3521\epsilon_{11}\sigma_{11}^3/k$ , respectively, with a correlation coefficient



**Figure 6.** Orthobaric density dependence of  $T \ln K^{\infty}$  for the infinitely dilute hard-sphere Yukawa system with  $\alpha_{11}\sigma_{11}=1.8$ ,  $(\sigma_{22}/\sigma_{11})=0.697$ , and  $(\epsilon_{22}/\epsilon_{11})=0.142$ .

Arrow indicates the location of the solvent's critical density. Temperature and density are reduced as  $(kT/\epsilon_{11})$  and  $(\rho\sigma_{11}^3)$ , respectively.

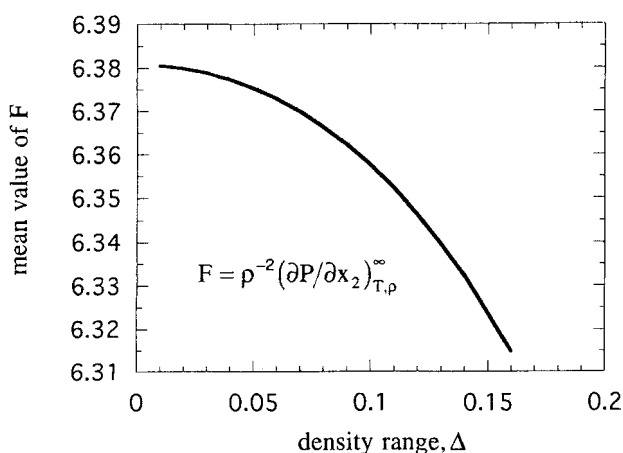


**Figure 7. Orthobaric density dependence of  $\rho^{-2}(\partial P/\partial x_2)_{T,\rho}^\infty$  for the infinitely dilute hard-sphere Yukawa system with  $\alpha_{11}\sigma_{11}=1.8$ ,  $(\sigma_{22}/\sigma_{11})=0.697$ , and  $(\epsilon_{22}/\epsilon_{11})=0.142$ .**

Vertical and horizontal arrows indicate the location of the solvent's critical density and the mean value of the function, respectively. Function and density are reduced as  $[\rho^{-2}(\partial P/\partial x_2)_{T,\rho}^\infty/\sigma_{11}^3]$  and  $(\rho\sigma_{11}^3)$ , respectively.

greater than 0.9998. If we assume the asymptotic expressions 1 and 2, then these slopes predict  $0.5919\epsilon_{11}/\sigma_{11}^3$  and  $0.6219\epsilon_{11}/\sigma_{11}^3$  for Krichevskii's parameters, respectively, in comparison to the actual value of  $0.6246\epsilon_{11}/\sigma_{11}^3$ , that is, within a 5% range.

In Figure 7 we show that the integrand of Eq. 30,  $\rho^{-2}(\partial P/\partial x_2)_{T,\rho}^\infty$ , evidently does not present the type of density dependence required to satisfy condition 45, yet its mean value in the density range  $\rho\sigma_{11}^3 = \rho_c\sigma_{11}^3 \pm 0.1529$  [ $(\rho/\rho_c)=1 \pm 0.488$ ] is  $6.315\epsilon_{11}\sigma_{11}^3$ , which compares quite well with either  $6.046\epsilon_{11}\sigma_{11}^3$  and  $6.352\epsilon_{11}\sigma_{11}^3$  from the regressed slopes of the  $T \ln K^\infty$  vs.  $\rho^l$  and  $T \ln(H_{2,1}/f_1^0)$  vs.  $\rho^l$  plots, respectively, or  $6.3795\epsilon_{11}\sigma_{11}^3$  from the actual Krichevskii's parameter. Note,



**Figure 8. Dependence of the mean value of  $\rho^{-2}(\partial P/\partial x_2)_{T,\rho}^\infty$  with the density range  $\Delta$  for the infinitely dilute hard-sphere Yukawa system with  $\alpha_{11}\sigma_{11}=1.8$ ,  $(\sigma_{22}/\sigma_{11})=0.697$ , and  $(\epsilon_{22}/\epsilon_{11})=0.142$ .**

Function and density are reduced as  $[\rho^{-2}(\partial P/\partial x_2)_{T,\rho}^\infty/\sigma_{11}^3]$  and  $(\rho\sigma_{11}^3)$ , respectively.

however, that the mean value of  $\rho^{-2}(\partial P/\partial x_2)_{T,\rho}^\infty$  decreases slightly,  $\sim 1\%$  in the range  $\rho\sigma_{11}^3 = \rho_c\sigma_{11}^3 \pm 0.1529$ , as the density range in the integrand of Eq. 45 increases (Figure 8).

## Discussion and Conclusions

This article encompasses the generalization of our previous solvation formalism to fluid mixtures composed of anisotropic molecules, and it is aimed at gaining some insight into the molecular basis of gas solubility at sub- and near-critical conditions. The current analysis provides a rigorous statistical mechanical interpretation of the splitting between solvation (finite) and compressibility-driven (diverging) contributions to the thermodynamic properties of near critical systems. Specifically, it connects the changes of the solvent's local environment around an infinitely dilute solute (solute-induced local effects) with the solvation (finite) contribution to the infinite dilution solute partial molar properties.

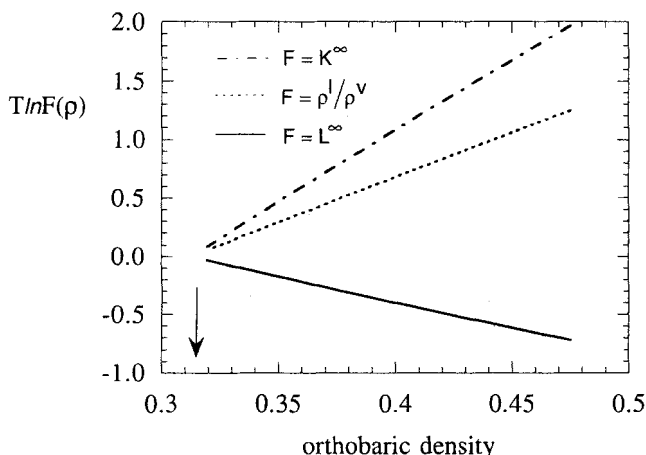
The statistical mechanical interpretation of  $(\partial P/\partial x_2)_{T,\rho}^\infty$  offers a convenient classification for dilute mixtures into two types of systems according to the sign of that derivative. In fact as noted by Chialvo and Cummings (Cummings et al., 1994; Chialvo and Cummings, 1995), the classification hinges upon the behavior of the quantity  $N_{ex}^\infty$ , Eq. 16, the excess number of solvent molecules around the infinitely dilute solute over that around a solvent molecule (i.e., around the solute when this is identical to the solvent molecule),

$$\begin{aligned} N_{ex}^\infty &= \rho(G_{11}^0 - G_{12}^\infty) \\ &= 1 - \rho\bar{v}_2^\infty. \end{aligned} \quad (55)$$

Because  $\kappa$  is positive definite, the sign of  $N_{ex}^\infty$ —intimately connected to the sign of the infinitely dilute solute partial molar volume—is given by  $(\partial P/\partial x_2)_{T,\rho}^\infty$ . Therefore, for  $(\partial P/\partial x_2)_{T,\rho}^\infty < 0$ , we have a *nonvolatile* solute and  $N_{ex}^\infty > 0$ , that is, the solute's solvation shell shows an excess of solvent in comparison to any solvent's solvation shell. Otherwise, for  $(\partial P/\partial x_2)_{T,\rho}^\infty > 0$ , we have a *volatile* solute and  $N_{ex}^\infty < 0$ , that is, the solute's solvation shell shows a depletion of solvent in comparison to any solvent's solvation shell. Note that  $(\partial P/\partial x_2)_{T,\rho}^\infty$  need not be at the solvent's critical conditions to define the type of solute involved.

Our integral equation calculations for the special case of an infinitely dilute spherically symmetric volatile solute in a near-critical solution of hard core Yukawa fluid support the linearity depicted by the asymptotic expressions 1 and 2. These molecular-based calculations in conjunction with the proposed statistical mechanical analysis provide some clues to the mechanism behind the unexpected agreement between the asymptotic expressions and the actual behavior beyond the asymptotic region. For example, the fact that  $\rho^{-2}(\partial P/\partial x_2)_{T,\rho}^\infty$  shows a nonlinear dependence with the orthobaric density (Figure 7), with a mean value close to the regressed slope of the quasi-linear  $a_x^\infty$  vs.  $\rho^l$  representation (Figure 4), that is,

$$\overline{\rho^{-2}(\partial P/\partial x_2)_{T,\rho}^\infty} \approx \frac{\Delta a_x^\infty}{\Delta \rho_\sigma} = \frac{\Delta}{\Delta \rho_\sigma} \int_0^{\rho_\sigma} \rho^{-2}(\partial P/\partial x_2)_{T,\rho}^\infty d\rho \quad (56)$$



**Figure 9.** Orthobaric density dependence of  $T \ln F$ ,  $F = K^\infty$ ,  $\rho^l/\rho^v$ ,  $L^\infty$ , for the infinite dilute hard-sphere Yukawa system with  $\alpha_{11}\sigma_{11}=1.8$ ,  $(\sigma_{22}/\sigma_{11})=0.697$ , and  $(\epsilon_{22}/\epsilon_{11})=0.142$ .

Arrow indicates the location of the solvent's critical density. Temperature and density are reduced as  $(kT/\epsilon_{11})$  and  $(\rho\sigma_{11}^3)$ , respectively.

suggests, according to Eq. 39, some sort of compensation between the volumetric and entropic solute-induced local effects in the condensed phase.

Regarding the behavior of Ostwald's coefficient  $L^\infty$ , Figure 9, the fact that the two contributions to  $T \ln L^\infty$ ,  $T \ln K^\infty$ , and  $T \ln(\rho^l/\rho^v)_\sigma$ , show opposite density dependence gives support to Wilhelm's suggestion that  $T \ln L^\infty$  vs.  $(\rho^l - \rho_c)$ , may show a better linear relationship than  $T \ln K^\infty$  vs.  $(\rho^l - \rho_c)$  in a wider range of orthobaric densities (Wilhelm, 1992). For our model system, both  $T \ln K^\infty$  and  $T \ln(\rho^l/\rho^v)_\sigma$  present linear dependence with  $\rho^l$  with correlation factors larger than 0.9997. Therefore, it is not likely under this circumstance to observe any improvement in the linear regression of  $T \ln L^\infty$  vs.  $\rho^l$  over the other solvation quantities.

It is worth mentioning that  $T \ln L^\infty$  vs.  $(\rho^l - \rho_c)$  may also show a similar asymptotic behavior as described by Eqs. 1 and 2. For example, by starting from the definition,

$$\begin{aligned} T \ln L^\infty &= T \ln(\rho^l/\rho^v) - T \ln K^\infty \\ &= T \ln[(\rho_c + \Delta)/(\rho_c - \Delta)] - T \ln K^\infty, \\ \Delta &= \rho^l - \rho_c = \rho_c - \rho^v \end{aligned} \quad (57)$$

and after replacing  $T \ln K^\infty$  in the righthand side of Eq. 57 by Eq. 1 we obtain

$$T \ln L^\infty = \left( \frac{2}{\rho_c} \right) \left[ T_c - \left( \frac{1}{k\rho_c} \right) \left( \frac{\partial P}{\partial x_2} \right)_{T_c, \rho_c} \right] (\rho^l - \rho_c), \quad (58)$$

where we have invoked the fact that  $T \ln[(\rho_c + \Delta)/(\rho_c - \Delta)] \approx 2T_c(\Delta/\rho_c)$  around the critical point. If we assume Eq. 58 to be also valid beyond the asymptotic region, based on the observed linear behavior of  $T \ln K^\infty$  and  $T \ln(\rho^l/\rho^v)_\sigma$  vs.  $\rho^l$  for our model system, then the regressed Krichevskii's parameter is  $(\partial P/\partial x_2)_{T_c, \rho_c}^\infty = 0.6101\epsilon_{11}/\sigma_{11}^3$ , that is, between those obtained by regression of  $T \ln K^\infty$  and  $T \ln(H_{2,1}/f_1^0)$ .

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## Appendix A: Derivation of the Multicomponent Analogs of Eqs. 3 and 4

The residual chemical potential of a component  $i$ ,  $\mu_i^r(T, P, x_i)$ , in a multicomponent system is given by (Modell and Reid, 1983)

$$\begin{aligned}\mu_i^r(T, P, x_i) &= \mu_i(T, P, x_i) - \mu_i^{IG}(T, P, x_i) \\ &= \beta^{-1} \ln \phi_i \\ &= - \int_{\infty}^{\rho(P)} \left[ \left( \frac{\partial P}{\partial N_i} \right)_{T, V, N_{j \neq i}} - \frac{kT}{V} \right] dV \\ &\quad - kT \ln \left( \frac{P}{\rho kT} \right), \quad i = 1, 2, \dots, c, \quad (\text{A1})\end{aligned}$$

where  $\phi_i$  is the fugacity coefficient of component  $i$ ,  $k$  is the Boltzmann constant,  $T$  is the absolute temperature,  $V$  is the total volume,  $P$  is the pressure,  $\rho$  is the total number density,  $c$  is the number of components,  $N_i$  is the number of molecules of component  $i$ , and  $x_i$  its corresponding mole fraction. The superscripts  $r$  and  $IG$  denote a residual quantity at the indicated state conditions and an ideal gas property, respectively. By invoking the chain rule for the derivatives (Chialvo and Cummings, 1995) we have

$$N \left( \frac{\partial P}{\partial N_i} \right)_{T, V, N_{j \neq i}} = \frac{\rho \bar{v}_i}{\kappa}, \quad i = 1, 2, \dots, c \quad (\text{A2})$$

so that, after some rearrangements, the integrand of A1 becomes

$$\begin{aligned}\mu_i^r(T, P, x_i) &= \int_0^{\rho(P)} \left[ \frac{\bar{v}_i}{\kappa} - kT \right] \frac{d\rho}{\rho} \\ &\quad - kT \ln(P/\rho kT), \quad i = 1, 2, \dots, c, \quad (\text{A3})\end{aligned}$$

where  $\bar{v}_i$  is the partial molar volume of component  $i$  and  $\kappa$  is the system's isothermal compressibility. Alternatively, we can write (Chialvo and Cummings, 1995),

$$\left( \frac{\partial P}{\partial x_i} \right)_{T, \rho, x_{j \neq i}} = \frac{\rho(\bar{v}_i - \bar{v}_1)}{\kappa}, \quad i \geq 2, \quad (\text{A4})$$

where the solvent is always component 1, and in the partial differentiation the solvent mole fraction,  $x_1$ , is regarded as a dependent variable (i.e.,  $x_1 = 1 - \sum_{i=2}^c x_i$ ). Finally, from Eqs. A3 and A4 the residual chemical potential for solute  $i$  becomes,

$$\begin{aligned}\mu_i^r(T, P, x_i) &= \mu_i(T, P, x_i) - \mu_i^{IG}(T, P, x_i) \\ &= \int_0^{\rho(P)} \left[ \rho^{-1} \left( \frac{\partial P}{\partial x_i} \right)_{T, \rho, x_{j \neq i}} + \frac{\bar{v}_1}{\kappa} - kT \right] \frac{d\rho}{\rho} - kT \ln(P/\rho kT), \\ &\quad i \geq 2 \quad (\text{A5})\end{aligned}$$

so that (Van Ness and Abbott, 1982)

$$\begin{aligned}\mu_i^r(T, \rho, x_i) &= \mu_i(T, \rho, x_i) - \mu_i^{IG}(T, \rho, x_i) \\ &= \int_0^{\rho(P)} \left[ \rho^{-1} \left( \frac{\partial P}{\partial x_i} \right)_{T, \rho, x_{j \neq i}} + \frac{\bar{v}_1}{\kappa} - kT \right] \frac{d\rho}{\rho}, \quad i \geq 2. \quad (\text{A6})\end{aligned}$$

Note that Eq. A5 differs from Eq. A6 in view of the difference in the thermodynamic variables held constant in the definition of the residual properties. Moreover, the difference of chemical potentials between any solute  $i$  and the solvent reads

$$\begin{aligned}\mu_i^r(T, P, x_i) - \mu_1^r(T, P, x_i) &= \mu_i^r(T, \rho, x_i) - \mu_1^r(T, \rho, x_i) \\ &= \int_0^{\rho(P)} \left( \frac{\partial P}{\partial x_i} \right)_{T, \rho, x_{j \neq i}} \frac{d\rho}{\rho^2}, \quad i \geq 2, \quad (\text{A7})\end{aligned}$$

or alternatively, in terms of fugacity coefficients,

$$\begin{aligned}\ln[\phi_i(T, P, x_i)/\phi_1(T, P, x_i)] \\ &= \beta \int_0^{\rho(P)} \left( \frac{\partial P}{\partial x_i} \right)_{T, \rho, x_{j \neq i}} \frac{d\rho}{\rho^2}, \quad i \geq 2, \quad (\text{A8})\end{aligned}$$

where  $\beta = 1/kT$ .

## Appendix B: $(\partial P/\partial x_i)_{T, \rho, x_{j \neq i}}$ for Multicomponent Systems

Following the matrix expressions of the Kirkwood-Buff formalism given by O'Connell (1971), we can write

$$\frac{\rho \bar{v}_i}{\kappa} = \rho kT[(I + \rho XG)^{-1t} \mathbf{1}]_i, \quad (\text{B1})$$

where  $I$  is the identity matrix,  $\mathbf{1}$  is a unit column vector, with the superscripts  $-1$  and  $t$  indicating an inverse and a transpose matrix, respectively. Moreover, the composition matrix  $X$  and the TCFI matrix  $G$  are defined as

$$X \equiv \{x_i \delta_{ij}\} \quad (\text{B2})$$

$$G \equiv \{G_{ij}\}, \quad G_{ij} = G_{ji} = \int [g_{ij}(r) - 1] dr. \quad (\text{B3})$$

Now, by substituting Eq. B1 into Eq. A4, we have

$$\left( \frac{\partial P}{\partial x_i} \right)_{T, \rho, x_{j \neq i}} = \rho kT \{ [(I + \rho XG)^{-1t} \mathbf{1}]_i - [(I + \rho XG)^{-1t} \mathbf{1}]_i \}, \quad i \neq 1. \quad (\text{B4})$$

Consequently, for an infinitely dilute solution, that is, with  $x_i \rightarrow 0$  for all  $i \neq 1$ , we have

$$\left( \frac{\partial P}{\partial x_i} \right)_{T, \rho, x_{j \neq i}}^{\infty} = \frac{kT \rho^2 (G_{11}^0 - G_{1i}^{\infty})}{1 + \rho G_{11}^0}, \quad i \neq 1, \quad (\text{B5})$$

which is the multicomponent counterpart of Eq. 7.

## Appendix C: Relationship between Molecular and Atomic Ornstein–Zernike Equations

The molecular Ornstein–Zernike (MOZ) equation connects the molecular total pair correlation function  $h_{ij}(\mathbf{r}_{ij}, \omega_i, \omega_j) = g_{ij}(\mathbf{r}_{ij}, \omega_i, \omega_j) - 1$  to the molecular direct correlation function  $c_{ij}(\mathbf{r}_{ij}, \omega_i, \omega_j)$  where  $\mathbf{r}_{ij}$  is the vector joining the centers of mass of the molecular species  $i$  and species  $j$ , and  $\omega_k$  is a vector containing the specification of the orientation of molecule  $k$ . For linear molecules,  $\omega_k$  will contain the two angles  $(\theta, \phi)$ , while for nonlinear molecules  $\omega_k$  will contain three Euler angles (Gray and Gubbins, 1985). The MOZ equation is given by

$$h_{ij}(\mathbf{r}_{ij}, \omega_i, \omega_j) = c_{ij}(\mathbf{r}_{ij}, \omega_i, \omega_j) + \frac{1}{\Omega} \sum_{k=1}^c \rho_k \int \int c_{ik}(\mathbf{r}_{ik}, \omega_i, \omega_k) h_{kj}(\mathbf{r}_{kj}, \omega_k, \omega_j) d\mathbf{r}_k d\omega_k, \quad (\text{C1})$$

where  $\Omega = \int d\omega$  and so is  $4\pi$  for linear molecules and  $8\pi^2$  for nonlinear molecules. Kirkwood–Buff theory is based on the use of the much simpler atomic Ornstein–Zernike (AOZ) equation given by

$$h_{ij}(\mathbf{r}_{ij}) = c_{ij}(\mathbf{r}_{ij}) + \sum_{k=1}^c \rho_k \int c_{ik}(\mathbf{r}_{ik}) h_{kj}(\mathbf{r}_{kj}) d\mathbf{r}_k. \quad (\text{C2})$$

If one defines the orientationally averaged pair distribution function  $g_{ij}(r) = \langle g_{ij}(\mathbf{r}_{ij}, \omega_i, \omega_j) \rangle_{\omega_i, \omega_j}$  and total correlation function

$$h_{ij}(r) = \langle h_{ij}(\mathbf{r}_{ij}, \omega_i, \omega_j) \rangle_{\omega_i, \omega_j} = g_{ij}(r) - 1, \quad (\text{C3})$$

Eq. C2 serves to define a spherically symmetric direct correlation function  $c_{ij}(r)$ . It should be noted that  $c_{ij}(r)$  is *not* the orientationally averaged direct correlation function, that is,  $c_{ij}(r) \neq \langle c_{ij}(\mathbf{r}_{ij}, \omega_i, \omega_j) \rangle_{\omega_i, \omega_j}$  (Gray and Gubbins, 1985). Thus, one cannot invoke known asymptotic results for  $c_{ij}(\mathbf{r}_{ij}, \omega_i, \omega_j)$  and use these to derive asymptotic properties for  $c_{ij}(r)$ .

Thus the quantity  $c_{ij}(r)$  has largely unknown mathematical properties except for its volume integral. If one takes the orientational average of Eq. C1 over  $\omega_i$  and  $\omega_j$ , and additionally integrates over  $\mathbf{r}_{ij}$ , one obtains (Gray and Gubbins, 1985)

$$\bar{H}_{ij} = \bar{C}_{ij} + \sum_{k=1}^c \rho_k \bar{C}_{ik}(r_{ik}) \bar{H}_{kj} \quad (\text{C4})$$

where

$$\bar{H}_{ij} = \int \langle h_{ij}(\mathbf{r}_{ij}, \omega_i, \omega_j) \rangle_{\omega_i, \omega_j} d\mathbf{r}_{ij}, \quad \bar{C}_{ij} = \int \langle c_{ij}(\mathbf{r}_{ij}, \omega_i, \omega_j) \rangle_{\omega_i, \omega_j} d\mathbf{r}_{ij}. \quad (\text{C5})$$

Equation C4 is only valid provided that there are no long-range interactions with charge-multipole symmetry and spatial dependence. For mixtures of electroneutral molecules, this will be the case. For mixtures containing ions and polar molecules, however, this will not be the case and a more complex form of Eq. C4 is obtained. Likewise, integrating Eq. C2 over  $\mathbf{r}_{ij}$  yields

$$H_{ij} = C_{ij} + \sum_{k=1}^c \rho_k C_{ik}(r_{ik}) H_{kj} \quad (\text{C6})$$

where

$$H_{ij} = \int h_{ij}(\mathbf{r}_{ij}) d\mathbf{r}_{ij}, \quad C_{ij} = \int c_{ij}(\mathbf{r}_{ij}) d\mathbf{r}_{ij}. \quad (\text{C7})$$

Given the relationship Eq. C3,  $\bar{H}_{ij} = H_{ij}$  and so  $\bar{C}_{ij} = C_{ij}$ . Thus, although  $c_{ij}(r) \neq \langle c_{ij}(\mathbf{r}_{ij}, \omega_i, \omega_j) \rangle_{\omega_i, \omega_j}$ , the volume integrals of the two functions are equal provided there are no long-range interactions of charge-multipole form. The consequence is that formally the manipulations based on the direct correlation function presented in our previous paper (Chialvo and Cummings, 1994) proceed as described in the case of a fluid composed of molecular (nonspherical) species subject only to the condition that there be no long-range interactions of charge-multipole form. However, the conclusions about long-rangedness and short-rangedness of the various contributions is not as straightforwardly established in the case of molecular fluids since the asymptotic properties of  $c_{ij}(r)$  are unknown. Thus it is very useful to be able to establish the alternative derivation presented in this article which bypasses the direct correlation function formalism.

## Appendix D: Critical Behavior of $(G_{ij}^{\infty}/G_{ii}^0)$ and $(G_{ij}^{\infty}/G_{ij}^0)$ for Binary Mixtures of Spherically Symmetric Molecules

We can unambiguously split the total correlation function integrals into direct (finite) and indirect (divergent) correla-

tion function integrals by invoking the Ornstein-Zernike equation as follows (Chialvo and Cummings, 1994):

$$\begin{aligned}\rho G_{11}^0 &= C_{11}^0 + \kappa \rho k T (C_{11}^0)^2 \\ \rho G_{12}^\infty &= C_{12}^\infty + \kappa \rho k T C_{11}^0 C_{12}^\infty \\ \rho G_{22}^\infty &= C_{22}^\infty + \kappa \rho k T (C_{12}^\infty)^2.\end{aligned}\quad (D1)$$

Therefore, at the solvent's critical point we have

$$\begin{aligned}\left[ \frac{G_{12}^\infty}{G_{11}^0} \right]_{T_c, \rho_c} &= \lim_{\kappa \rightarrow \infty} \frac{(C_{12}^\infty/\kappa) + \rho k T C_{11}^0 C_{12}^\infty}{(C_{11}^0/\kappa) + \rho k T (C_{11}^0)^2} \\ &= \left( \frac{C_{12}^\infty}{C_{11}^0} \right)_{T_c, \rho_c} = (C_{12}^\infty)_{T_c, \rho_c}\end{aligned}\quad (D2)$$

and

$$\begin{aligned}\left[ \frac{G_{12}^\infty}{G_{22}^\infty} \right]_{T_c, \rho_c} &= \lim_{\kappa \rightarrow \infty} \frac{(C_{12}^\infty/\kappa) + \rho k T C_{11}^0 C_{12}^\infty}{(C_{22}^\infty/\kappa) + \rho k T (C_{12}^\infty)^2} \\ &= \left( \frac{C_{11}^0}{C_{12}^\infty} \right)_{T_c, \rho_c} = (C_{12}^\infty)_{T_c, \rho_c}^{-1}\end{aligned}\quad (D3)$$

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

$$C_{ij} = \rho \int c_{ij} d\mathbf{r} = \rho \hat{c}_{ij}(\mathbf{0}), \quad (D4)$$

where  $\hat{c}_{ij}(\mathbf{k})$  is the Fourier transform of the direct  $ij$ -pair correlation function, and  $(C_{11}^0)_{T_c, \rho_c} = 1$ . Equations D1–D3 indicate that even though the individual TCFIs diverge as the solvent approaches its critical conditions, the ratios of TCFIs remain finite.

## Appendix E: Derivation of Eq. 36

By recalling the notation of Japas and Levelt Sengers (1989), and according to Eq. 3, we have that

$$\begin{aligned}a_\alpha^{r\infty} &\equiv \left( \frac{\partial a^r}{\partial \alpha_2} \right)_{T, \rho}^\infty \\ &= \int_0^\rho \left( \frac{\partial P}{\partial \alpha_2} \right)_{T, \rho} \frac{d\rho}{\rho^2}, \quad \alpha = x, y \\ &= \int_0^\rho \frac{(G_{11}^0 - G_{12}^\infty)_{\sigma(\alpha)}}{\rho \kappa} d\rho, \quad \alpha = x, y \quad \text{and} \quad \sigma(\alpha) = l, v\end{aligned}\quad (E1)$$

since  $P = (\rho/\beta) - (\partial a^r/\partial v)_{T, x}$ . Now, the temperature derivative of  $a_\alpha^{r\infty}$  is

$$\begin{aligned}\left( \frac{\partial a_\alpha^{r\infty}}{\partial T} \right)_\rho &= \lim_{\alpha_2 \rightarrow 0} \left( \frac{\partial^2 a^r}{\partial \alpha_2 \partial T} \right)_\rho \\ &= - \lim_{\alpha_2 \rightarrow 0} \left( \frac{\partial s^r}{\partial \alpha_2} \right)_{T, \rho} = - \left( \frac{\partial s^r}{\partial \alpha_2} \right)_{T, \rho}, \quad \alpha = x, y,\end{aligned}\quad (E2)$$

which after invoking  $d\beta = -k\beta^2 dT$  becomes,

$$\begin{aligned}\left( \frac{\partial a_\alpha^{r\infty}}{\partial T} \right)_\rho &= -k\beta^2 \int_0^\rho \left( \frac{\partial (\partial P/\partial \alpha_2)_{T, \rho}^\infty}{\partial \beta} \right)_{\rho, x} \frac{d\rho}{\rho^2} \\ &= -k\beta^2 \int_0^\rho \left( \frac{\partial [(G_{11}^0 - G_{12}^\infty)/\kappa]_{\sigma(\alpha)}}{\partial \beta} \right)_{\rho, x} \frac{d\rho}{\rho}, \\ &\quad \alpha = x, y \quad \text{and} \quad \sigma(\alpha) = l, v\end{aligned}\quad (E3)$$

Finally, from Eqs. E2, E3 and 25 we obtain,

$$\begin{aligned}\left( \frac{\partial s^r}{\partial \alpha_2} \right)_{T, \rho}^\infty &= [\bar{s}_2^{r\infty}(\text{SR}) - s_1^{r0}]_{T, \rho}^{\sigma(\alpha)}, \\ &\quad \alpha = x, y \quad \text{and} \quad \sigma(\alpha) = l, v.\end{aligned}\quad (E4)$$

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