PHYSICAL REVIEW A VOLUME 40, NUMBER 11 DECEMBER 1, 1989

Critical behavior of the hypernetted-chain equation for a Lennard-Jones mixture

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(Received 6 July 1989)

The hypernetted-chain (HNC) approximation is applied to study the critical behavior of a Lennard-Jones mixture. The parameters of the model potential are appropriate to describe a He-Xe mixture in the thermodynamic region where "gas-gas phase separation" is known to occur. The locus of points in the temperature-concentration plane where the $k \rightarrow 0$ limit of the concentration-concentration structure factor $S_{cc}(k)$ diverges, i.e., the spinodal line, is determined through an extrapolation of the HNC results from the region where this integral equation is solvable, toward the phase stability boundary, where the algorithm becomes highly unstable and no solution can be found. The extrapolation is based on a power-law behavior of $S_{cc}(0)$ that is verified to hold in the realm of the available results. The critical temperature and concentration so obtained compare quite favorably with the experimental data.

I. INTRODUCTION

In recent years various authors[1-8] have studied the behavior of one-component fluids near the critical point in the context of integral-equation theories. Special attention has been received by the critical behavior of the hypernetted-chain (HNC) equation which has been carefully investigated in a recent paper by Poll and Ashcroft.[4] These authors showed that for a model fluid system described by a pair potential with a highly repulsive core and an attractive well, there exists a locus of temperature below which no physical solution to the HNC can be found, and on which the isothermal compressibility κ_T remains finite. Such a behavior persists up to densities near the triple point density where κ_T actually diverges, following a power law and a true spinodal exists.

Similar studies involving the HNC, or other approximations, have been performed for charged fluids,[9,10] and charged fluid mixtures,[11,12] where it is found that the HNC solution procedure becomes highly unstable in the approach to the phase stability boundary; in this case the location of the "spinodal" is obtained through an extrapolation procedure of the available results.

The integral-equation approach has also been used for studying the critical behavior of mixtures of simple fluids. Mixtures of hard-sphere Yukawa fluids have been investigated elsewhere[13] in the framework of the mean spherical approximation, while soft-sphere potential mixtures have been studied through the Roger-Young equation.[14]

In this paper we extend the investigation of the critical behavior of the HNC equation to Lennard-Jones (LJ) mixtures. We follow the approach to the phase stability boundary in these systems through the calculation of the $k=0$ limit of the concentration-concentration structure factor $S_{cc}(k)$. The LJ parameters we choose correspond to those of a He-Xe mixture, and the pressure is fixed high enough so as to correspond to the thermodynamic conditions where "gas-gas phase separation" is experimentally known to occur.[15-17] In the He-Xe mixture the atomic sizes and the interaction potential parameters differ substantially from one species to another so that, also according to recent computer simulation studies of LJ mixtures,[18-21] phase separation should occur relatively easily in our model.

The basic theoretical approach is described in Sec. II, while the results are reported and discussed in Sec. III. Section IV contains some concluding remarks.

II. THEORY

Concentration fluctuations in fluid mixtures are described by the concentration-concentration structure factor $S_{cc}(k)$ which for a binary mixture can be expressed in terms of the partial structure factors,[22,23]

$$S_{cc}(k)=c(1-c)\{(1-c)S_{11}(k)+cS_{22}(k) -2[c(1-c)]^{0.5}S_{12}(k)\} \ . \tag{1}$$

Here c is the concentration of species (1) defined as

$$c=N_1/(N_1+N_2)$$

and N_1 and N_2 are the number of particles of the type 1 and 2, respectively.

As is well known,[22,23] the long-wavelength limit $(k \rightarrow 0)$ of $S_{cc}(k), S_{cc}(0)$, is related to the second derivative of the Gibbs free energy of mixing G_M, with respect to the concentration

$$S_{cc}(0)=N\,k_B T/(\partial^2 G_M/\partial c^2)_{T,P} \ , \tag{2}$$

where N is the total number of particles.

From Eq. (2) it follows that $S_{cc}(0)$ diverges for all points where the concavity of the G_M versus c curve changes sign, that is, where

$$(\partial^2 G_M/\partial c^2)_{T,P}=0 \ . \tag{3}$$

The locus of points in the T-c plane on which, for every fixed pressure, Eq. (3) is satisfied, is the spinodal line of the mixture. The portion of the plane inside the curve corresponds to the instability region of the mixture. The spinodal line lies inside the so-called binodal line, or the phase diagram, which can be obtained from the Gibbs free energy of mixing through the common tangent procedure.[24] The two curves coincide at the critical consolution points(s), for which critical temperature(s) and concentration(s), $T_{\rm cr}$ and $c_{\rm cr}$, can be defined.

The interaction potential for the particles of the binary mixture is the LJ (12-6) potential

$$v_{ij}(r)=4\epsilon_{ij}[(\sigma_{ij}/r)^{12}-(\sigma_{ij}/r)^{6}],\quad i,j=1,2\ . \tag{4}$$

In order to calculate $S_{cc}(0)$ we make use of the hypernetted-chain integral equation (HNC) which for our model can be written as

$$g_{ij}(r)=\exp[-\beta v_{ij}(r)+h_{ij}(r)+c_{ij}(r)]\ , \tag{5}$$

where $g_{ij}(r)=h_{ij}+1$ is the radial distribution function, $\beta=(k_BT)^{-1}$, and $c_{ij}(r)$ is the Ornstein-Zernike direct correlation function defined by the relation

$$h_{ij}(r)=c_{ij}(r)+\sum_{l=1}^{2}\rho_l\int d\mathbf{r}'h_{il}(|\mathbf{r}-\mathbf{r}'|)c_{lj}(r')\ , \tag{6}$$

where ρ_i is the number density of the ith species. In our case $\rho_1=c\rho$ and $\rho_2=(1-c)\rho$, ρ, being the total number density of particles.

For numerical convenience Eq. (6) is rewritten in terms of $c_{ij}(r)$ and $\theta_{ij}(r)=h_{ij}(r)-c_{ij}(r)$ to obtain

$$c_{ij}(r)=\exp[-\beta v_{ij}(r)+\theta_{ij}(r)]-\theta_{ij}(r)-1\ . \tag{7}$$

Equations (6) and (7) are solved for a given density ρ, concentration c, and temperature T through an iterative procedure which has been described in detail elsewhere.[25]

From the knowledge of $h_{ij}(r)$ the partial structure factors are calculated via Fourier transform and from them, finally, the concentration-concentration structure factor $S_{cc}(k)$. Most of the calculations were carried out on a grid with a real-space step $\Delta r=0.02\sigma_{\text{Xe-Xe}}$ and a total number of points $N=1024$; however, checks have been made of the stability of the results for those cases where convergence was more difficult to obtain, by using $N=2048$ and various Δr. No significant variation was found with these different grids.

We approach the phase stability boundary along a thermodynamic path for which the concentration is initially fixed, and for each chosen temperature the density of the mixture is varied until the HNC estimate of the pressure attains a prefixed value. We obtain in this manner the value of $S_{cc}(0)$ corresponding to, say, pressure P^*, temperature T^*, and concentration c^*, denoted in what follows $S(P^*,T^*,c^*)$. This calculation is then repeated, at the same prefixed pressure, for a discrete set of concentration values. If T^* is sufficiently high, solutions exist to the HNC equation all over the concentration range from $c=0$ to $c=1$. By reporting the values of $S_{cc}(0)$ as a function of the concentration we obtain a bell-shaped curve $S(P^*,T^*,c)$ (see Fig. 1), which is obviously zero at the pure component limits and, in the present case, has a maximum at $c\simeq0.5$.

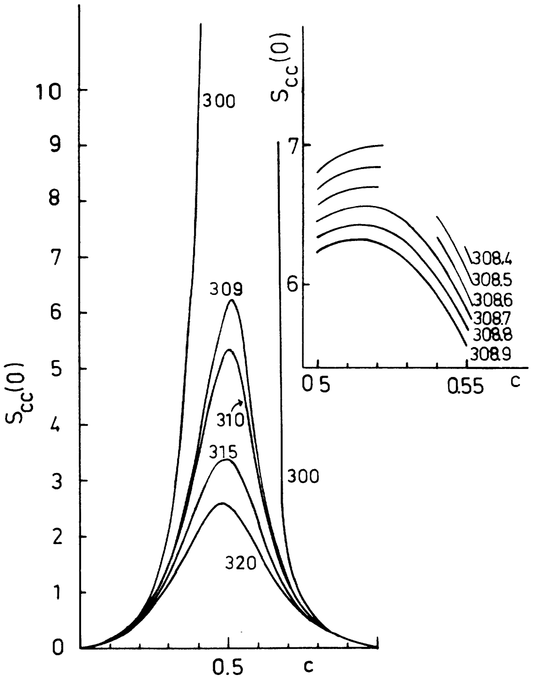

FIG. 1. $S_{cc}(0)$ plotted as a function of the concentration for the He-Xe mixture at a pressure of 695 bar and various temperatures. In the inset: an expanded representation of the critical point region.

As the temperature decreases, and the spinodal is approached, $S_{cc}(0)$ increases for every value of c, with a rate which is higher in correspondence approximately of the maximum of the curve, and the convergence rate becomes slower and slower, until no solution can be found.

If we consider a fixed value of the concentration c^* and report the value of $S_{cc}(0)$ as function of temperature we obtain a curve $S(P^*,T,c^*)$ which increases as the temperature decreases. A description of this behavior can be attempted by using a power law, as detailed in Sec. III.

III. RESULTS

As mentioned above, phase separation in the He-Xe mixture has been experimentally investigated in the past (De Swaan Arons and Diepen,[15] J. Zanderbergen *et al.*,[16] Trappeniers and Schouten[17]). We consider this mixture subject to a pressure of 695 bar, for which the experimental upper critical mixing point is located at $T_{\rm cr}=305.2$ K and $c_{\rm cr}=0.51$. The He-Xe mixture has been investigated by Hoheisel[20] in the high-pressure regime, and we shall assume for the parameters ϵ_{ij} and σ_{ij}, appearing in the potential (4), the same values as those used in his molecular-dynamics simulation. Before discussing the results, it is worth observing that these LJ parameters were obtained in Ref. 20 through a series of computer simulation runs, where the densities were fixed on the basis of the Redlich-Kwong equation of state, and the experimental compressibility factors were fitted in the high-pressure range. For the particular pressure chosen we can there-

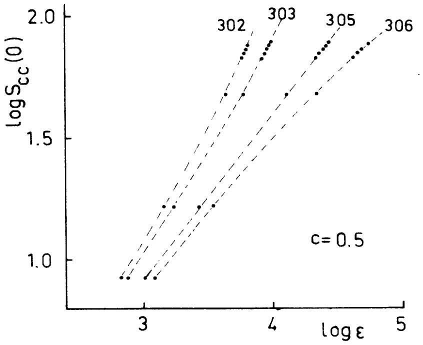

FIG. 2. Log-log plot of $S_{cc}(0)$ vs the reduced temperature ϵ at fixed concentration $c=0.5$; labels on the curve are values of T_∞ (see text for the definitions). The dots correspond to calculated values; the dashed lines are guides for the eye.

fore regard the potential adopted as very accurate, in the sense that the "exact" numerical procedure reproduces the experimental values for the pressure.

In Fig. 1 $S_{cc}(0)$ is shown as a function of the concentration at different temperatures. At the higher temperature considered, $T=320$ K, the curve has a maximum at $c_M=0.48$. As the temperature is decreased, $S_{cc}(0)$ increases at each value of the concentration. The maximum shifts slightly toward higher values of the concentration and, at $T=308.6$ K, we find $c_M=0.52$. Below this temperature the HNC algorithm fails to reach convergence in a range of concentrations which becomes wider and wider the more the temperature is lowered.

The HNC failure is attained before a real divergence of $S_{cc}(0)$ is reached, so that, in order to find the temperature $T_\infty(c)$ at which, for the given concentration, $S_{cc}(0)$ diverges, we need some extrapolation procedure. For this purpose, similarly to what has been done elsewhere,[11,12] we assume that $S_{cc}(0)$ tends to diverge as

$$S_{cc}(0) \propto (T-T_\infty)^{-\gamma}, \quad T \to T_\infty^+ .$$

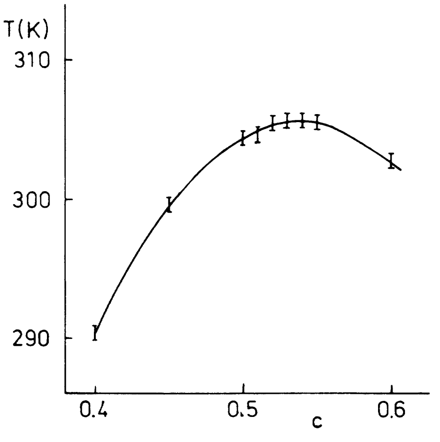

FIG. 3. Spinodal curve estimated from the HNC for the He-Xe mixture at 695 bar. The vertical bars correspond to the estimated error in T_∞ induced by the numerical procedure adopted.

In order to check if our results conform to such a law we report in a log-log plot $S_{cc}(0)$ versus the reduced temperature $\epsilon=(T-T_\infty)/T_\infty$. For each value of the concentration we find it possible to adjust the value of T_∞ so to produce a linear behavior in such a plot. This is shown in Fig. 2 for the particular case $c=0.5$, and confirms that $S_{cc}(0)$, obtained from the HNC calculations, diverges with $\epsilon \to 0$ following a power law. The value of γ does not vary very much with concentration, ranging about $\gamma=0.75$. The experimental value is $\gamma \simeq 1.2$.[26]

We report the temperature T_∞ as a function of c, in Fig. 3. This curve defines our spinodal line; it shows a maximum which corresponds to the critical temperature of mixing T_{cr}, and the critical concentration c_{cr}. We estimate from our figure $c_{cr} \simeq 0.515$ and $T_{cr} \simeq 305.6$; these values are remarkably close to the experimental data.

IV. CONCLUDING REMARKS

We have shown how the HNC approximation scheme can be used in order to describe the critical behavior of dense simple fluid mixtures. For the particular case investigated, that is, the He-Xe mixture, the predictions of the theory compare quite favorably with the experimental data for both the critical temperature and concentration. Moreover, the theory shows a power-law behavior in the approach to the phase separation boundary.

This behavior of the HNC seems similar to the one exhibited by this same theory for the model potential investigated by Poll and Ashcroft;[4] in fact, in that case the isothermal compressibility diverged with a power law in the high-density regime.

Obviously, if the HNC solution could be obtained closer to the spinodal line, the extrapolation described above would become more and more accurate. Such an improvement requires stabilizing the algorithm of solution in the approach to the critical region. Attempts in this sense are reported in the recent literature and seem encouraging.[27]

The HNC estimate of the critical exponent is not correct; however, with reference to this point, it is necessary to remember that the HNC neglects the contribution of bridge diagrams, which play an important role[3,4] in determining the power-law behavior of the integral equation.

Finally, we observe that in recent years there has been substantial progress in the achievement of new computer simulation techniques aimed to tackle the problem of phase coexistence in fluids.[18–21,28] However, these simulations are quite demanding, requiring a great number of particles and a substantial sampling of the phase space. In such a situation the predictions of a microscopic theoretical approach, even with the limitations discussed above, could prove useful for a comparison with simulation results.

ACKNOWLEDGMENTS

This work was supported by the Centro Interuniversitario Struttura della Materia of Ministero Italiano della Pubblica Istruzione and Gruppo Nazionale Struttura della Materia of Consiglio Nazionale delle Ricerche.

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