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Local density augmentation in attractive supercritical solutions: Inhomogeneous fluid approach

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We study the local solute–solvent structure in supercritical solutions, using as a model system a dilute Lennard-Jones solute in a supercritical Lennard-Jones fluid. The study is focused on attractive mixtures, which are characterized by enhanced local solvent density around the solute molecule. We employ the integral equation theory for inhomogeneous fluids to calculate the solute–solvent radial distribution function and the local coordination number of the solute. We show that this theory is in excellent agreement with Monte Carlo simulations and provides a substantial improvement over the integral equation theory formulated for homogeneous fluids. Using the inhomogeneous fluid theory, we perform a detailed study of the local density enhancement in attractive supercritical mixtures, and analyze its dependence on the model potential parameters and on the solvent thermodynamic conditions. © 2000 American Institute of Physics. [S0021-9606(00)51416-0]

I. INTRODUCTION

Supercritical fluids (SCFs) are currently attracting significant industrial and scientific interest due to their unique physical properties.^{1–4} SCFs are characterized by high dissolving power and enhanced mass-transfer rates, thereby providing an attractive alternative to conventional liquid solvents for a variety of technological applications, such as extraction, separation and reaction processes.^{2,5,6} In addition, the high compressibility of near-critical solvents allows one to adjust their density dependent properties to desired values by applying relatively small changes in pressure. This tunability makes it possible to tailor rates, yields, and selectivities of chemical reactions carried out in near-critical fluids.

The aforementioned industrial applications of SCFs generally involve highly asymmetric solutions, in which the solute differs significantly from the solvent in size, mass, and interaction strength. There exists substantial experimental and theoretical evidence that the local environment around a dilute solute in such systems can differ dramatically from that around a solvent molecule.^{7–28} Dilute supercritical solutions are typically classified into attractive and repulsive mixtures, depending on whether the solute–solvent attraction is stronger or weaker compared to the solvent–solvent attraction.^{19,29} Both types of systems have been extensively studied theoretically.^{7,14,18–29} It has been shown that the local solvent density is enhanced in the vicinity of an attractive solute and depleted in the vicinity of a repulsive one. The former case is of particular importance since the vast majority of industrial and technological applications of SCFs involve attractive mixtures. The local solvent density enhancement in these systems is believed to be related to the outstanding solvation properties of SCFs.

The theoretical studies mentioned above have utilized both simulation techniques and integral equation theories to calculate the structural properties of dilute supercritical mixtures. The main advantage of the first approach lies in the fact that for a given model it produces exact results (albeit

with inevitable statistical noise). Unfortunately, in order to obtain converged simulation results for near-critical solvent states, one needs to employ very large system sizes, which makes extensive simulation studies of such states computationally prohibitive. On the other hand, the approach based on the integral equation theories is very inexpensive computationally, but suffers from unavoidable approximations.

In a recent study, the accuracy of two integral equation theories (Percus–Yevick and hybrid mean spherical approximation³⁰) has been tested for infinitely dilute supercritical solutions, in which solvent–solvent and solute–solvent interactions were modeled with the isotropic pairwise additive potentials of the Lennard-Jones (LJ) form.³¹ Three particular systems were studied: an attractive LJ mixture (Xe in Ne), a repulsive LJ mixture (Ne in Xe), and a neat LJ fluid (i.e., solute identical to the solvent). The solute–solvent radial distribution functions calculated from the integral equation theories were compared to the simulation results for a wide range of solvent temperatures and densities. The main focus was on *short-range* structural properties (e.g., local coordination number of the solute) determined by the first peak of the solute–solvent radial distribution function. The integral equation theories generally agreed well with the simulation for the neat fluid and the repulsive mixture, but failed for the attractive mixture, especially in the near-critical region. Given the primary importance of attractive mixtures for practical applications of SCFs, it is desirable to understand the reasons for this failure and to provide the necessary refinements which would allow one to obtain accurate results for the local structural properties of supercritical solutions.

The traditional integral equation approach is formulated for homogeneous fluids, which are characterized by spatially uniform density. However, as was mentioned above, in attractive supercritical mixtures the local solvent density in the vicinity of the solute particle can substantially exceed the bulk density. Therefore, in calculating the solute–solvent pair distribution function, it would seem appropriate to ac-

count for the solvent density enhancement induced by the solute. This goal can be achieved by employing the extended version of the integral equation theory, which was formulated specifically for inhomogeneous fluids.^{32–42} One well-known example of inhomogeneous systems involves liquids near macroscopic surfaces, where spatial variation of density arises from the presence of a liquid–solid interface.^{40–42} In the case of dilute asymmetric mixtures, an analogous non-uniform solvent density profile is created by the solute molecule. The integral equation theory of inhomogeneous fluids provides a framework for calculating this density profile, thereby yielding the solute–solvent pair distribution function.

Given the failure of the standard integral equation theories for attractive supercritical mixtures, it is of interest to apply the theory developed for nonuniform fluids to study the local solvent structure around a dilute solute in these systems. In the present work we carry out such calculations and assess the accuracy of this approach by comparing our theoretical results with simulations. It is shown that the theory for inhomogeneous fluids does indeed provide a substantial improvement over the standard integral equation approach for calculating the solute–solvent pair distribution functions.

Equipped with an accurate theory of the local structural properties of supercritical solutions, we set out to perform a detailed quantitative analysis of the local density augmentation around dilute solutes in attractive supercritical mixtures. Some work along these lines has already been reported in Ref. 31. However, in view of the failure of the homogeneous integral equation theory for attractive mixtures, the latter study relied entirely on Monte Carlo (MC) simulations. Due to large system sizes required to obtain converged MC results for near-critical solvent states, only one model attractive mixture (Xe in Ne) was studied in Ref. 31. The local coordination number of the solute was calculated for a variety of solvent densities and temperatures, and various ways of analyzing the local solvent density around the solute were discussed. The origin of the local density enhancement in attractive supercritical mixtures was rationalized in terms of a crossover between energy-dominated low-density and packing-dominated high-density behavior of the solute's local coordination number.³¹

It is desirable to extend the above study by analyzing the dependence of the local density enhancement on the model potential parameters, such as the solute–solvent interaction strength and the solute size, and on the solvent density and temperature. This requires performing extensive calculations of the solute–solvent pair distribution functions for several model attractive mixtures, and therefore would be extremely time-consuming within the simulation-based approach. On the other hand, the inhomogeneous integral equation theory, although more computationally demanding than its homogeneous counterpart, is still much less expensive than simulation studies. We will therefore employ this theory to perform the analysis of the local density enhancement in several model supercritical mixtures.

One additional issue that should be mentioned here concerns the long-range decay of the distribution functions in

the vicinity of the solvent's critical point. In this regard, we note that the emphasis of the present study is on the *short-range* solute–solvent structural properties exemplified by the solute's local coordination number. For this reason, we do not address here the issue of the long-range decay of the distribution functions. However, one still needs to be extremely careful in choosing the system sizes employed in the calculations. In fact, the first peak of the distribution function is quite sensitive to the choice of the cutoff distance in the numerical implementation of the integral equation theory. Therefore, in performing calculations near the critical point, we must be sure to employ the cutoff distance large enough that the first peak of the distribution function is converged.

The paper is organized as follows. In Sec. II we briefly outline the theory we use to calculate the pair distribution functions. In Sec. III we compare theoretical results with MC simulations. In Sec. IV we present results of our model calculations for several attractive supercritical mixtures and analyze the dependence of the local density enhancement on the solute–solvent potential parameters and thermodynamic conditions of the solvent. In Sec. V we conclude.

II. RADIAL DISTRIBUTION FUNCTIONS

In the present study we are concerned with two-component fluids where one of the components (the solute) is present at infinite dilution. We assume that the solute interacts with the solvent atoms via a spherically symmetric pair potential, $\phi(r)$, and that the solvent atoms interact with each other via another isotropic pair potential, $\phi_s(r)$.

Following Attard's "source particle method,"^{35–37} we treat this mixture as a spherically symmetric inhomogeneous system, where the source of inhomogeneity is the solute particle fixed at the origin, and the singlet density of the non-uniform fluid, $\rho(r)$, is a function of the distance from the origin. Within this formalism, the solute–solvent pair distribution function, $g(r)$, is obtained directly from the singlet density profile,

$$g(r) = \rho(r)/\rho, \quad (1)$$

where ρ is the bulk solvent number density.

The essential steps of Attard's method are as follows.^{35–37} One starts by writing the inhomogeneous Ornstein–Zernike (OZ) equation for two solvent particles located at \mathbf{r}_1 and \mathbf{r}_2 ,

$$h(\mathbf{r}_1, \mathbf{r}_2) = c(\mathbf{r}_1, \mathbf{r}_2) + \int d\mathbf{r}_3 \rho(r_3) c(\mathbf{r}_1, \mathbf{r}_3) h(\mathbf{r}_3, \mathbf{r}_2), \quad (2)$$

where $h(\mathbf{r}_1, \mathbf{r}_2)$ and $c(\mathbf{r}_1, \mathbf{r}_2)$ are the total and direct solvent pair correlation functions, respectively. Since the system is characterized by spherical symmetry, these anisotropic correlation functions depend only on the distances r_1 and r_2 of the two solvent particles from the origin and on the angle θ_{12} formed by \mathbf{r}_1 and \mathbf{r}_2 . Accordingly, the OZ equation takes the following form:

$$h(r_1, r_2, \cos \theta_{12}) = c(r_1, r_2, \cos \theta_{12}) + \int d\mathbf{r}_3 \rho(r_3) c(r_1, r_3, \cos \theta_{13}) \times h(r_3, r_2, \cos \theta_{32}). \quad (3)$$

Equation (3) can be further simplified by expanding the angular dependent correlation functions in Legendre polynomials. For the total solvent pair correlation function one writes

$$h(r_1, r_2, \cos \theta_{12}) = \sum_{n=0}^{\infty} \hat{h}_n(r_1, r_2) P_n(\cos \theta_{12}), \quad (4)$$

where $P_n(x)$ is the Legendre polynomial of degree n , and the expansion coefficients are given by

$$\hat{h}_n(r_1, r_2) = \frac{2n+1}{2} \int_{-1}^1 dx h(r_1, r_2, x) P_n(x). \quad (5)$$

Analogous relations hold for the direct correlation function $c(r_1, r_2, \cos \theta_{12})$.

Taking the Legendre transform of Eq. (3) and using the addition theorem for spherical harmonics, the OZ equation for a spherically symmetric inhomogeneous fluid can be written as follows:

$$\hat{h}_n(r_1, r_2) = \hat{c}_n(r_1, r_2) + \frac{4\pi}{2n+1} \times \int_0^\infty dr_3 r_3^2 \rho(r_3) \hat{c}_n(r_1, r_3) \hat{h}_n(r_3, r_2). \quad (6)$$

In analogy to the integral equation theory for uniform fluids, the inhomogeneous OZ equation needs to be supplemented with a closure, which relates the total and direct pair correlation functions. In the present work, we use the inhomogeneous Percus–Yevick (PY) closure,

$$c(r_1, r_2, \cos \theta_{12}) = [h(r_1, r_2, \cos \theta_{12}) + 1] \times [1 - \exp(\beta \phi_s(r_{12}))], \quad (7)$$

where $\beta = 1/k_B T$ and $r_{12} = |\mathbf{r}_1 - \mathbf{r}_2|$.

In addition to the anisotropic pair correlation functions, the OZ equation for a nonuniform fluid contains one more unknown function—the density profile $\rho(r)$. Several exact relations between the density profile and the pair correlation functions are known.^{43–46} Here we employ the Lovett–Mou–Buff–Wertheim equation,^{44,45} which for a spherically symmetric inhomogeneous system takes the following form:

$$\rho'(r_1) = -\beta \rho(r_1) \phi'(r_1) + \frac{4\pi}{3} \rho(r_1) \times \int_0^\infty dr_2 r_2^2 \hat{c}_1(r_1, r_2) \rho'(r_2), \quad (8)$$

where the prime denotes differentiation with respect to argument.

By solving Eqs. (6), (7), and (8) simultaneously, one obtains the inhomogeneous pair correlation functions and the density profile in a self-consistent manner. The solute–solvent pair distribution function, which is of primary interest for the present study, is then calculated from Eq. (1).

Regarding the numerical implementation of the procedure described above, it is important to note that the focus of the present study is on near-critical systems, which are characterized by long-ranged total correlation functions. In the computational procedure, all the functions are calculated on a finite grid with spacing Δr and cutoff distance R . As the decay range of correlation functions increases, one needs to employ large cutoff distances (up to 15 solvent diameters) in order to obtain converged results for the first peak of $g(r)$. To keep the memory requirements for the computation practical, we employ a nonuniform grid spacing; we set $\Delta r = 0.02$ (in units of the solvent diameter) around the first peak of $g(r)$ and $\Delta r = 0.1$ beyond the first peak. In the computations, the Legendre polynomial expansion given by Eq. (4) is also limited to a finite number of terms; we found that keeping the first 100 terms in the sum in Eq. (4) was sufficient to make the truncation errors negligible.

Before proceeding to the comparison of the inhomogeneous PY theory with simulation, we will briefly outline its homogeneous counterpart, since it is instructive to compare the approximations involved in each of the two approaches. Within the standard integral equation theory, mixtures are described by a system of homogeneous OZ equations, which for an infinitely dilute solution take the following form:³⁰

$$\tilde{h}_s(r_1) = \tilde{c}_s(r_1) + \rho \int d\mathbf{r}_2 \tilde{h}_s(r_2) \tilde{c}_s(r_{12}), \quad (9)$$

$$\tilde{h}(r_1) = \tilde{c}(r_1) + \rho \int d\mathbf{r}_2 \tilde{h}(r_2) \tilde{c}_s(r_{12}). \quad (10)$$

In the above, $\tilde{h}_s(r)(\tilde{h}(r))$ and $\tilde{c}_s(r)(\tilde{c}(r))$ are the isotropic solvent–solvent (solute–solvent) total and direct correlation functions, respectively. In contrast to the inhomogeneous OZ relation given by Eq. (2), the density of the solvent is taken to be spatially uniform.

In order to solve Eqs. (9) and (10), one supplements *each of them* with an approximate closure relation. In particular, the homogeneous PY closure reads

$$\tilde{c}_s(r) = [\tilde{h}_s(r) + 1][1 - \exp(\beta \phi_s(r))], \quad (11)$$

$$\tilde{c}(r) = [\tilde{h}(r) + 1][1 - \exp(\beta \phi(r))]. \quad (12)$$

Note that Eqs. (9) and (11) are uncoupled from the solute–solvent quantities and therefore can be solved independently to yield the solvent–solvent total and direct correlation functions. Using $\tilde{c}_s(r)$ from the above, one solves Eqs. (10) and (12) for $\tilde{c}(r)$ and $\tilde{h}(r)$, and thus obtains the homogeneous theory result for the solute–solvent radial distribution function, $\tilde{h}(r) + 1$. Clearly, the function $\tilde{c}_s(r)$ utilized in solving Eq. (10) is identical to the direct correlation function of a neat solvent. In other words, no account is made for the fact that the correlation function for the two solvent particles in the vicinity of a solute can be different from the solvent correlation function in the bulk.

From the above discussion of the homogeneous and inhomogeneous fluid theories, the following comparisons can be made. The homogeneous integral equation method for an infinitely dilute solution involves two (exact) OZ equations, each of which is supplemented by an approximate closure

relation. On the other hand, the theory for inhomogeneous fluids involves three relations; the equation for the nonuniform density profile, the inhomogeneous OZ equation, and the closure. The first two relations are *exact*, and the only approximation in the theory is the closure relation between the solvent–solvent total and direct anisotropic pair correlation functions. Furthermore, in contrast to the homogeneous formulation, the latter functions depend on the positions of the two solvent particles *relative to the solute*, which accounts for the solvent density inhomogeneities induced by the solute particle. On the basis of the above comparison, one would expect the theory for nonuniform fluids to provide more accurate results for the structural properties of dilute solutions, especially when the local environment around the solute differs dramatically from the bulk. In the next section we will demonstrate that this is indeed the case.

III. COMPARISON OF THEORY WITH SIMULATION

We start by specifying the solute–solvent and solvent–solvent model potentials. We assume that the solvent particles interact with each other via the familiar LJ potential,

$$\phi_s(r) = 4\epsilon_s \left[\left(\frac{\sigma_s}{r} \right)^{12} - \left(\frac{\sigma_s}{r} \right)^6 \right], \quad (13)$$

where ϵ_s is the potential well depth and σ_s is the effective diameter of the solvent particle. The solute–solvent pair potential has the same form, but with different ϵ and σ parameters,

$$\phi(r) = 4\epsilon \left[\left(\frac{\sigma}{r} \right)^{12} - \left(\frac{\sigma}{r} \right)^6 \right]. \quad (14)$$

As was already discussed in the Introduction, the present study is focused primarily on attractive supercritical mixtures, since these systems are of major importance for practical applications of SCFs, and at the same time have been shown to be the most problematic for the standard integral equation treatments.³¹ For the purpose of testing the theory of inhomogeneous fluids, we consider a model attractive mixture roughly corresponding to Xe in Ne, with the following values of the model potential parameters: $\sigma/\sigma_s = 1.22$ and $\epsilon/\epsilon_s = 2.47$. Extensive simulation results for this system have been reported in Ref. 31.

Using Attard's "source particle method,"^{35–37} we calculate the solute–solvent distribution function for a series of solvent densities from $\rho^* = 0.01$ to 0.9 ($\rho^* = \rho\sigma_s^3$), on three supercritical isotherms, $T^* = 1.338$, 1.41, and 1.70 ($T^* = k_B T/\epsilon_s$). Note that the best estimates for the critical density and temperature of a LJ fluid are $\rho_c^* = 0.316$ and $T_c^* = 1.312$.⁴⁷ Our density range therefore extends from a dilute gas, through the critical region, to a dense fluid (the triple point density for the LJ fluid is $\rho_t^* \approx 0.85$). Defining a reduced temperature by $T_r = T/T_c$, our three isotherms correspond to $T_r = 1.02$, 1.07, and 1.30, respectively.

We start by considering the near-critical region of the phase diagram, where the inadequacy of the standard integral equation approach was found to be the most pronounced. Figure 1 depicts the solute–solvent radial distribution function calculated for the lowest temperature isotherm at the

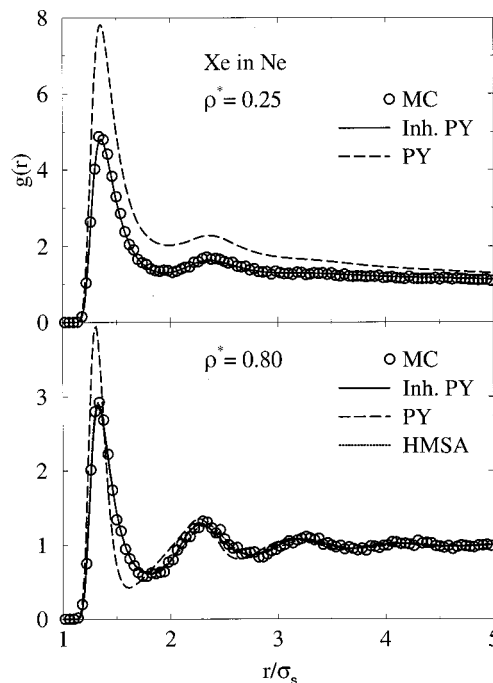


FIG. 1. Solute–solvent radial distribution function for the Xe in Ne attractive mixture at $T^* = 1.338$, at two different densities. The open symbols are MC simulation results (Ref. 31); the solid line is from the inhomogeneous PY theory, the dashed line is from the homogeneous PY theory, and the dotted line in the lower panel is from the homogeneous HMSA theory [the latter is nearly indistinguishable from the solid line for the first peak of $g(r)$].

density $\rho^* = 0.25$, i.e., somewhat below the solvent's critical density. Also shown are $g(r)$ calculated from MC simulations and from the homogeneous PY theory.³¹ One sees that the theory for inhomogeneous fluids is in excellent agreement with the simulation, while the standard PY method significantly overestimates the height of the first peak of $g(r)$.

As was pointed out in the previous section, one of the important features of the inhomogeneous fluid theory is the explicit treatment of the solute's influence on the solvent pair correlations. To illustrate that this influence can be significant, we show in Fig. 2 the anisotropic direct correlation function $c(r_1, r_2, \cos \theta_{12})$ calculated from the inhomogeneous PY theory. In plotting this function, we have fixed the values of its first two arguments, i.e., the distances between the solute and each of the solvent particles. Specifically, we have set $r_1 = r_2 = 1.4\sigma_s$, which roughly corresponds to the first peak of the solute–solvent pair distribution function. By varying the angle θ_{12} between 0 and π , we plot $c(r_1 = 1.4\sigma_s, r_2 = 1.4\sigma_s, \cos \theta_{12})$ as a function of the separation between the two solvent particles, $r_{12} = \sqrt{r_1^2 + r_2^2 - 2r_1r_2 \cos \theta_{12}}$. Also shown in Fig. 2 is the *isotropic* direct solvent correlation function, $\bar{c}_s(r_{12})$, obtained from the homogeneous PY theory [Eqs. (9) and (11)] for the same thermodynamic conditions of the solvent. Clearly, the two functions differ substantially at small distances [the magnitude of $\bar{c}_s(0)$ is nearly 50% smaller than $c(1.4\sigma_s, 1.4\sigma_s, 0)$], which demonstrates the pronounced effect of the solute on the solvent pair correlations. In fact, the anisotropic correlation function is remarkably similar to the isotropic one calculated at the same temperature but at a

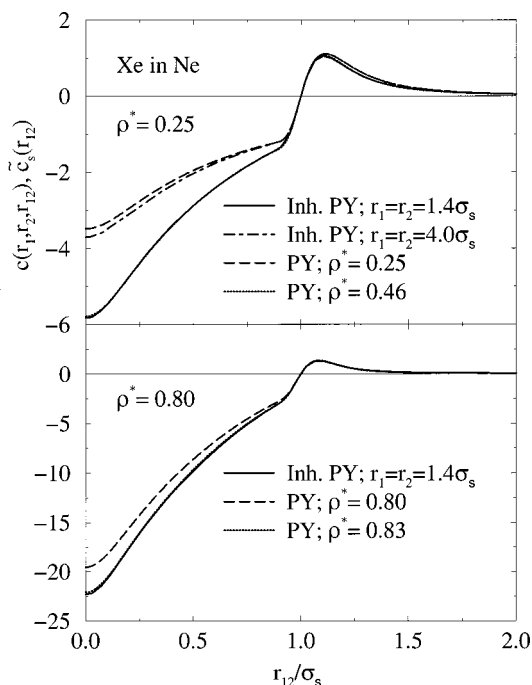


FIG. 2. Solvent-solvent direct pair correlation functions for the Xe in Ne attractive mixture at $T^*=1.338$, at two different densities. Solid and dotted-dashed lines are from the inhomogeneous PY theory for two different values of the solute-solvent separation; the dashed line is from the homogeneous PY theory at the actual value of the bulk density, the dotted line is from the homogeneous PY theory at a different (higher) value of the bulk density, as indicated (the dotted line is nearly indistinguishable from the solid line).

significantly *higher* bulk solvent density, $\rho^*=0.46$, which is also shown in Fig. 2. This is hardly surprising, since the local solvent density around an attractive solute is expected to be higher than the bulk value, especially at near-critical conditions. We also note that the above result is rather insensitive to a particular choice of the solute-solvent separation, as long as $r_1(=r_2)$ is within the first solute's coordination shell. This suggests that the above value ($\rho^*=0.46$) can be considered as a rough estimate of the local solvent density around the solute; we will return to this point in the next section. As one would expect, for larger values of the solute-solvent separation, the anisotropic correlation function approaches the isotropic one calculated at the actual value of the bulk density. To illustrate this, we consider two solvent particles, both of which are located at a distance $4\sigma_s$ from the solute. The corresponding anisotropic direct correlation function, i.e., $c(r_1=4\sigma_s, r_2=4\sigma_s, r_{12})$, is also shown in Fig. 2. The latter function is indeed very close to $\tilde{c}_s(r_{12})$ evaluated at $\rho^*=0.25$.

Turning next to liquidlike densities, the second panel of Fig. 1 depicts theoretical and simulation results for the solute-solvent distribution function at $\rho^*=0.80$, $T^*=1.338$. Once again, the inhomogeneous PY theory is in excellent agreement with the simulation, while its homogeneous counterpart is much less accurate, albeit its inadequacy is somewhat less dramatic than in the near-critical region. Also shown in the second panel of Fig. 1 is $g(r)$ calculated from the homogeneous hybrid mean spherical approximation (HMSA) theory, which involves a more refined closure

based on thermodynamic self-consistency.³⁰ While the HMSA theory agrees very well with the simulation in the present case, in the near-critical region this method suffers from severe convergence problems. We note that for the lowest temperature isotherm we were unable to obtain converged HMSA results for the density range between $\rho^*=0.12$ and 0.35 , and therefore we could not present $g(r)$ from this theory for the near-critical state considered above ($\rho^*=0.25$, $T=1.338$). We reiterate that the HMSA result shown in Fig. 1 is obtained within the *homogeneous* integral equation approach, i.e., solvent pair correlations from the bulk are utilized in calculating solute-solvent correlation functions. The fact that this approach works well at the present density suggests that the neglect of the solute's effect on the solvent correlations is much less problematic at liquidlike densities than at near-critical conditions. This is confirmed by the second panel of Fig. 2, where we plot the anisotropic direct correlation function $c(r_1=1.4\sigma_s, r_2=1.4\sigma_s, r_{12})$ at the present thermodynamic point together with the corresponding isotropic PY result, $\tilde{c}_s(r_{12})$. One sees that the difference between the two functions is much smaller than in the previous case [the magnitude of $\tilde{c}_s(0)$ is only $\approx 12\%$ smaller than $c(1.4\sigma_s, 1.4\sigma_s, 0)$]. Furthermore, the anisotropic correlation function is very close to the isotropic one evaluated at $\rho^*=0.83$, which is only slightly higher than the actual value of the bulk density. This is consistent with the fact that the local solvent density augmentation becomes less pronounced in going from near-critical to liquidlike densities (see also next section).

In view of the above, one can argue that the homogeneous PY method fails at higher densities due to the inaccuracy of the PY closure itself, which is applied to both solute-solvent and solvent-solvent correlation functions [see Eqs. (7) and (12)]. The inhomogeneous approach, on the other hand, involves only one closure relation—for the solvent pair correlations—and therefore its results for the solute-solvent distribution function are likely to be less sensitive to the approximations involved in the closure.

The two thermodynamic points considered above were chosen as being representative of near-critical and liquidlike solvent conditions, and in both cases the solute-solvent radial distribution function obtained from the theory for non-uniform fluids was found to be in excellent agreement with the simulation. The same holds true for all other thermodynamic conditions studied in the present work, as will be illustrated by our results for the coordination number of the solute.

We define the solute's local coordination number, i.e., the average number of solvent particles within the first coordination shell of the solute, by

$$N_c = 4\pi\rho \int_0^{\sigma_s + \sigma/2} dr r^2 g(r), \quad (15)$$

where the upper limit on the integral ($\sigma_s + \sigma/2$) roughly corresponds to the first minimum in $g(r)$. It is clear from the above definition that N_c is entirely determined by the first peak of the radial distribution function, and therefore a comparison between theoretical and simulation results for the

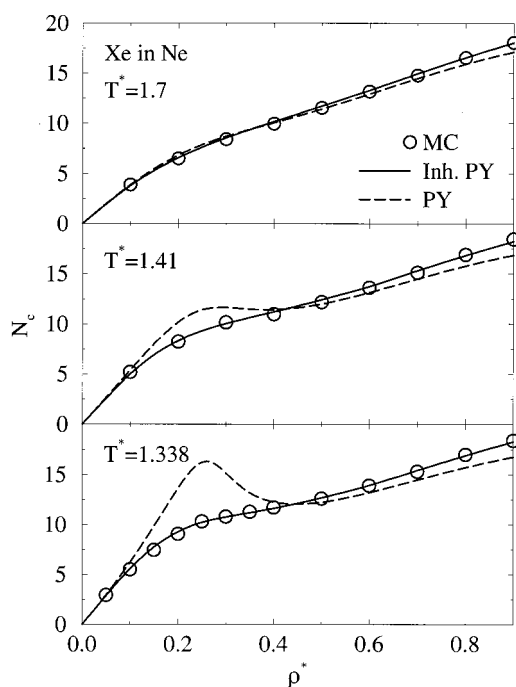


FIG. 3. N_c vs ρ^* for Xe in the Ne attractive mixture at three temperatures. The open symbols are MC simulation results (Ref. 31); the solid line is from the inhomogeneous PY theory, and the dashed line is from the homogeneous PY theory.

coordination number provides an indication of the accuracy of the theory in calculating local structural properties.

To perform such a comparison, we have calculated N_c as a function of the solvent density for three isotherms studied; the results are shown in Fig. 3 together with the previously reported results³¹ from the MC simulations and the homogeneous PY theory. One sees that for all thermodynamic conditions the inhomogeneous PY theory is in excellent agreement with the simulation, while its homogeneous counterpart grossly overestimates N_c in the near-critical region at the two lower temperatures, and underestimates it in the high-density region for all three isotherms. As discussed above, the theory for homogeneous fluids fails for attractive mixtures at near-critical conditions due to the assumption that the solvent pair correlation functions in the vicinity of the solute are identical to those in the bulk. The above approximation is inherent in the homogeneous OZ equation [Eq. (10)] and therefore choosing a different closure is not expected to improve the accuracy of the theory significantly. In fact, the HMSA method does not even converge for the near-critical attractive mixture studied here, and therefore we do not present the HMSA results for N_c . The situation is different at liquid-like densities, where the local solvent density enhancement becomes less pronounced, and employing a more refined closure (e.g., HMSA instead of PY) allows one to improve the accuracy of the homogeneous integral equation approach.

Clearly, the theory for inhomogeneous fluids is much more robust than its homogeneous counterpart, since it produces accurate results for the local structure of attractive supercritical mixtures over the whole range of densities and temperatures examined in this work. The reasons for this superior performance are twofold. Firstly, the method oper-

ates with *anisotropic* solvent pair correlation functions, which depend explicitly on the positions of the solvent atoms relative to the solute. Secondly, the (approximate) closure relation is applied only to solvent–solvent correlations, while the solvent density profile around the solute is obtained from the exact LMBW equation. We note that in the present application of the inhomogeneous fluid theory we have limited ourselves to the PY closure. In principle, other closures commonly used within the standard integral equation approach can be easily incorporated into the theory for nonuniform fluids (e.g., the HMSA closure was employed in Refs. 38, 39, and 41, and the hypernetted chain and Duh–Haymet–Henderson closures were used in Ref. 34). However, since the PY closure produces sufficiently accurate results, we have not explored these possibilities in the present study.

Returning to our results for the solute's coordination number shown in Fig. 3, we observe a nonlinear density dependence of N_c , which is especially pronounced at the lowest temperature isotherm ($T^* = 1.338$). This behavior of N_c indicates a local solvent density enhancement around a dilute solute at near-critical conditions, which is a characteristic feature of attractive mixtures. Having demonstrated the accuracy of the inhomogeneous integral equation approach in calculating the local solute–solvent structure of attractive mixtures, we are now in a position to perform a detailed quantitative analysis of the local density enhancement in these systems, and its dependence on thermodynamic conditions and solute–solvent model potential parameters.

Before doing that, however, we will briefly discuss two other systems studied in Ref. 31; neat LJ fluid and a repulsive mixture (roughly corresponding to Ne in Xe). These two types of systems, unlike the attractive mixtures, do not exhibit significant local solvent density enhancement; the solute's local coordination number depends almost linearly on the solvent density and is nearly temperature independent. Furthermore, it has been shown in Ref. 31 that the results for N_c from standard integral equation theories (PY and HMSA closures) agree well with MC simulations, except that the PY method slightly underestimates N_c at higher densities and the HMSA method does not converge in the near-critical region.

In order to perform a comprehensive test of the integral equation theory for nonuniform fluids, we have employed the inhomogeneous PY method to calculate N_c as a function of solvent density for neat LJ fluid and for a repulsive mixture (Ne in Xe). The calculations were performed for the same three isotherms considered above. Theoretical results were found to be in good agreement with simulation at all thermodynamic conditions, with the accuracy of the inhomogeneous PY method in the high-density region being slightly better compared to its homogeneous counterpart (the same improvement has been observed by Duh *et al.*³⁴ in their study of the neat LJ fluid). Apart from that, there are no major improvements over the standard PY theory—which is already fairly accurate and less demanding computationally—and therefore we will not discuss these results in detail here.

Satisfactory performance of the standard integral equation theory for neat fluid and repulsive mixture is likely to stem from the absence of significant local solvent density enhancements in these systems. In other words, approximat-

ing solvent pair correlation functions in the vicinity of the solute by the corresponding functions from the bulk is less problematic in this case. By the same token, the homogeneous PY theory produces satisfactory results for the attractive system at the highest isotherm considered here ($T^* = 1.7$), since at this temperature one is sufficiently far away from the critical point, and the local density enhancement is much less pronounced (see also next section).

IV. LOCAL DENSITY ENHANCEMENT IN ATTRACTIVE MIXTURES: MODEL CALCULATIONS

Over the past decade, several attempts have been made to quantify the concept of local density enhancement in supercritical solutions by calculating local solvent density around a dilute solute and comparing it to the bulk density.^{7,21–23,28,31} Generally, local density is taken to be proportional to the solute's coordination number, and various definitions proposed in the literature differ from each other mainly in the choice of the corresponding proportionality factor. For a given definition of the local density, its behavior as a function of the bulk solvent density depends both on the solvent temperature and on the solute–solvent potential parameters.⁷

Several simulation and integral equation studies have examined local density enhancement in dilute attractive LJ mixtures.^{21–23,27,28,31} Simulation studies, being computationally demanding, are typically restricted to a single system, such as pyrene in CO₂,²² DTBN in C₂H₆,²⁸ Xe in Ne,³¹ etc. Each model system is characterized by a different set of LJ parameters, and therefore a comparison between several studies does not allow one to isolate the effect of a given single parameter on the local density enhancement. At the same time, the approach based on the integral equation theories makes it possible to perform more extensive calculations, but it is clear from the previous section that the integral equation theory for homogeneous fluids—irrespective of the choice of the closure—cannot be expected to produce accurate results for attractive mixtures in the near-critical region, especially in the case of high asymmetry between solute and solvent potential parameters. In view of the above, the integral equation theory for inhomogeneous fluids, given its accuracy and relatively modest computational demands, becomes a natural choice for an extensive model study of attractive supercritical mixtures.

Following previous studies of the local density enhancement, we assume the local solvent density to be proportional to the solute's coordination number. The proportionality factor is obtained by comparing the actual density dependence of N_c to a certain reference density dependence.^{7,22,31} If the solute's local coordination number depended linearly on density, from $\rho^* = 0$ up to some high liquidlike density, say, $\rho^* = 0.9$, then one could define a reference coordination number by $N_c^{\text{ref}} = \rho N_c^{\text{max}} / \rho_{\text{max}}$, where in this case $\rho_{\text{max}}^* = 0.9$ and N_c^{max} is the value of N_c at ρ_{max} . The local solvent density enhancement results in nonlinear density dependence of N_c , and therefore the actual coordination number at a given density is generally different from N_c^{ref} . Hence, one can define the local density ρ_l by equating, for each bulk density, the

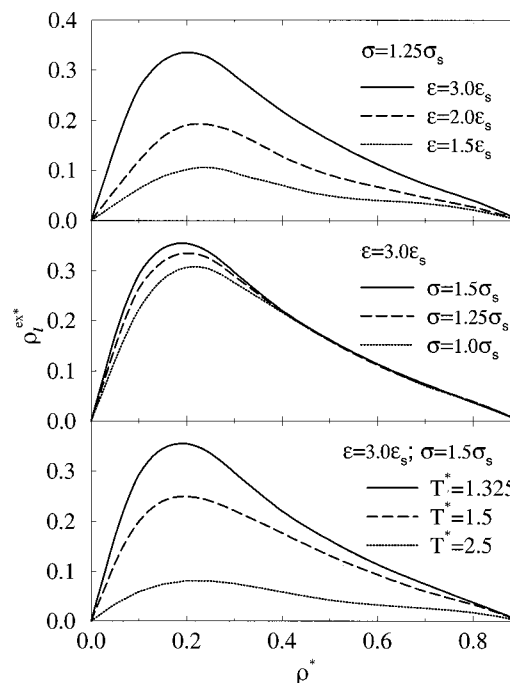


FIG. 4. Excess local density vs bulk solvent density for various model attractive mixtures.

reference coordination number evaluated at ρ_l to the actual coordination number N_c . This procedure leads to $\rho_l = N_c \rho_{\text{max}} / N_c^{\text{max}}$.

In order to illustrate that the above definition provides a reasonable estimate of the local density, we apply it to the Xe in the Ne system. Using our results for N_c at $T^* = 1.338$, we obtain $\rho_l^* = 0.50$ at the bulk density $\rho^* = 0.25$, and $\rho_l^* = 0.83$ at $\rho^* = 0.80$. At the same time, we recall that, for a given bulk density, the anisotropic direct correlation function for two Ne atoms in the vicinity of Xe agrees well with the corresponding isotropic result evaluated at a *higher* bulk density. The latter can be considered as an alternative estimate of the local solvent density, which gives $\rho_l^* = 0.46$ at $\rho^* = 0.25$ and $\rho_l^* = 0.83$ at $\rho^* = 0.80$ (see Fig. 2). One sees that the two estimates of ρ_l are in good agreement with each other. In what follows, we employ the definition $\rho_l = N_c \rho_{\text{max}} / N_c^{\text{max}}$ with $\rho_{\text{max}}^* = 0.9$. Since we are primarily interested in the local density *enhancement*, we do not consider ρ_l itself, but instead focus on the excess quantity, $\rho_l^{\text{ex}} = \rho_l - \rho$, which goes to zero both at $\rho^* = 0$ and at $\rho^* = 0.90$ for the present definition of ρ_l .

Proceeding to the model studies, we first examine the effect of the solute–solvent potential well depth on the local density enhancement. To this end, we set $\sigma/\sigma_s = 1.25$ and consider three model systems with the following values of the solute–solvent potential well depths, $\epsilon/\epsilon_s = 1.5, 2.0$, and 3.0 . The inhomogeneous PY theory results for ρ_l^{ex} in these three systems are shown in Fig. 4 as a function of bulk density along the isotherm $T^* = 1.325$ ($T_r = 1.01$). One sees that all three systems exhibit significant solvent density augmentation; ρ_l^{ex} first increases rapidly with density, passes through a maximum in the vicinity of $\rho^* \approx 0.2$ ($\rho_r \approx 0.6$), and then decreases gradually as one proceeds to liquidlike densities. It

is also clear that the increase in the solute–solvent potential well depth has a pronounced effect on ρ_l^{ex} ; in going from $\epsilon/\epsilon_s=1.5$ to $\epsilon/\epsilon_s=3.0$, the height of the maximum in the excess local density increases more than threefold. This is hardly surprising, since larger ϵ enhances the attractive behavior of the solute.²⁹ At the same time, changing the solute–solvent potential well depth does not affect the position of the maximum significantly; for all three systems ρ_l^{ex} peaks in the vicinity of $\rho_r \approx 0.6$, with the peak position shifting only slightly to lower densities as ϵ increases.

Next we turn to the effect of the solute size on the local density enhancement. Assuming that the size parameter σ in the solute–solvent potential is obtained using the Lorenz–Berthelot combining rules,⁴⁸ the solute diameter is equal to $(2\sigma - \sigma_s)$. To examine its effect on the excess local density, we set $\epsilon/\epsilon_s=3.0$ and calculate ρ_l^{ex} at $T^*=1.325$ for the following three model systems, $\sigma/\sigma_s=1.0, 1.25$, and 1.5 , i.e., the solute of the same size as the solvent, 50% larger, and twice as large as the solvent, respectively. The results for ρ_l^{ex} vs ρ are also presented in Fig. 4. One sees that the three curves are much closer to each other compared to the case of different ϵ values. This indicates that the solute size has a much weaker effect on the excess local density than the solute–solvent potential well-depth—at least, for the definition of ρ_l^{ex} employed in the present work. At liquidlike densities all three systems exhibit essentially the same local density, and the only significant differences are observed below the critical density; the maximum value of the excess density increases somewhat and the position of the maximum shifts slightly to lower densities as the solute size increases. We note in passing that the homogeneous PY theory (not shown here) is not only quantitatively in error, grossly overestimating ρ_l^{ex} in all cases, but is also qualitatively incorrect; it predicts a significant increase in the excess local density with increasing solute size for a given potential well depth.

Finally, from our results for Xe in Ne it can be anticipated that the local density enhancement for a given system depends on the solvent temperature. Taking $\epsilon/\epsilon_s=3.0$ and $\sigma/\sigma_s=1.5$, we calculate ρ_l^{ex} as a function of bulk density along the following three isotherms: $T^*=1.325, 1.5$, and 2.5 ($T_r=1.01, 1.14$, and 1.91); the results are also shown in Fig. 4. One sees that the maximum in the excess local density decreases substantially as the temperature is increased. This behavior explains the satisfactory performance of the homogeneous PY theory for the Xe in Ne mixture observed at the highest isotherm in Fig. 3; at this temperature the local density enhancement becomes small enough for the homogeneous integral equation approach to produce accurate results.

To summarize, given the presently adopted definition of the local solvent density, its enhancement around a dilute solute in attractive mixtures increases with the solute–solvent attraction strength, decreases with temperature, and is only weakly dependent on the solute size.

V. CONCLUSION

In this work we studied the local solute–solvent structure in dilute supercritical solutions. We employed a model based on isotropic pairwise additive potentials of the LJ

form, and focused on attractive LJ mixtures, which are characterized by a local solvent density enhancement around the solute molecule. To calculate the solute–solvent radial distribution function, we employed the inhomogeneous fluid theory, in which the solute particle serves as a source of the local solvent density inhomogeneity.

We first considered a particular attractive mixture (Xe in Ne), for which extensive simulation results are available. We calculated the solute–solvent radial distribution function and the solute’s local coordination number as a function of the solvent density at several temperatures. The integral equation theory for inhomogeneous fluids was found to be in excellent agreement with simulation at all thermodynamic conditions, and was shown to provide a substantial improvement over the theory formulated for uniform fluids. It was suggested that the reasons for this superior performance are twofold. First, the inhomogeneous fluid theory explicitly takes into account the effect of the solute on the solvent pair correlation functions, which is crucial when the local environment around the solute differs dramatically from the bulk. Second, the theory involves only one approximate closure relation, as opposed to two such relations in its homogeneous counterpart.

Equipped with an accurate theory of the local structure of supercritical solutions, we performed a quantitative study of the local solvent density enhancement in dilute attractive mixtures. In particular, we analyzed its dependence on the solute–solvent potential parameters, and on the solvent thermodynamic conditions. It was shown that the local density augmentation increases with the solute–solvent attraction strength, decreases with temperature, and is only weakly varying with the solute size.

Finally, we note that the local solute–solvent structure studied in this work can be probed experimentally in spectroscopic studies. The local solvent density enhancement is reflected in the unusual density dependence of solvatochromic shifts, which has been observed in numerous experimental studies of supercritical solutions.^{7–9} The inhomogeneous fluid theory can be employed to perform a quantitative analysis of the experimental spectroscopic data; this will be the subject of future research.

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¹ *Supercritical Fluid Engineering Science*, edited by E. Kiran and J. F. Brennecke, ACS Symposium Series No. 514 (American Chemical Society, Washington, D.C., 1993).

² *Supercritical Fluids: Fundamentals for Applications*, edited by E. Kiran and J. M. H. Levelt Singers (Kluwer, Dordrecht, 1994).

³ C. A. Eckert, B. L. Knutson, and P. G. Debenedetti, *Nature (London)* **383**, 313 (1996).

⁴ J. Kauffman, *Anal. Chem.* **68**, 248 (1996).

⁵ K. P. Johnston and C. Haynes, *AIChE. J.* **33**, 2017 (1987).

⁶ T. L. Chester, J. D. Pinkston, and D. E. Raynie, *Anal. Chem.* **70**, 301R (1998).

⁷ S. C. Tucker, *Chem. Rev.* **99**, 391 (1999).

- ⁸Y.-P. Sun and C. E. Bunker, Ber. Bunsenges. Phys. Chem. **99**, 976 (1995).
- ⁹R. Biswas, J. E. Lewis, and M. Maroncelli, Chem. Phys. Lett. **310**, 485 (1999).
- ¹⁰O. Kajimoto, M. Futakami, T. Kobayashi, and K. Yamasaki, J. Phys. Chem. **92**, 1347 (1988).
- ¹¹S. Kim and K. P. Johnston, AIChE. J. **33**, 1603 (1987).
- ¹²J. F. Brennecke, D. L. Tomasko, J. Peshkin, and C. A. Eckert, Ind. Eng. Chem. Res. **29**, 1682 (1990).
- ¹³C. Carlier and T. W. Randolph, AIChE. J. **39**, 876 (1993).
- ¹⁴J. Zhang, L. L. Lee, and J. F. Brennecke, J. Phys. Chem. **99**, 9268 (1995).
- ¹⁵R. D. Schulte and J. F. Kauffman, Appl. Spectrosc. **49**, 31 (1995).
- ¹⁶K. Takahashi, K. Abe, S. Sawamura, and C. D. Jonah, Chem. Phys. Lett. **282**, 361 (1998).
- ¹⁷J. Lu, B. Han, and H. Yan, Ber. Bunsenges. Phys. Chem. **102**, 695 (1998).
- ¹⁸L. W. Flanagan, P. B. Balbuena, K. P. Johnston, and P. J. Rossky, J. Phys. Chem. **99**, 5196 (1995).
- ¹⁹R.-S. Wu, L. L. Lee, and H. D. Cochran, Ind. Eng. Chem. Res. **29**, 977 (1990).
- ²⁰R.-S. Wu, L. L. Lee, and H. D. Cochran, J. Supercrit. Fluids **5**, 192 (1992).
- ²¹A. A. Chialvo and P. T. Cummings, AIChE. J. **40**, 1558 (1994).
- ²²B. L. Knutson, D. L. Tomasko, C. A. Eckert, P. G. Debenedetti, and A. A. Chialvo, *Supercritical Fluid Technology*, edited by F. V. Bright and M. E. McNally (American Chemical Society, Washington, D.C., 1992).
- ²³J. W. Tom and P. G. Debenedetti, Ind. Eng. Chem. Res. **32**, 2118 (1993).
- ²⁴T. W. Li, F. Munoz, and E. H. Chimowitz, AIChE. J. **39**, 1985 (1993).
- ²⁵I. B. Petsche and P. G. Debenedetti, J. Chem. Phys. **91**, 7075 (1989).
- ²⁶H. Tanaka, J. W. Shen, K. Nakanishi, and X. C. Zeng, Chem. Phys. Lett. **239**, 168 (1995).
- ²⁷F. Munoz and E. H. Chimowitz, Fluid Phase Equilibria **71**, 237 (1992).
- ²⁸J. A. O'Brien, T. W. Randolph, C. Carlier, and S. Ganapathy, AIChE. J. **39**, 1061 (1993).
- ²⁹I. B. Petsche and P. G. Debenedetti, J. Phys. Chem. **95**, 386 (1991).
- ³⁰J. P. Hansen and I. R. McDonald, *Theory of Simple Liquids*, 2nd ed. (Academic, London, 1986).
- ³¹S. A. Egorov, A. Yethiraj, and J. L. Skinner, Chem. Phys. Lett. **317**, 558 (2000).
- ³²D. Henderson, in *Fundamentals of Inhomogeneous Fluids*, edited by D. Henderson (Dekker, New York, 1992), p. 177.
- ³³D. Henderson and S. Sokolowski, J. Chem. Phys. **62**, 1544 (1975).
- ³⁴D. M. Duh, D. Henderson, L. Mier-Y-Teran, and S. Sokolowski, Mol. Phys. **90**, 563 (1997).
- ³⁵P. Attard, J. Chem. Phys. **91**, 3072 (1989).
- ³⁶P. Attard, J. Chem. Phys. **91**, 3083 (1989).
- ³⁷P. Attard, J. Chem. Phys. **95**, 4471 (1991).
- ³⁸M. Fushiki, Mol. Phys. **74**, 307 (1991).
- ³⁹B. Bildstein and G. Kahl, Phys. Rev. E **52**, 2668 (1995).
- ⁴⁰M. Plischke and D. Henderson, J. Chem. Phys. **84**, 2846 (1986).
- ⁴¹R. Kjellander and S. Sarman, Mol. Phys. **70**, 215 (1990).
- ⁴²J. D. Weeks, K. Katsov, and K. Vollmayr, Phys. Rev. Lett. **81**, 4400 (1998).
- ⁴³D. G. Trizenberg and R. Zwanzig, Phys. Rev. Lett. **28**, 1183 (1972).
- ⁴⁴R. A. Lovett, C. Y. Mou, and F. P. Buff, J. Chem. Phys. **58**, 1880 (1976).
- ⁴⁵M. S. Wertheim, J. Chem. Phys. **65**, 2377 (1976).
- ⁴⁶M. Born and H. S. Green, Proc. R. Soc. London, Ser. A **188**, 10 (1946).
- ⁴⁷J. J. Potoff and A. Z. Panagiotopoulos, J. Chem. Phys. **109**, 10914 (1998).
- ⁴⁸M. P. Allen and D. J. Tildesley, *Computer Simulation of Liquids* (Clarendon, Oxford, 1987).