

Solute-solute correlations in infinitely dilute supercritical mixtures

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Asymptotic expressions for the solute-solute pair correlation integral and for the limiting slope of the composition dependence of the solute's activity coefficient are derived for the situation in which the solvent's critical point is approached while the mixture is kept at infinite dilution. Both quantities diverge to plus infinity and scale as the solvent's compressibility, with prefactors that depend on the temperature, solvent density, and the infinite dilution limit of the solute-solvent direct correlation function integral.

INTRODUCTION

Fluctuation theory^{1,2} is an important tool in the analysis of mixture behavior. Central to the formalism are the volume integrals of molecular distribution functions (the correlation function integrals). Thermodynamic quantities such as the isothermal compressibility, component partial molar volumes, the isobaric heat capacity, and the isobaric-isothermal composition derivatives of the chemical potential can be expressed in terms of correlation function integrals. Thus, the theory provides a link between molecular quantities and bulk fluid properties.

The integrals of the total correlation function exhibit some common features near critical points. In this region, the correlation length becomes very large^{3,4} and all pair-distribution functions decay to their bulk values over a distance of the order of the correlation length. Thus, the corresponding total correlation function integrals become large in absolute value. The behavior of correlation function integrals in binary mixtures close to consolute points was analyzed by Munster.⁵ Recently, McGuigan and Monson⁶ studied the relationship between the solute-solvent and the solvent-solvent total correlation function integrals at infinite dilution in supercritical mixtures.

In this work, we investigate the behavior of the solute-solute total correlation function integral at infinite dilution and near the solvent's critical point. As is the case with the corresponding solvent-solvent and solute-solvent quantities, this total correlation function integral scales as the solvent's compressibility. We show that the proportionality constant is positive definite. Thus, near the solvent's critical point, the solute-solute pair-distribution function (g_{11}) decays slowly to unity from above ($g > 1$), and the distribution of solute molecules around each other is solute rich with respect to bulk conditions. This is in contrast with the corresponding solute-solvent quantity, which can approach unity

from above (attractive behavior^{7,8}) or from below (repulsive behavior^{7,8}: the distribution function exhibits a long-ranged correlation hole). We also derive an expression for the composition dependence of the solute's activity coefficient near the solvent's critical point in terms of a short-ranged correlation function integral (the direct correlation function integral) and the solvent's compressibility.

Diluteness and proximity to criticality characterize most supercritical mixtures of practical interest. Such systems have received much attention in recent years.⁶⁻²⁸ Because of the low solute mole fractions involved (typically less than 10^{-2}), the investigation of solute-solvent interactions is the natural starting point in the quest for a molecular-based understanding of supercritical mixtures, and several studies have, in fact, addressed the behavior of solute-solvent and solvent-solvent pair-correlation functions and their integrals.^{6,19,20-22,28} In contrast, very little work aimed at studying solute-solute correlations in such systems has been done to date.²² Our derivations provide a first step toward filling this gap in our current understanding of supercritical mixtures.

In the following section we use fluctuation theory to derive asymptotic expressions for the solute-solute total correlation function integral and for the composition dependence of the solute's activity coefficient, in infinitely dilute mixtures in the vicinity of the solvent's critical point. The implications of the new equations are addressed in the Discussion section, with emphasis on dilute supercritical mixtures.

DERIVATION

The fluctuation theory of mixtures^{1,2} relates integrals of molecular distribution functions to thermodynamic derivatives, such as the partial molar volume, the isothermal compressibility, or the composition dependence of the chemical potential. Therefore, in what follows, we begin with thermodynamic identities involving such derivative quantities, we then relate these derivatives to the corresponding distribution function integrals, and then we investigate the behavior of the resulting expressions at infinite dilution and near the solvent's critical point. We first write the thermodynamic identity

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$$\left(\frac{\partial\mu_1}{\partial N_1}\right)_{T,V,N_2} = \left(\frac{\partial\mu_1}{\partial N_1}\right)_{T,P,N_2} + \frac{\bar{v}_1^2}{VK_T}, \quad (1)$$

where \bar{v}_1 is a partial molar volume, K_T is the mixture's isothermal compressibility, and V is the volume within which the average number of molecules of species 1 and 2 is N_1 and N_2 , respectively. Then, with $\rho_i = N_i/V$, $\rho = N/V$, and $N = N_1 + N_2$, we write²⁹ (see also the Appendix)

$$N\left(\frac{\partial\mu_1}{\partial N_1}\right)_{T,V,N_2} = \rho\left(\frac{\partial\mu_1}{\partial\rho_1}\right)_{T,\rho_2} = kT\left(\frac{1}{x_1} - C_{11}\right), \quad (2)$$

where k is Boltzmann's constant, x_1 is a mole fraction, and C_{11} is the 1-1 direct correlation function integral,

$$C_{11} = \rho \int c_{11} d^3r. \quad (3)$$

In Eq. (2), c_{ij} , the direct correlation function, is a short-ranged quantity related to the direct influence of molecules of type i on molecules of type j . For the isobaric composition derivative of μ_1 , we write

$$\begin{aligned} N\left(\frac{\partial\mu_1}{\partial N_1}\right)_{T,P,N_2} &= kT(1-x_1) \left[\frac{1}{x_1} + \left(\frac{\partial \ln \gamma_1}{\partial x_1}\right)_{T,P} \right] \\ &= kT(1-x_1) \left[\frac{1}{x_1} + \left(\frac{\partial \ln \phi_1}{\partial x_1}\right)_{T,P} \right], \end{aligned} \quad (4)$$

where γ_1 and ϕ_1 are component 1's activity and fugacity coefficients, respectively. Then, with 1 denoting the solute, using the notation³⁰

$$K = -\lim_{x_1 \rightarrow 0} \left(\frac{\partial \ln \gamma_1}{\partial x_1}\right)_{T,P} = -\lim_{x_1 \rightarrow 0} \left(\frac{\partial \ln \phi_1}{\partial x_1}\right)_{T,P} \quad (5)$$

and taking into account Equations (1), (2), and (4), we obtain

$$K = \bar{v}_1^\infty \left(\frac{\delta}{kT} + \frac{C_{11}^\infty - 1}{\bar{v}_1^\infty}\right) = \frac{\delta^2 K_T}{\rho kT} + (C_{11}^\infty - 1), \quad (6)$$

where the superscript ∞ denotes infinite dilution with respect to component 1. In Eq. (6) we have used the identity,⁸

$$\rho \bar{v}_1^\infty = \delta K_T, \quad (7)$$

$$\delta = \lim_{x_1 \rightarrow 0} \left[N \left(\frac{\partial P}{\partial N_1}\right)_{T,V,N_2} \right] = \rho kT(1 - C_{12}^\infty), \quad (8)$$

where C_{12}^∞ is the unlike direct correlation function integral at infinite dilution,

$$C_{12}^\infty = \rho \int c_{12} d^3r. \quad (9)$$

Returning now to Eq. (6), and noting that $|\bar{v}_1^\infty| \rightarrow \infty$ as the solvent's critical point is approached^{3,4,26,27} while C_{11}^∞ and δ remain finite, we have

$$K \rightarrow \frac{\delta^2 K_T}{\rho kT} = (1 - C_{12}^\infty)^2 \rho kTK_T, \quad (10)$$

where the symbol \rightarrow signifies that the ratio of the left- and right-hand sides tends to unity as the solvent's critical point is approached along any path at infinite dilution and where K_T and ρ are now solvent properties. Note, however, that

$C_{11}^\infty - 1$, the difference between K and $\delta^2 K_T / \rho kT$ is, in general, nonzero; see Eq. (6). Equation (10) relates the composition dependence of the solute's fugacity coefficient to the unlike direct correlation function integral and the solvent's compressibility.

We now seek expressions for the solute-solute direct correlation function integral. To this end, we write the fluctuation identity¹ (see the Appendix)

$$\begin{aligned} \frac{1}{kT} \left(\frac{\partial\mu_1}{\partial x_1}\right)_{T,P} - \frac{1}{x_1} \\ = \frac{-\rho_2(G_{11} + G_{22} - 2G_{12})}{1 + x_1\rho_2(G_{11} + G_{22} - 2G_{12})}, \end{aligned} \quad (11)$$

where G_{ij} is the total correlation function integral (or Kirkwood-Buff integral)

$$G_{ij} = \int (g_{ij} - 1) d^3r \quad (12)$$

and where g_{ij} is the pair correlation function of species i and j . Therefore, taking into account Eq. (5) we must have, at infinite dilution,^{31,32}

$$K = \rho(G_{11}^\infty + G_{22}^0 - 2G_{12}^\infty), \quad (13)$$

where, as before, the superscript ∞ denotes infinite dilution with respect to the solute and, correspondingly, the superscript 0 on solvent quantities denotes the pure solvent. Invoking the fluctuation identities⁸

$$\rho G_{12}^\infty = \rho kTK_T C_{12}^\infty = \rho kTK_T \left(1 - \frac{\delta}{\rho kT}\right), \quad (14)$$

$$\rho G_{22}^0 = -1 + \rho kTK_T, \quad (15)$$

as well as Eq. (10), we immediately obtain, by substitution into Eq. (13),

$$\rho G_{11}^\infty = C_{11}^\infty + \rho kTK_T (C_{12}^\infty)^2. \quad (16)$$

Therefore, upon approaching the solvent's critical point,

$$G_{11}^\infty \rightarrow kTK_T (C_{12}^\infty)^2, \quad (17)$$

$$\lim_{(T_r, \rho_r \rightarrow 1)} \left(\frac{G_{11}^\infty}{G_{12}^\infty}\right) = C_{12}^\infty, \quad (18)$$

where the meaning of the symbol \rightarrow has already been explained and T_r, ρ_r denote T/T_c and ρ/ρ_c , respectively. Note that Eq. (18) is a stronger condition than Eq. (17), since in Eq. (18) the difference between the left- and right-hand sides vanishes as the solvent's critical point is approached at infinite dilution along any path, whereas in Eq. (17), the ratio of the left- and right-hand sides tends to unity, but their difference, $C_{11}^\infty \rho^{-1}$, is finite. Invoking now Eqs. (14)–(16), we obtain

$$\lim_{(T_r, \rho_r \rightarrow 1)} \left(\frac{(G_{12}^\infty)^2}{G_{11}^\infty G_{22}^0}\right) = 1, \quad (19)$$

$$\lim_{(T_r, \rho_r \rightarrow 1)} \left(\frac{G_{11}^\infty}{G_{22}^0}\right) = (C_{12}^\infty)^2, \quad (20)$$

$$\lim_{(T_r, \rho_r \rightarrow 1)} \left(\frac{G_{12}^\infty}{G_{22}^0}\right) = C_{12}^\infty. \quad (21)$$

It is interesting to note that, although it applies to a different

situation, Eq. (19) is identical to the corresponding finite concentration relationship obtained by Munster⁵ for a binary mixture at its critical point.

DISCUSSION

The main results of this paper are Eqs. (17) and (10) [Equations (18)–(21) follow trivially from the former]. Because the isothermal compressibility diverges to $+\infty$ at the solvent's critical point, Eq. (17) says that the solute–solute correlation function integral is positively divergent irrespective of the type of mixture (attractive, weakly attractive, repulsive^{7,8}). Identical conclusions follow from Eq. (20), since G_{22}^0 is also positively divergent [see Eq. (15)]. Because near criticality pair-correlation functions decay to their bulk value without oscillations, this means that, as the solvent's critical point is approached, the probability of finding solute molecules separated by any distance greater than the repulsive core is systematically greater than if the molecules were randomly distributed.

Recent experimental^{23,24,25} and numerical²² work appears to suggest that short-ranged interactions among solute molecules can be important at supercritical conditions, even at very low solute concentrations. This includes the observation^{23,24} that cholesterol aggregation plays an important role during its enzyme-catalyzed oxidation in supercritical carbon dioxide under conditions where the mole fraction of cholesterol in the supercritical fluid does not exceed 10^{-4} . In addition, enhancements in the rate of photodimerization of dilute cyclohexenone, and in the corresponding regioselectivity toward the more polar head-to-head dimer (versus the less polar head-to-tail dimer), have been shown to increase as the pressure of the supercritical solvent (ethane) is decreased toward its critical point; this effect has been attributed to enhanced solute–solute interactions which increase both the number of encounters and the local polarity.²⁵ In the aforementioned examples, there appear to be important interactions among solute molecules. These interactions become significant when the solvent becomes very compressible and seem to be occurring even though the solute mole fraction is very low. Integral equation calculations of the spatial distribution of molecules in dilute binary Lennard–Jones mixtures at supercritical conditions have shown exceptionally large enhancements in the local density of solute molecules around each other with respect to bulk conditions.²² The theoretical substantiation of these experimental observations and numerical calculations, however, cannot be provided by analyzing the asymptotic behavior of the solute–solute total correlation function integral close to criticality: its divergence is a long-ranged phenomenon. Therefore, the intriguing question of short-ranged enhancements in the solute–solute distribution function remains open. It must be answered on a case-by-case basis, and requires detailed knowledge of the full pair-correlation function itself (as opposed to its integral). This is clearly an area that deserves the attention of experimentalists and theoreticians. At present, all that can be said is that the systematic deviation from randomness in the distribution of solute molecules implied by Eq. (17) suggests that the notion of infinite dilution

needs to be applied with care near the solvent's critical point. Clearly, it is of both theoretical and practical significance to develop quantitative criteria based upon which a given mixture can be considered “effectively infinitely dilute.”

The derivations are completely general and apply to both the classical and nonclassical cases. Since both K and G_{11}^∞ scale as K_T , they diverge with the latter quantity's exponents. For example, K (the absolute value of the limiting slope of the $\ln \gamma_1$ vs x_1 relationship) diverges as $t^{-1.24}$ along the solvent's critical isochore for real fluids,⁴ and as t^{-1} for classical fluids [$t = (T - T_c)/T_c$], but Eq. (10) is always satisfied. Equation (10) suggests that close proximity to the boundary between attractive and weakly attractive behavior^{7,8} ($C_{12}^\infty \approx 1$, or, equivalently, $\delta \approx 0$) tends to narrow the critical region where the solute's activity coefficient becomes arbitrarily sensitive to composition. In fact, Eq. (10) raises the interesting possibility of the existence of regions close to the solvent's critical point where borderline attractive-weakly attractive mixtures exhibit almost ideal solution-type behavior, in the sense defined by Denbigh³³ ($\phi_1 \approx \phi_1^\infty$; $\gamma_1 \approx \gamma_1^\infty$; $\mu_1 \propto \ln x_1$), in spite of their asymmetry. Geometrically, this condition represents a plateau in the $\gamma_1(x_1)$ functionality³⁴ which, in preliminary calculations for the van der Waals mixture,³⁵ we have found to extend in some cases up to solute mole fractions as high as 0.8. Of course, Eq. (10) is not accurate away from the critical point, and this matter merits further and careful investigation.

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APPENDIX

We outline the derivation of Eqs. (11) and (2) (the latter follows from the former). Details can be found in Refs. 1, 2, 34, and 36. Double differentiation of the grand partition function yields ($\beta = 1/kT$, $i, j = 1, \dots, n$; $n =$ number of components in a mixture)

$$\beta \langle \delta N_i \delta N_j \rangle = \left(\frac{\partial N_i}{\partial \mu_j} \right)_{\mu_{(j)}, T, V}, \quad (\text{A1})$$

where δN_i denotes an instantaneous fluctuation in the number of molecules of species i in volume V about the equilibrium value, $\mu [j]$ denotes constancy of all chemical potentials except for μ_j , and the angular brackets denote thermodynamic averaging in an open, isothermal system of volume V . Changing the independent variables from chemical potentials to compositions (which can be conveniently done by invoking the properties of Legendre transforms³⁶), we obtain

$$\beta \langle \delta N_i \delta N_j \rangle = \frac{|B|_{ij}}{|B|}, \quad B_{ij} = \left(\frac{\partial \mu_i}{\partial N_j} \right)_{N[j], T, V}, \quad (\text{A2})$$

where $|B|_{ij}$ denotes the cofactor of the (i, j) element in the symmetric determinant $|B|$, with elements B_{ij} ; $N[j]$ denotes constancy of all species molecule numbers within V , except for N_j . Inversion of the matrix equation (A2) yields

$$\beta \left(\frac{\partial \mu_i}{\partial N_j} \right)_{N[j], T, V} = \frac{|\Delta|_{ij}}{|\Delta|}, \quad \Delta_{ij} = \langle \delta N_i \delta N_j \rangle, \quad (\text{A3})$$

where $|\Delta|_{ij}$ denotes the cofactor of the (i, j) element in the symmetric determinant $|\Delta|$, with elements Δ_{ij} . Invoking the thermodynamic identity, Eq. (1), the Gibbs–Duhem equation, and the identity $V = \sum_{i=1}^n \bar{v}_i N_i$ yields, after some algebra,^{1,36}

$$\beta \left(\frac{\partial \mu_i}{\partial N_j} \right)_{T, P, N[j]} = \frac{|\Delta|_{ij}}{|\Delta|} - \left(\sum_k x_k |\Delta|_{kj} \right) \left(\sum_l x_l |\Delta|_{il} \right) \left[|\Delta| \sum_k \sum_l x_k x_l |\Delta|_{kl} \right]^{-1}, \quad (\text{A4})$$

where x_i is the mole fraction of species i and additional fluctuation-explicit equations are also obtained for the isothermal compressibility and the partial molar volumes.^{1,36} We now invoke the normalization condition for the pair-correlation function in the grand canonical ensemble,¹

$$\frac{1}{V} G_{ij} = \frac{\langle \delta N_i \delta N_j \rangle}{\langle N_i \rangle \langle N_j \rangle} - \frac{\delta_{ij}}{\langle N_i \rangle}, \quad (\text{A5})$$

where G_{ij} is defined in Eq. (12). Substituting Eq. (A5) in Eq. (A4) (binary mixture case; $n = 2$) and rearranging, we obtain Eq. (11).

To obtain Eq. (2) one combines Eqs. (A3), (1), and the integrated form of the multicomponent Ornstein–Zernicke equation.^{2,29,37} Matrix manipulations^{2,29} then yield equations relating thermodynamic derivatives (such as the isothermal compressibility or chemical potential compositional derivatives) to direct correlation function integrals. When the compositional derivatives are expressed using the independent variables appropriate to the canonical ensemble (T, V, N_j) , Eq. (2) is the result (binary mixture case).²⁹

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