# Mean Field Calculations of Thermodynamic Properties of Supercritical Fluids

**Ioannis G. Economou**
**Marc D. Donohue**
Department of Chemical Engineering
Johns Hopkins University
Baltimore, MD 21218

The partial molar volume of a solute near a solvent critical point can be large and negative at concentrations near infinite dilution. This unusual behavior was first observed experimentally by Khazanova and Sominskaya (1968) and the thermodynamic reasons for this behavior have been discussed both for nonclassical fluids (Wheeler, 1972) and for classical fluids (Rozen, 1976). More recently, the thermodynamic behavior of dilute mixtures in the vicinity of a solvent critical point has received renewed attention because of interest in supercritical extraction as a separation process. Experiments have been presented by Eckert and coworkers (Eckert et al., 1983, 1986) and molecular simulations have been performed by Debenedetti and coworkers (Debenedetti et al., 1989; Petsche and Debenedetti, 1989). The integral equation theory has been also used by Cochran and Lee (1989) to study the thermodynamic properties of supercritical fluids. The implications of these results have been discussed by Chang et al. (1984), Chang and Levelt Sengers (1986), Debenedetti (1987), Debenedetti and Kumar (1988), Debenedetti et al. (1989), and Kim and Johnston (1987a). The partial molar volume of a solute at infinite dilution, $\bar{v}_2^\infty$, can be large and negative near the solvent critical point where the compressibility of the solvent is greatest. For example, $\bar{v}_2^\infty$ for naphthalene dissolved in carbon dioxide at 35°C and 80 bar is $-8$ L/mol. As the molar volume of carbon dioxide is about 0.1 L/mol, Debenedetti (1987), as well as Kim and Johnston (1987a), has suggested that the negative partial molar volume is due to clustering of solvent molecules around the solute molecules. While there can be some enhancement in the density of solvent molecules in the vicinity of the solute molecules, in this paper we show that the large negative partial molar volume of a solute in a supercritical solvent is due predominantly to the high compressibility of the solvent in the critical region irrespective of any clustering that may be occurring.

Eckert et al. (1983) were the first to suggest that molecular clustering might be used to explain the large negative partial molar volumes that are observed in supercritical fluids. In their paper, they showed that the Peng-Robinson (PR), Redlich-Kwong (RK) and Soave-Redlich-Kwong (SRK) equations of state, three empirical cubic equations of state, describe quite reasonably the large negative partial molar volumes observed. They also showed that chemical theory could be used to correlate the data with about the same accuracy. They showed that the infinite dilution partial molar volume of naphthalene dissolved in carbon dioxide near its critical point could be predicted qualitatively using ideal chemical theory with a cluster size of 50 solvent molecules per solute molecule. They also showed that the partial molar volume of naphthalene dissolved in ethylene could be predicted qualitatively with a cluster size of 10 solvent molecules per solute molecule. They suggested that a combined physical-chemical model could improve the results leading to quantitative agreement with the experimental data. Although Eckert et al. (1983) never stated that the ability of chemical theory to empirically mimic the behavior of the partial molar volume in the critical region suggested that any such clusters physically exist, several papers published subsequently seem to suggest that such a conclusion not only was reached but was proven.

Kim and Johnston (1987a) stated: "The partial molar volume of naphthalene in supercritical carbon dioxide at infinite dilution is $-7{,}800$ cm$^3$/mol, which corresponds to the condensation of about 80 solvent molecules around a solute molecule. This large degree of condensation corresponds to macroscopic clusters that extend over many coordination shells." Debenedetti (1987) seems to be implying the same thing when he states: "Clustering is thus the physical mechanism whereby the volume decrease occurs, namely, through the collapse of a large number of solvent molecules around a single solute molecule." He compared calculations from Kirkwood-Buff fluctuation analysis with the experimental data of Eckert et al. (1983), and concluded that these clusters are approximately 100 solvent

---

Correspondence concerning this paper should be addressed to M. D. Donohue.

molecules per solute molecule for the case of naphthalene dissolved in supercritical carbon dioxide. However, in his analysis he implicitly assumes that "cluster" formation is responsible for the large negative values of $\bar{v}_2^\infty$.

In this paper, it is shown that mean field theory, which explicitly does not take into account either clustering or local composition effects, predicts qualitatively the behavior of $\bar{v}_2^\infty$ in the critical region of the solvent. Therefore, despite the spectroscopic evidence that there is some enhancement in local density of solvent molecules around a solute molecule, the extent of this density enhancement has significance only if it is beyond that due to changes in the mean field.

## Mean Field Theory

To many, the term "mean field" implies only that the properties of a mixture are calculated, in the sense of corresponding states, from some average molecular size and average attractive force. Therefore, any equation of state of the form

$$P = P(\bar{\epsilon}, \bar{\sigma}, T, V) \tag{1}$$

where $\bar{\epsilon}$ and $\bar{\sigma}$ are measures of the composition average attractive forces and composition average molecular size, would satisfy this definition. Similarly, equations of the form

$$P = P(\bar{a}, \bar{b}, T, V) \tag{2}$$

and

$$P = P(\overline{T}_c, \overline{P}_c, T, V) \tag{3}$$

or

$$P = P(\overline{T}_c, \overline{V}_c, T, V) \tag{4}$$

where $\bar{a}$ and $\bar{b}$ are average van der Waals constants and $\overline{T}_c$, $\overline{P}_c$, and $\overline{V}_c$ are composition averages of the critical constants, also would satisfy this definition.

While the van der Waals equation as well as many of the other popular cubic equations of state can be written in this form and can predict the existence of large negative solute partial molar volumes in the vicinity of the solvent critical point, we do not use them here because it could be argued that they are empirical equations and hence their predictions of partial molar volumes might be taking clustering into account implicitly rather than explicitly.

To avoid any ambiguity as to whether this might be true, we adopt a more rigorous and restricted definition of the term "mean field." We use the term "mean field theory" in the context of first-order perturbation theory so that we can prove unequivocally the point of the last paragraph of the previous section. We use mean field theory in this way because "first-order perturbation theory ... does not allow for clustering" (Alder et al., 1974).

In perturbation theory, the total potential of the system is written as a sum of two terms (Barker and Henderson, 1967)

$$U = U^r + U^p \tag{5}$$

where $U^r$ is the potential energy of the unperturbed or reference system and $U^p$ is the perturbation; usually the reference potential is the hard-sphere potential and the perturbation results from molecular attractions. With this approach, the Helmholtz free energy, $A$, can be written as

$$\frac{A}{NkT} = \frac{A^r}{NkT} + \frac{A^p}{NkT} \tag{6}$$

where $A^r$ and $A^p$ are the Helmholtz free energy of the unperturbed system and the perturbation, respectively.

Carnahan and Starling (1969) have evaluated a quite accurate expression for the Helmholtz free energy of a system of hard spheres

$$\frac{A^r}{NkT} = -\ln v + \frac{4\tau\dfrac{v^*}{v} - 2\left(\tau\dfrac{v^*}{v}\right)^2}{\left(1 - \tau\dfrac{v^*}{v}\right)^2} + f(T) \tag{7}$$

where $\tau = \pi\sqrt{2}/6$ and $v^*$ is the close-packed volume of the fluid.

Following Alder and Hecht (1969) and Alder et al. (1972), we write $A^p/NkT$ as a Taylor series expansion over the hard-sphere reference state so that

$$\frac{A^p}{NkT} = \sum_{n=1}^{\infty} \frac{A_n}{T^n}\left(\frac{\epsilon}{k}\right)^n \tag{8}$$

where the $A_n$ are functions only of reduced density. Alder et al. (1972) have evaluated the first four terms in the perturbation expansion for the square-well molecules (with $R = 1.5$) using molecular dynamics calculations and have fitted their results to polynomials of the form

$$A_n = \sum_{m=1}^{M} \frac{A_{nm}}{(v/v^*)^m} \tag{9}$$

where the $A_{nm}$ are constants. In mean field theory the Taylor series expansion is truncated after the first term so that nonrandomness corrections of the higher order perturbation terms are neglected (Alder et al., 1974; Donohue and Prausnitz, 1978; Henderson, 1974). As a result, only bulk properties are taken into account. The resulting equation of state, if written for the compressibility factor, has the following form

$$Z = \frac{Pv}{NkT} = 1 + \frac{4\tau\dfrac{v^*}{v} - 2\left(\tau\dfrac{v^*}{v}\right)^2}{\left(1 - \tau\dfrac{v^*}{v}\right)^3} + \frac{\epsilon}{kT}\sum_{m=1}^{M} \frac{mA_{1m}}{(v/v^*)^m} \tag{10}$$

In order to use this equation to calculate partial molar volumes, one must write mixing rules for both the repulsive (the second term on the righthand side) and the attractive term (the last term on the righthand side) in Eq. 10. In general, this is not an easy task. Mansoori et al. (1970) and Machat and Boublik (1985) have shown how the repulsive equation of state can be written for mixtures of hard spheres of different sizes. Gubbins (1983) and Smit and Cox (1988a,b) have discussed how this can be done for the attractive form. However, for mixtures of square-well molecules of the same size but with different energies of attraction, Eq. 11 is exact (within the limitations of mean field theory) if one simply writes the energy parameter for the mixture as

$$\epsilon_M = \sum_i \sum_j x_i x_j \epsilon_{ij} \tag{11}$$

In the next section, we present sample calculations for a mixture of this type to demonstrate, unambiguously, that small changes in the mean field have a significant effect on the volume and hence partial molar volume in the critical region. We also present calculations for naphthalene dissolved in near critical carbon dioxide. These calculations necessarily require an additional mixing rule for the size parameter, $v^*$, for the mixture. For the calculations of naphthalene in carbon dioxide, we use the conventional van der Waals mixing rules for the parameters

$$v^*_M = \sum_i x_i v^*_i \tag{12}$$

$$[(\epsilon/k)v^*]_M = \sum_i \sum_j x_i x_j \frac{\epsilon_{ij}}{k} \frac{\sigma_{ji}^3}{\sqrt{2}} \tag{13}$$

Although these mixing rules are not exact, they should be sufficiently accurate to demonstrate the importance of the mean field to the partial molar volume.

## Results and Discussion

In Figure 1 the critical isotherm for carbon dioxide has been calculated from Eq. 10. The energy parameter, $\epsilon/k$, and the size parameter $v^*$ were obtained from the constraints

$$\left(\frac{\partial P}{\partial V}\right)_{T,cr} = \left(\frac{\partial^2 P}{\partial V^2}\right)_{T,cr} = 0 \tag{14}$$

applied at the critical point. In Table 1, values for $\epsilon/k$ and $v^*$ are presented for carbon dioxide and naphthalene. Also shown in Figure 1 is the same isotherm for a mixture of carbon dioxide with a hypothetical species of the same size but with an attractive energy approximately twice as large ($\epsilon_{22}/k = 400$ K). The geometric mean was used to calculate the cross interactions. In these calculations, this hypothetical second species is present at a mole fraction of 0.0001. The addition of the solute decreases the molar volume of the system at constant temperature and pressure significantly in the critical region. In the critical region the compressibility of the solvent is very large, so the addition of a small amount of the solute causes a large decrease in the volume of the system. In Figure 1, the horizontal dashed line shows the large change in volume at constant $T$ and $P$. This is proportional to the partial molar volume of the solute. In these calculations, this change in volume can only be caused by the high compressibility of the solvent near its critical point since mean field theory does not take into account structural effects of the fluid.

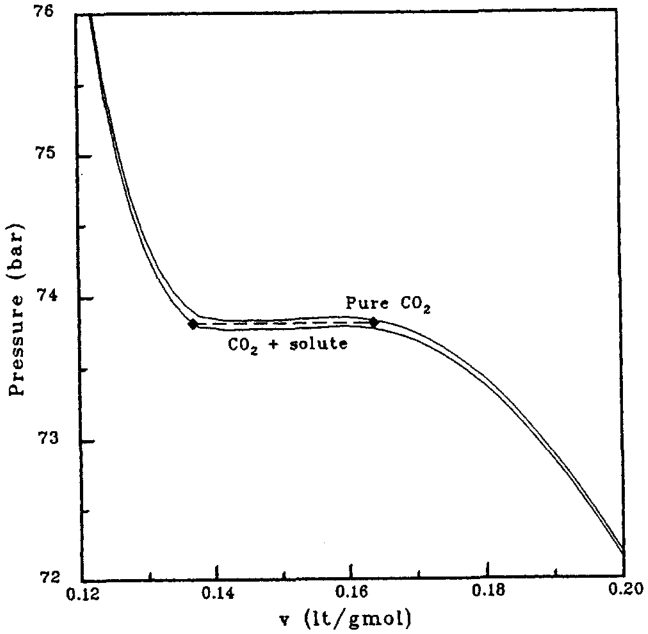

**Figure 1. Carbon dioxide isotherms.**

Critical isotherm for $CO_2$ from mean field theory and (at $T = 31.06°C$) for a mixture of $CO_2$ with a solute of the same size and $\epsilon_{22}/k = 400$ K, at near infinite dilution, $x_2 = 0.0001$.
– – – shows the large change in volume for constant $T$ and $P$ that is proportional to the partial molar volume of the solute

In Figure 2, the infinite dilution partial molar volume of the hypothetical solute in supercritical carbon dioxide ($T = 35°C$) is shown as a function of pressure. Also shown are partial molar volume for a second hypothetical solute with an even larger energy of interaction ($\epsilon_{22}/k = 600$ K). The effect of solute energy parameter, $\epsilon_{22}/k$, in $\bar{v}_2^\infty$ is remarkable. A large negative value for $\bar{v}_2^\infty$ is obtained at 78 bar and its absolute value depends on $\epsilon_{22}/k$. The absolute value of $\bar{v}_2^\infty$ increases as the energy parameter of the solute increases.

In Figure 3, $\bar{v}_2^\infty$ is calculated from mean field theory for naphthalene dissolved in carbon dioxide at 35°C using the mixing rules given in Eqs. 12 and 13. The size and energy parameters for naphthalene are shown in Table 1. Again, a large negative value is obtained near 78 bar. For comparisons we also present the experimental data of Eckert et al. (1983) for the same system. As one can see, there is qualitative agreement between these calculations and the experimental data. Since mean field theory does not take into account any local composition effects, and hence is incapable of predicting any physical behavior that is based on the existence of clusters, the large negative $\bar{v}_2^\infty$ must be attributed entirely to the high compressibility of the solvent in this region. For a quantitative agreement with the experimental data more sophisticated mixing rules probably are necessary. Nevertheless, the mean field theory is able to predict large negative partial molar volumes for solutes dissolved in supercritical fluid solvents.

**Table 1. Parameters for Mean Field Theory**

| Component | $\epsilon/k$ K | $v^*$ L/mol |
|---|---|---|
| Carbon dioxide | 217.45 | 0.0329 |
| Naphthalene | 560.54 | 0.11109 |

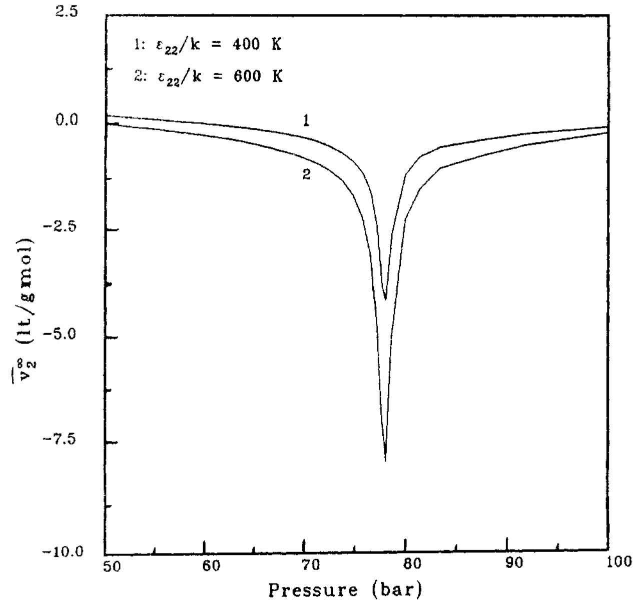

**Figure 2. Partial molar volumes for two solutes dissolved in $CO_2$ at 35°C.**

Both solutes the same size as the solvent, but have larger energies of interaction; partial molar volumes are calculated near infinite dilution ($x_2$ = 0.0001) using mean field theory

### *Kirkwood-Buff fluctuation theory*

Debenedetti (1987) and Kim and Johnston (1987b) defined the size of the cluster of solvent *A* molecules about a solute *B* molecule in dilute solution as

$$\xi_c \equiv \rho G_{12} \tag{15}$$

where $\rho$ is the number density and $G_{12}$ is the Kirkwood fluctuation integral (Kirkwood and Buff, 1951) defined with respect to concentration fluctuations in the grand canonical ensemble as follows

$$G_{12} \equiv 4\pi \int [g_{12}(r) - 1] r^2 dr = V\left(\frac{\langle N_1 N_2\rangle - \langle N_1\rangle\langle N_2\rangle}{\langle N_1\rangle\langle N_2\rangle} - \frac{\delta_{12}}{c_1}\right) \tag{16}$$

where ⟨ ⟩ denotes a thermodynamic average on an open system of volume $V$, $N$ is the number of molecules, and $c_l$ is the bulk molecular concentration of species 1. According to the compressibility equation, the compressibility of a system can be calculated from the density fluctuations through the expression

$$kT\left(\frac{\partial \rho}{\partial P}\right)_{T,N} = 1 + 4\pi\rho \int [g(r) - 1] r^2 dr \tag{17}$$

As the critical point is approached the compressibility of the system approaches infinity, $\partial\rho/\partial P \rightarrow \infty$, and thus the Kirkwood integral diverges because $h(r) = g(r) - 1$ approaches zero less rapidly than $r^{-3}$. However, the divergence of the Kirkwood integral and also the large negative partial molar volumes of solutes near a solvent critical point are due to long-range correlations in the radial distribution function and not to any significant enhancement in the density of solvent molecules in the layers immediately adjacent to a solute molecule (Fisher, 1964; Sengers and Levelt Sengers, 1978). Therefore, the definition in Eq. 15 and the use of terms like "clustering" and "condensation" are confusing and misleading.

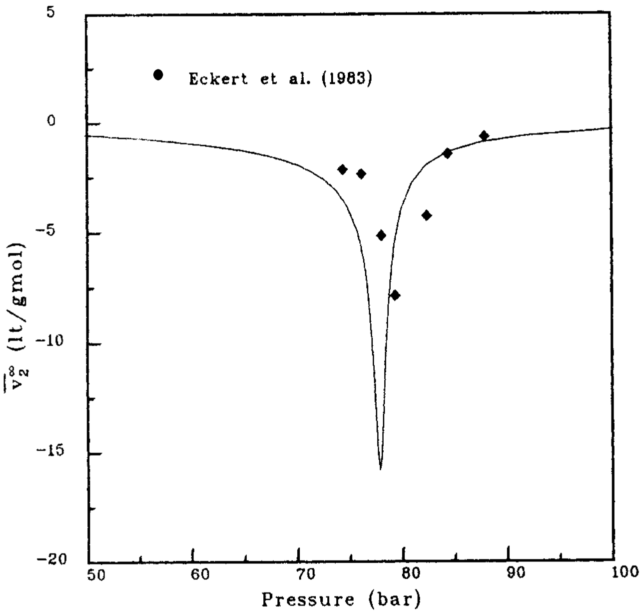

**Figure 3. Partial molar volume for naphthalene dissolved in $CO_2$ at 35°C at near infinite dilution ($x_2$ = 0.0001) using mean field theory.**

Experimental data from Eckert et al. (1983)

### *Significance of clustering*

Although we have shown that 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 these can affect both solubility and partial molar volume to some extent. Molecular simulation studies show some enhancement in local density around a solute molecule when one is near the solvent critical point (Debenedetti et al., 1989; Petsche and Debenedetti, 1989). In addition, Kim and Johnston (1987a) presented experimental measurements of the solvatochromic shift of phenol blue in supercritical carbon dioxide with the cosolvents acetone, methanol, ethanol, and *n*-octane. The solvatochromic shift in the absorption spectrum of phenol blue suggested an increase in local density in the region of high compressibility that was in agreement with their calculations for local compositions. Other experimental results that can be taken as evidence of some clustering are the Stokes shift and charge transfer to normal fluorescence of (N,N-dimethylamino)benzonitrile in supercritical $CF_3H$ (Kajimoto et al., 1988) and the results from fluorescence spectroscopic studies of both nonpolar and polar solutes in supercritical $CO_2$, $C_2H_4$, and $CF_3H$ (Brennecke and Eckert, 1989).

Further, the prediction of the solid hydrocarbon solubilities in supercritical fluids obtained using the first-order Carnahan–Starling–van der Waals model, which is a mean field theory, is improved by using a second-order attractive term to account for nonrandomness (Johnston et al., 1982). Similarly, Kim and Johnston (1987a) showed that predictions of solubilities of acridine in carbon dioxide–acetone and carbon dioxide–methanol mixtures are improved when local composition effects are included. These results are consistent with the results presented here.

Nonetheless, while there can be enhancement in solvent density in the vicinity of a solute molecule near the solvent critical point, the magnitude of this density enhancement and its effect on the solute partial molar volume is small compared to the mean field effect. Cochran and Lee (1989) and McGuigan and Monson (1990) have used the integral equation theory to show that "the physical effects associated with the divergence of $\bar{v}_2^\infty$ are due to the development of long-range correlations in the solvent and not to drastic changes in the local structure about the solute" (McGuigan and Monson, 1990). Cochran and Lee correctly suggest that the divergence of the Kirkwood integral is caused by the long tail of the radial distribution function, $g_{12}(r)$, and not by any enhancement in the first shell next to the solute molecule. As Debenedetti et al. (1989) state, the "long-range behavior results in large volume contractions . . . ," and a distinction must be made between long-range correlations (which cause the divergence of the Kirkwood integral) and the short-range effects. We therefore contend that the use of terminology like "clustering is thus the physical mechanism whereby the volume decrease occurs," "the highly compressible solvent condenses or clusters about the highly polarizable solute," and "the collapse of a large number of solvent molecules around a single solute molecule" paints an incorrect picture of the physical phenomena.

## Acknowledgment

Support of this research by the Division of Chemical Sciences of the Office of Basic Energy Sciences, U.S. Department of Energy under Contract No. DE-FG02-87ER13777 is gratefully acknowledged. The authors also would like to acknowledge constructive comments on the manuscript by P. G. Debenedetti, C. A. Eckert, J. R. Elliot, K. P. Johnston, L. L. Lee, J. M. H. Levelt Sengers, and M. A. McHugh.

## Notation

$A_{nm}$ = Alder's universal constants
$c$ = bulk molecular concentration
$g$ = radial distribution function
$G$ = Kirkwood fluctuation integral
$k$ = Boltzmann's constant
$N$ = number of molecules
$P$ = pressure
$r$ = radial coordinate
$T$ = temperature
$U$ = potential energy
$v$ = molar volume
$v^*$ = characteristic volume per mole
$x$ = mole fraction
$Z$ = compressibility factor
$\langle\,\rangle$ = thermodynamic average

### *Greek letters*

$\delta$ = Kronecker's delta function
$\epsilon$ = characteristic energy parameter per molecule
$\xi_c$ = cluster size
$\rho$ = number density
$\sigma$ = soft core diameter of a molecule
$\theta = \pi\sqrt{2}/6$

### *Subscripts and superscripts*

1 = solvent
2 = solute
$\infty$ = infinite dilution
$-$ = average properties
*att* = attractions
$c$ = critical properties
$M$ = mixture properties
$p$ = perturbed system
$r$ = reference system
*rep* = repulsions

## Literature Cited

Alder, B. J., and C. E. Hecht, "Studies in Molecular Dynamics. VII: Hard-Sphere Distribution Functions and an Augmented van der Waals Theory," *J. Chem. Phys.*, **50**(5), 2032 (1969).

Alder, B. J., D. A. Young, and M. A. Mark, "Studies in Molecular Dynamics. X: Corrections to the Augmented van der Waals Theory for the Square-Well Fluid," *J. Chem. Phys.* **56**(6), 3013 (1972).

Alder, B. J., W. E. Alley, and M. Rigby, "Corrections to the van der Waals Model for Mixtures and for the Diffusion Coefficient," *Physica*, **73**, 143 (1974).

Barker, J. A., and D. Henderson, "Perturbation Theory and Equation of State for Fluids: The Square-Well Potential," *J. Chem. Phys.*, **47**(8), 2856 (1967).

Brennecke, J. F., and C. A. Eckert, "Fluorescence Spectroscopy Studies of Intermolecular Interactions in Supercritical Fluids," *Supercritical Fluid Science and Technology*, K. P. Johnston, J. M. L. Penninger, eds., ACS Symp. Ser. 406, 14 (1989).

Carnahan, N. F., and K. E. Starling, "Equation of State for Nonattracting Rigid Spheres," *J. Chem. Phys.*, **51**(2), 635 (1969).

Chang, R. F., and J. M. H. Levelt Sengers, "Behavior of Dilute Mixtures Near the Solvent's Critical Point," *J. Phys. Chem.*, **90**, 5921 (1986).

Chang, R. F., G. Morrison, and J. M. H. Levelt Sengers, "The Critical Dilemma of Dilute Mixtures," *J. Phys. Chem.*, **88**, 3389 (1984).

Cochran, H. D., and L. L. Lee, "Solvation Structure in Supercritical Fluid Mixtures Based on Molecular Distribution Functions," *Supercritical Fluid Science and Technology*, K. P. Johnston, J. M. L. Penninger, eds., ACS Symp. Ser. 406, 27 (1989).

Debenedetti, P. G., "Clustering in Dilute, Binary Supercritical Mixtures: A Fluctuation Analysis," *Chem. Eng. Sci.*, **42**, 2203 (1987).

Debenedetti, P. G., and S. K. Kumar, "The Molecular Basis of Temperature Effects in Supercritical Extraction," *AIChE J.*, **34**(4), 645 (1988).

Debenedetti, P. G., I. B. Petsche, and R. S. Mohamed, "Clustering in Supercritical Mixtures: Theory, Applications and Simulations," *Fluid Phase Equil.*, **52**, 347 (1989).

Donohue, M. D., and J. M. Prausnitz, "Perturbed Hard Chain Theory for Fluid Mixtures: Thermodynamic Properties for Mixtures in Natural Gas and Petroleum Technology," *AIChE J.*, **24**(5), 849 (1978).

Eckert, C. A., D. H. Ziger, K. P. Johnston, and T. K. Ellison, "The Use of Partial Molal Volume Data to Evaluate Equations of State for Supercritical Fluid Mixtures," *Fluid Phase Equil.*, **14**, 167 (1983).

Eckert, C. A., D. H. Ziger, K. P. Johnston, and S. Kim, "Solute Partial Molal Volumes in Supercritical Fluids," *J. Phys. Chem.*, **90**, 2738 (1986).

Fisher, M. E., "Correlation Functions and the Critical Region of Simple Fluids," *J. Math. Phys.*, **5**(7), 944 (1964).

Gubbins, K. E., "Equations of State—New Theories," *Fluid Phase Equil.*, **13**, 35, (1983).

Henderson, D., "Perturbation Theory for a Mixture of Hard Spheres and Square-Well Molecules," *J. Chem. Phys.*, **61**(3), 1 (1974).

Johnston, K. P., D. H. Ziger, and C. A. Eckert, "Solubilities of Hydrocarbon Solids in Supercritical Fluids. The Augmented van der Waals Treatment," *Ind. Eng. Chem. Fundam.*, **21**, 191 (1982).

Kajimoto, O., M. Futakami, T. Kobayashi, and K. Yamasaki, "Charge-Transfer-State Formation in Supercritical Fluid: (N,N-Dimethylamino)benzonitrile in $CF_3H$," *J. Phys. Chem.*, **92**, 1347 (1988).

Khazanova, N. E., and E. E. Sominskaya, "Volume Properties of Binary Gaseous Solutions Close to the Critical Pressures and Temperatures of the Pure Components," *Russ. J. Phys. Chem.*, **42**(5), 676 (1968).

Kim, S., and K. P. Johnston, "Clustering in Supercritical Fluid Mixtures," *AIChE J.*, **33**(10), 1603 (1987a).

———, "Molecular Interactions in Dilute Supercritical Fluid Solutions," *Ind. Eng. Chem. Res.*, **26**, 1206 (1987b).

Kirkwood, J. K., and F. P. Buff, "The Statistical Mechanical Theory of Solutions. I," *J. Chem. Phys.*, **19**(6), 774 (1951).

Machat, V., and T. Boublik, "Vapor-Liquid Equilibrium at Elevated Pressures from the BACK Equation of State. II: Binary Systems," *Fluid Phase Equil.*, **21**, 11 (1985).

Mansoori, G. A., N. F. Carnahan, K. E. Starling, and T. W. Leland, "Equilibrium Thermodynamic Properties of the Mixture of Hard Spheres," *J. Chem. Phys.*, **54**(4), 1523 (1970).

McGuigan, D. B., and P. A. Monson, "Analysis of Infinite Dilution Partial Molar Volumes Using a Distribution Function Theory," *Fluid Phase Equil.*, **57**, 227 (1990).

Petsche, I. B., and P. G. Debenedetti, "Solute–Solvent Interactions in Infinitely Dilute Supercritical Mixtures: A Molecular Dynamics Investigation," *J. Chem. Phys.*, **91**(11), 7075 (1989).

Rozen, A. M., "The Unusual Properties of Solutions in the Vicinity of the Critical Point of the Solvent," *Russ. J. Phys. Chem.*, **50**(6), 837 (1976).

Sengers, J. V., and J. M. H. Levelt Sengers, "Critical Phenomena in Classical Fluids," *Progress in Liquid Physics*, C. A. Croxton, ed., Wiley, New York, 103 (1978).

Smit, B., and K. R. Cox, "A New Approach for Calculating the Accessible Volume in Equations of Sate for Mixtures. I: Theory and Implementation in the van der Waals Equation of State," *Fluid Phase Equil.*, **43**, 171 (1988a).

———, "A New Approach for Calculating the Accessible Volume in Equations of Sate for Mixtures. II: Application to Lennard-Jones Mixtures," *Fluid Phase Equil.*, **43**, 181 (1988b).

Wheeler, J. C., "Behavior of a Solute Near the Critical Point of an Almost Pure Solvent," *Ber. Bunsenges. Phys. Chem.*, **76**, 308 (1972).

*Note: See the "Letters to the Editor" Section on p. 1927 in this issue for comments.*

*Manuscript received June 8, 1990, and revision received Sept. 7, 1990.*

## Correction

In the Note titled "Viscosity Effects in Cocurrent Three-Phase Fluidization" (October 1990, p. 1613), the order of authorship should be changed to read: B. P. A. Grandjean, P. J. Carreau, I. Nikov, and J. Paris.