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Integral equation approaches to mixtures of atomic and molecular fluids

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A recent extension to mixtures of Verlet's closure is applied in conjunction with the Ornstein–Zernike relation to solve the structure and thermodynamics of mixtures of hard-spheres and homonuclear hard-dumbbells. This integral equation (IE), which is proven to be very accurate when compared with simulation data, is used to explore the possibility of phase separation in an asymmetric mixture. While our results do not show evidence of such phase separation in the asymmetric binary hard-sphere mixture studied by Biben and Hansen [T. Biben and J. P. Hansen, *Phys. Rev. Lett.* **66**, 2215 (1991)], an equivalent mixture of hard-dumbbells and large hard-spheres seems to exhibit a certain tendency to phase separate as far as the integral equation results are concerned. Finally, given the ability of this integral equation to reproduce the hard-core system, we have incorporated these results into a previous Reference Hypernetted Chain scheme to treat a mixture of N_2 and Ar modeled by means of site–site Lennard-Jones potentials. In consonance with the results for pure fluids, the parameterization of a hard-core reference system with the same molecular shape leads to excellent results both for the structure and thermodynamics of real systems. © 1997 American Institute of Physics. [S0021-9606(97)50605-2]

I. INTRODUCTION

A great amount of work has been dedicated over the years to the development of accurate integral equation approximations (IE) for simple fluids, both from first principles: Percus–Yevick (PY), Hypernetted Chain (HNC), Reference Hypernetted Chain (RHNC), and from more empirical approaches, as is the case of the Verlet's Modified closure (VM),¹ or the more recent family of closures based on the renormalization of the indirect correlation function (see Duh and Haymet² and Duh and Henderson³) which in some case might incorporate thermodynamic self-consistency criterion.⁴

In this connection, one of the most successful approaches, both for atomic and very specially for molecular fluids, results from the combination of the RHNC with a semiempirical integral equation (VM) which is used to evaluate the properties of an appropriate reference fluid which adequately accounts for the geometry of the particles of the real fluid. An additional empirical assumption is required in order to establish the optimum reference fluid (which typically is a hard-core system). In Refs. 5 and 6 various parametric formulas were derived fitting simulation data for selected thermodynamic states. An alternative, slightly more demanding computationally speaking, would imply the use of some consistency criterion. This later path has led to excellent results for the calculation of phase diagrams of molecular fluids.⁷ Along the same lines, related approximations have been proposed to deal with mixtures of simple fluids such as the optimized RHNC,⁸ Hybrid Mean Spherical Approximation (HMSA),⁹ or Duh–Henderson's empirical closure.³ For the special case of mixtures of additive hard-spheres, Henderson *et al.*¹⁰ have very recently pre-

sented an extension of the modified Verlet's closure which yields excellent results for a wide range of densities and compositions. An obvious step forward is the treatment of mixtures of molecular and atomic fluids. This problem is not only relevant in itself, since it is by no means clear that those approximations valid for the simple fluid mixtures will be equally accurate now, but it is of significance in problems such as the high-pressure gas–gas separation of noble and molecular gases (such as the separation found in the He- H_2 mixture¹¹). Therefore, we present here a straightforward extension of Henderson *et al.* variant of the VM integral equation, which we have tested for mixtures of hard-sphere plus a hard-dumbbell fluids. With this closure we have explored the possibility of a phase separation for highly asymmetric mixtures, both of hard-spheres (HS), a system studied by Biben and Hansen few years ago in the HMSA,¹² and large hard-spheres plus small hard-dumbbells (HS-HD). Although inconclusive as the integral equation results may be, there seems to be a clear indication of a demixing tendency in the HS-HD system, which is completely absent in the HS mixture results for the size ratios considered herein.

Once the quality of the IE results for the HS-HD mixture was assessed, we proceed to incorporate the resulting bridge functions in a RHNC scheme for a mixture of N_2 +Ar in which N_2 interactions are modeled with a two-center LJ potential and Ar interactions are defined in terms of a simple LJ potential. Using the expressions previously introduced to define hard-core reference systems for two-center heteronuclear LJ fluids,⁶ one can describe the geometry of our new reference system and solve it in the VM approach. This combination, again denoted by RHNC-VM, will show once more an excellent ability to describe the properties of real systems, in this case the N_2 -Ar mixture. The study of high pressure

demixing for other systems of interest seems now attainable by this type of IE methods and will be the subject of forthcoming work.

The rest of the paper is organized as follows. In Sec. II we present the key equations relevant to the VM approximation for the HS-HD mixtures and we recall the essentials of the RHNC-VM scheme, in particular the parameterization of the reference system. Results for the hard-core mixtures as well as the theoretical study of the demixing transition in the highly asymmetric case are presented in Sec. III. Finally the most significant results for the N₂-Ar mixture are collected in Sec. IV.

II. THEORETICAL BACKGROUND

In a recent paper, Henderson *et al.*¹⁰ proposed an extension of the VM approximation for the bridge function $B^{\alpha\beta}(r)$ in mixtures of hard-spheres such that

$$B^{\alpha\beta}(r) = -\frac{1}{2} \frac{\gamma^{\alpha\beta}(r)^2}{1 + \vartheta^{\alpha\beta} \gamma^{\alpha\beta}(r)}, \quad (1)$$

where $\gamma^{\alpha\beta} = h^{\alpha\beta} - c^{\alpha\beta}$, being $h^{\alpha\beta}$ and $c^{\alpha\beta}$ the total and direct correlation function, respectively, and with the parameters $\vartheta^{\alpha\beta}$ adjusted so that $B^{\alpha\beta}(0)$ be exact at low densities. α, β superscripts denote the different species involved. Following previous work on pure hard-spheres,

$$\vartheta^{\alpha\beta} = a_{\alpha\beta} e^{2\xi} + 0.8 - 0.45\xi \quad (2)$$

with

$$\xi = \frac{\pi}{6} \rho (x_1 d_{11}^3 + x_2 d_{22}^3), \quad (3)$$

where ρ is the number density and x_i and d_{ii} are the mole fraction and hard-sphere diameter of component i , respectively. These authors found for $a_{\alpha\beta}$ the values

$$a_{11} = \frac{3}{4\pi\rho(x_1 d_{11}^3 + x_2 d_{12}^3)} \times \left[-\frac{16\pi^2(x_1 d_{11}^3 + x_2 d_{12}^3)^2}{9(x_1^2 C_{111} + 2x_1 x_2 C_{112} + x_2^2 C_{122})} - 1 \right],$$

$$a_{12} = a_{11}, \quad (4)$$

$$a_{22} = \frac{3}{4\pi\rho(x_1 d_{12}^3 + x_2 d_{22}^3)} \times \left[-\frac{16\pi^2(x_1 d_{12}^3 + x_2 d_{22}^3)^2}{9(x_1^2 C_{112} + 2x_1 x_2 C_{122} + x_2^2 C_{222})} - 1 \right],$$

where

$$C_{111} = -\frac{5\pi^2}{6} d_{11}^6,$$

$$C_{112} = -\frac{\pi^2}{18} (32d_{12}^3 - 18d_{11}d_{12}^2 + d_{11}^3)d_{11}^3,$$

$$C_{122} = -\frac{\pi^2}{18} (32d_{12}^3 - 18d_{22}d_{12}^2 + d_{22}^3)d_{22}^3,$$

$$C_{222} = -\frac{5\pi^2}{6} d_{22}^6. \quad (5)$$

An obvious extension to treat mixtures of hard dumbbells consists in replacing the hard-sphere diameter in Eqs. (4)–(5) by the equivalent sphere diameter,

$$d_{\text{eq}}^3 = \frac{1}{2} d_a \left[(1 + \gamma^3) + \frac{3}{2} L^* (1 + \gamma^2) - L^{*3} + \frac{3}{16} \frac{(1 - \gamma^2)^2}{L^*} \right], \quad (6)$$

where $\gamma = d_b/d_a$, $L^* = L/d_a$, with d_a and d_b being the diameters of the constituent spheres in the dumbbell and L is the elongation.

We have thus solved the Ornstein–Zernike (OZ) equation, which in the case of our mixture reads

$$\gamma^{\alpha\beta}(12) = \sum_{\lambda} \rho_{\lambda} \int C^{\alpha\lambda}(13) [\gamma^{\alpha\lambda}(32) + C^{\lambda\beta}(32)] d\mathbf{3} \quad (7)$$

coupled with the closure

$$c^{\alpha\beta}(12) = \exp[-u^{\alpha\beta}(12) + \gamma^{\alpha\beta}(12) - B^{\alpha\beta}(12)] - 1 - \gamma^{\alpha\beta}(12), \quad (8)$$

where $B^{\alpha\beta}(12)$ is given by Eq. (1). As usual our solution method will rely on the spherical harmonic expansion of the pair functions, which for some of them will be now particularly simple. Thus

$$f^{AA}(12) = f^{AA}(r),$$

$$f^{AM}(12) = \sqrt{4\pi} \sum_{m_1, \chi} f_{0m_1\chi}^{AM}(r) Y_{m_1\chi}(\omega_1),$$

$$f^{MA}(12) = \sqrt{4\pi} \sum_{m_2, \chi} f_{0m_2\chi}^{MA}(r) Y_{m_2\chi}(\omega_2),$$

$$f^{MM}(12) = 4\pi \sum_{m_1, m_2, \chi} f_{m_1 m_2 \chi}^{MM}(r) Y_{m_1\chi}(\omega_1) Y_{m_2\chi}(\omega_2),$$

where A and M refer to atomic and molecular species. With this, it has been shown elsewhere¹³ that the OZ equation decouples in Fourier space as

$$\tilde{\gamma}_{m_1 m_2 \chi}^{\alpha\beta}(k) = (-1)^{\chi} \sum_{\lambda} \rho_{\lambda} \sum_{m_3} \tilde{c}_{m_3 m_2 \chi}^{\alpha\lambda}(k) [\tilde{\gamma}_{m_3 m_2 \chi}^{\lambda\beta}(k) + \tilde{c}_{m_3 m_2 \chi}^{\lambda\beta}(k)]. \quad (9)$$

Now if we define matrices $\tilde{\Gamma}_{\chi}(k)$ and $\tilde{\mathbf{C}}_{\chi}(k)$ whose elements are in turn sub-matrices $\tilde{\Gamma}_{\chi}^{\alpha\beta}$ and $\tilde{\mathbf{C}}_{\chi}^{\alpha\beta}$ with elements

TABLE I. Compressibility factor results for hard-sphere plus hard-dumbbell mixtures.

Z	$\rho^*=0.6 \quad x_m=1/2$			$\rho^*=0.6 \quad x_m=1/3$			$\rho^*=0.45 \quad x_m=0.1$			$\rho^*=0.45 \quad x_m=0.9$		
	HNC	VM	MC	HNC	VM	MC	HNC	VM	MC	HNC	VM	MC
total	11.868	9.433	9.516±0.351	8.087	6.743	6.815±0.175	3.414	3.159	3.180±0.064	9.944	8.145	8.226±0.143
M-M	3.983	3.055	3.080±0.139	1.103	0.878	0.888±0.041	0.048	0.042	0.044±0.008	7.768	6.194	6.269±0.100
M-A	5.212	4.057	4.113±0.156	3.405	2.751	2.821±0.080	0.592	0.525	0.533±0.023	1.136	0.918	0.919±0.034
A-A	1.673	1.320	1.323±0.056	2.579	2.114	2.105±0.054	1.775	1.591	1.604±0.033	0.041	0.033	0.038±0.009

$\tilde{\gamma}_{m_1 m_2 \chi}^{\alpha\beta}(k)$ and $\tilde{c}_{m_1 m_2 \chi}^{\alpha\beta}(k)$ respectively, and $m_1, m_2 > \chi$, then it is possible to rewrite Eq. (9) in matrix form

$$\tilde{\Gamma}_\chi(k) = [(-1)^\chi \mathbf{I} - \mathbf{D}\tilde{\mathbf{C}}_\chi(k)]^{-1} \rho \tilde{\mathbf{C}}_\chi(k) \tilde{\Gamma}_\chi(k) \quad (10)$$

with \mathbf{D} and \mathbf{I} being, respectively, a diagonal matrix with elements ρ_λ and the identity matrix. Thus, the closure relation reads

$$c_{m_1 m_2 \chi}^{\alpha\beta}(r) = \langle \exp[-\beta u^{\alpha\beta}(12) + \gamma^{\alpha\beta}(12) + B^{\alpha\beta}(12)] | m_1 m_2 \chi \rangle - 1 - \gamma_{m_1 m_2 \chi}^{\alpha\beta}(r), \quad (11)$$

where $\langle \dots | m_1 m_2 \chi \rangle$ denotes the projection onto the spherical harmonic coefficients $Y_{m_1 \chi}(\omega_1) Y_{m_2 \chi}(\omega_2)$. The bridge function is given again by Eqs. (1)–(5), and finally one must recall that the $\gamma^{\alpha\beta}(12)$ functions for the molecule-molecule and atom-molecule contributions must be obtained by resummation of the spherical harmonic series, which for these particular functions is rapidly convergent. As seen in Ref. 10, the VM closure will yield an excellent approximation for the mixture of hard-core systems, but previous experience has shown that its use for potentials with attractive component is not encouraging. However, since use of modern numerical techniques makes feasible the solution of the complete set of equations in a relatively short computer time, we can incorporate the hard-core calculated bridge function, which will be denoted $B_{\text{HC}}^{\alpha\beta}(12)$, into a RHNC closure

$$c^{\alpha\beta}(12) = \exp[-u^{\alpha\beta}(12) + \gamma^{\alpha\beta}(12) - B_{\text{HC}}^{\alpha\beta}(12)] - 1 - \gamma^{\alpha\beta}(12) \quad (12)$$

for our system of interest, i.e. the mixture of a two-center LJ plus an atomic LJ fluid. As to the definition of the molecular geometry of the reference system, we have simply resorted to the parameterized expressions which have been shown to produce excellent results for heteronuclear diatomic systems.⁶ Hence the hard-core diameters corresponding to a given LJ interaction defined by the standard $\epsilon_{\alpha\alpha}$ and $\sigma_{\alpha\alpha}$ are given by

$$d_{\alpha\alpha} = \sigma_{\alpha\alpha} g(\gamma) [25 - \ln(k_B T / \epsilon_{\alpha\alpha})] [25 + \ln(\rho \sigma_{\alpha\alpha}^3)], \quad (13)$$

where

$$g(\gamma) = \alpha \left[1 - h \left(\frac{1-\gamma}{1+\gamma} \right)^2 \right] \quad (14)$$

with $\alpha = 1.62 \times 10^{-3}$, $h = 0.88$ and $\gamma = \sigma_{\beta\beta} / \sigma_{\alpha\alpha}$. This expression is only valid for a mixture of a homonuclear di-

atomic plus a monoatomic fluid. In a more general situation (as in the case of pure fluids with more than two different sites⁷) the simplest approach, although it requires slightly more work, is to drop the h term and optimize the parameter α using thermodynamic consistency (virial-fluctuation theorem) for just one state point. Nonetheless for the case we plan to study here ($\text{N}_2 + \text{Ar}$), Eq. (13) is perfectly suitable, taking $\sigma_{\beta\beta} = \sigma_{\text{ArAr}}$ and $\sigma_{\alpha\alpha} = \sigma_{\text{NN}}$.

III. THE MIXTURE OF HARD SPHERES AND HARD DUMBBELLS: STABILITY ANALYSIS

We have solved the VM equation for a mixture of hard-spheres and homonuclear hard-dumbbells with elongation $L^* = 0.6$ in the special case in which the hard-spheres constituent of the hard-dumbbell have the same size as the atomic species. In order to check the VM results we have performed various NVT Monte Carlo simulations with 500 particle samples using several compositions. The number of steps required (one step implies 500 attempted moves) to get good statistics varies from 10000 to 100000. The latter number is required to produce sensible distribution functions for the dilute samples. The only relevant thermodynamic property that can be compared with simulation is the compressibility factor, which is shown in Table I for the four samples considered (ranging from dilute hard-spheres to dilute hard-dumbbells). Results obtained from the HNC equation are in-

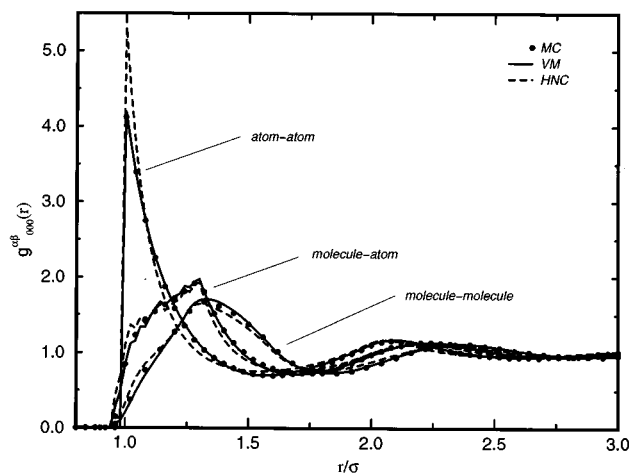


FIG. 1. Center-of-mass distribution functions in an equimolar hard-sphere plus hard-dumbbell mixture.

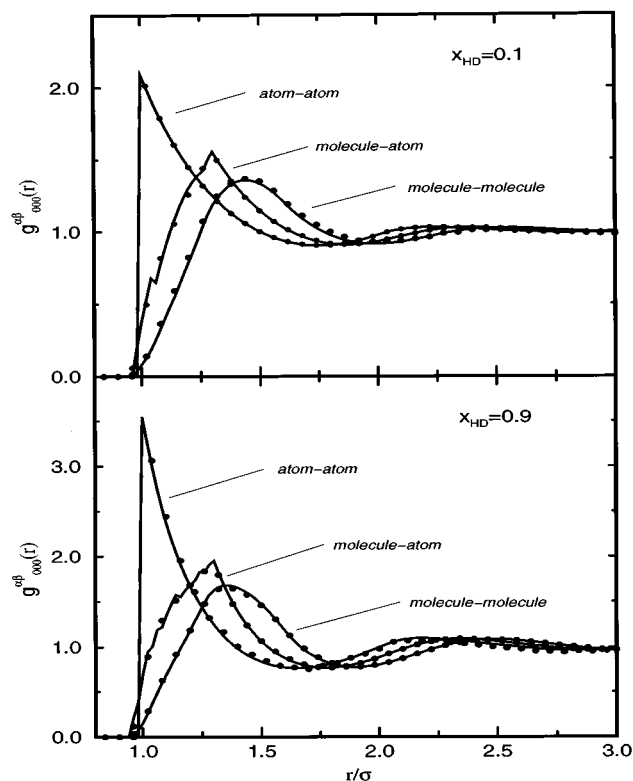


FIG. 2. Center-of-mass distribution functions in hard-sphere plus hard-dumbbell mixtures at different compositions: The figure above refers to a sample with dilute hard-dumbbells, and the figure below to a sample with dilute hard-spheres.

cluded for the sake of comparison. It is immediately apparent that all the VM results lie within the error bars of the simulated data for all the compositions.

As to the structure, in Fig. 1 we can see the center-of-mass to center-of-mass distribution functions, i.e., the radial coefficient in the expansion of the distribution functions, $g_{00}^{\alpha\beta}(r)$, for an equimolar mixture. Again the VM results exhibit an excellent agreement with Monte Carlo calculations. HNC results show the deviations typical of this approach. Finally in Fig. 2 we present the structural results for samples with dilute hard-dumbbells in a hard-sphere solvent and viceversa. These cases were particularly cumbersome to simulate given the poor statistics of the dilute species, being the signature of a non-converged simulation the incorrect decay of the dilute species correlation functions. Here we would like to underline that the molecule-atom $g_{00}(r)$ shows a sawtooth structure due to an artifact of the numerical integration, as a result of the discontinuities inherent to anisotropic hard-core potentials. Should one want to remove such effect, the number of integration points would be prohibitively large in this case. Nonetheless the influence on integrated thermodynamic properties is negligible.

Given the quality of the IE results we considered worthwhile to reexamine the problem of entropically driven demixing in hard-core systems. To this end we have first applied the VM approach as formulated by Henderson *et al.*¹⁰ to test the case that was first analyzed by Biben and

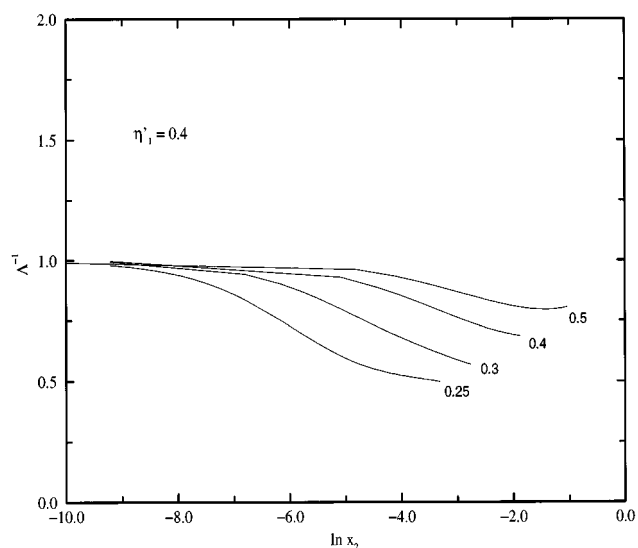


FIG. 3. Long-wavelength limit of the concentration-concentration structure factor, $\Lambda^{-1} = S_{cc}(0)/x_1 x_2$, vs the molar fraction of the large hard-sphere constituent of the HS mixture. η'_1 refers to the effective packing fraction of the small hard-spheres (see text). Curves are labeled with the corresponding size ratios.

Hansen.¹² These authors considered the mixture of additive asymmetric hard spheres with size ratios, $y = \sigma_1/\sigma_2$, ranging from 0.5 to 0.1, in a variety of integral equation approximations, finding evidences of demixing in the Rogers–Young’s approximation.¹⁴ As suggested by the same authors, being infeasible to perform the calculations at constant pressure, it is at least sensible to keep constant the effective density or packing fraction of the small spheres, i.e. the density relative to the volume available to the small spheres, which can be calculated from

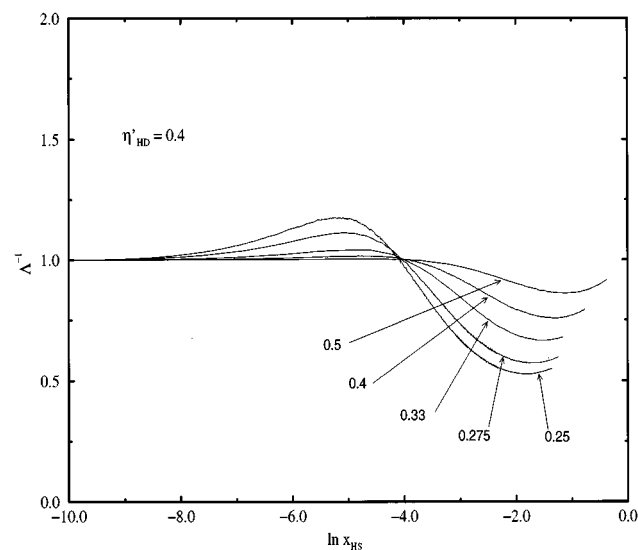


FIG. 4. Long-wavelength limit of the concentration-concentration structure factor, $\Lambda^{-1} = S_{cc}(0)/x_1 x_2$, vs. the molar fraction of the hard-sphere component of the HS-HD mixture. η'_{HD} refers to the effective packing fraction of the hard-dumbbell component of the mixture. Again curves are labeled with the corresponding size ratios.

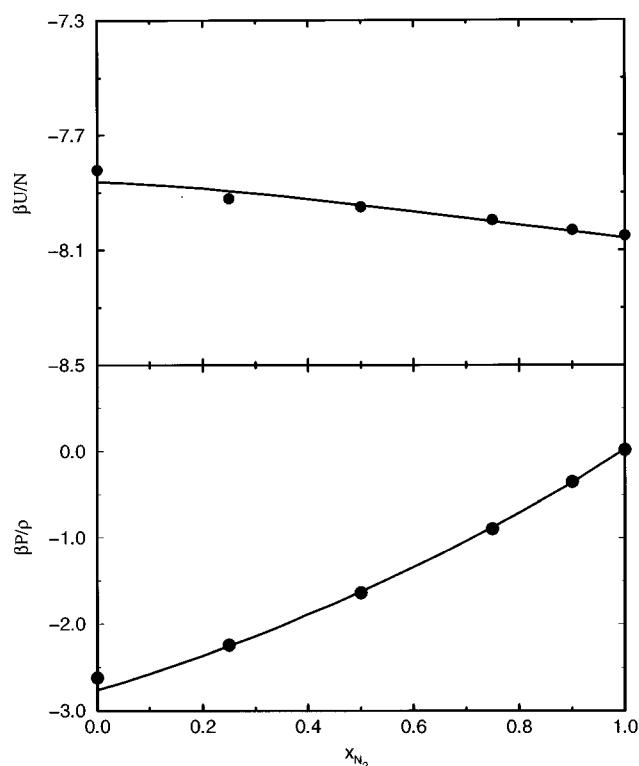


FIG. 5. Internal energy and compressibility factor results for the mixture N_2 -Ar. Solid line: RHNC-VM results. Filled circles: MC simulation data.

$$\eta'_1 = \frac{\eta_1}{1 - \eta_2} \exp \left[\frac{3\eta_2}{1 - \eta_2} y + \frac{3\eta_2}{(1 - \eta_2)^2} \left(1 + \frac{\eta_2}{2} \right) y^2 + \frac{\eta_2 + \eta_2^2 + \eta_2^3}{(1 - \eta_2)^3} y^3 \right] \quad (15)$$

with $\eta_i = \pi/6 \rho_i \sigma_i^3$. When the small particles are hard-dumbbells σ_1 is replaced by the equivalent sphere diameters given by Eq. (6). We have performed calculations at constant $\eta'_1 = 0.4$ for different size ratios, y , varying the mole fraction of the small spheres (or the hard dumbbells). In Fig. 3 we present the results of the long-wavelength limit of the concentration-concentration Bathia-Thornton structure factor for the hard-sphere mixture at size ratios from 0.25 to 0.5,

$$\Lambda^{-1} = \frac{S_{cc}(0)}{x_1 x_2} = \frac{1}{(\rho k_B T \chi_T) |I - \tilde{C}(0)|} \quad (16)$$

$S_{cc}(0)$ going to infinity implies a demixing transition. Results for the mixture of large hard-spheres plus hard-dumbbells are also shown in Fig. 4. It seems clear from the inspection of these figures that whereas the VM approach does not show evidence of the phase separation for the hard-sphere mixture, when hard dumbbells are present there seems to be a tendency for demixing, indicated by the presence of a maximum in Λ^{-1} around $x_{HS} \approx 10^{-5}$, which increases with decreasing size ratio. The transition probably occurs for size asymmetries that are unfortunately extremely hard to deal with (large asymmetries imply larger number of points and finer grids). On the other hand, an unfortunate

TABLE II. Thermodynamic results for a N_2 -Ar mixture: $T^* = 2.064$, $\rho^* = 0.63$.

x_{N_2}	$\beta p/\rho$			$\beta U/N$			
	MC	RHNC	HNC	MC	RHNC	HNC	
0.00	-2.62	-2.86	-1.51	-7.82	-7.86	-7.74	tot.
	0.00	0.00	0.00	0.00	0.00	0.00	M-M
	0.00	0.00	0.00	0.00	0.00	0.00	M-A
	-2.62	-2.86	-1.51	-7.82	-7.86	-7.74	A-A
0.25	-2.24	-2.25	-1.01	-7.92	-7.89	-7.61	tot.
	0.82	0.82	0.93	-0.50	-0.49	-0.48	M-M
	-1.14	-1.16	-0.66	-2.93	-2.93	-2.91	M-A
	-1.92	-1.91	-1.28	-4.49	-4.47	-4.22	A-A
0.50	-1.64	-1.625	0.15	-7.95	-7.94	-7.71	tot.
	0.40	0.41	0.94	-1.98	-1.99	-1.94	M-M
	-1.28	-1.30	-0.43	-3.97	-3.95	-3.89	M-A
	-0.76	-0.74	-0.36	-2.00	-2.00	-1.88	A-A
0.75	-0.895	-0.88	1.43	-7.995	-8.00	-7.77	tot.
	0.04	0.04	1.42	-4.50	-4.51	-4.36	M-M
	-0.78	-0.76	0.04	-2.995	-2.99	-2.91	M-A
	-0.16	-0.155	-0.04	-0.50	-0.50	-0.50	A-A
0.90	-0.35	-0.36	2.19	-8.03	-8.04	-7.755	tot.
	-0.03	-0.04	2.08	-6.51	-6.515	-6.28	M-M
	-0.29	-0.30	0.11	-1.44	-1.44	-1.40	M-A
	-0.02	-0.02	-0.00	-0.08	-0.08	-0.08	A-A
1.00	0.02	0.03	2.75	-8.05	-8.06	-7.745	tot.
	0.02	0.03	2.75	-8.05	-8.06	-7.745	M-M
	0.00	0.00	0.00	0.00	0.00	0.00	M-A
	0.00	0.00	0.00	0.00	0.00	0.00	A-A

property of the VM closure, i.e. the presence of poles in the denominator of Eq. (1), prevents the solution of the equation for all compositions for size ratios smaller or equal to 0.01. Actually, recent computer simulation results by Biben and Hansen¹⁵ seem to indicate the demixing occurs for size ratios around 0.1, and that the RY closure clearly overestimates the instability of the mixture. It is then possible that the VM results might be correct for the size ratios considered. In any case, the leading conclusion to be drawn is the fact that the anisotropy of the particle enhances the instability and thus obvious fluctuations (though not divergence) appears in the HS-HD mixture. In other words, steric effects will increase the tendency of the small dumbbells to stick together.

IV. THE N_2 -Ar MIXTURE

Our mixture of N_2 and Ar has been modeled using a standard two-center LJ potential for N_2 and a simple LJ to model Ar. Cross interactions have been determined using Lorentz-Berthelot mixing rules, $\varepsilon_{\alpha\beta} = \sqrt{\varepsilon_{\alpha\alpha}\varepsilon_{\beta\beta}}$ and $\sigma_{\alpha\beta} = (\sigma_{\alpha\alpha} + \sigma_{\beta\beta})/2$. Specifically, we have used $\sigma_{N-N} = 3.31$ Å, $\sigma_{Ar-Ar} = 3.405$ Å, $\varepsilon_{N-N}/k = 37.3$ and $\varepsilon_{Ar-Ar}/k = 119.8$. The elongation of the N_2 molecule has been set to $d_{N-N} = 1.09$ Å. Calculations have been performed at constant total density, $\rho \sigma_{N-N}^3 = (\rho_{Ar} + \rho_{N_2}) \sigma_{N-N}^3 = 0.63$ and $T^* = kT/\varepsilon_{NN} = 2.064$. With this potential parameters and using the empirical relations given by Eqs. (13) and (14), it is possible to define a hard-core reference system which is then solved in the VM approximation as shown in the previous section. The calculations have been complemented by a

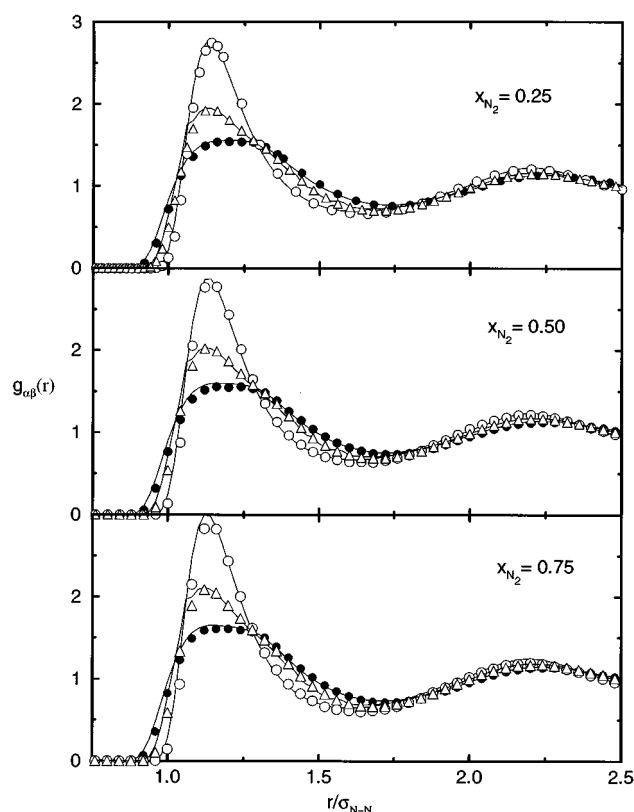


FIG. 6. Atom-atom distribution functions for the N_2 -Ar mixtures at different compositions. Solid lines refer to RHNC-VM results and symbols to MC simulation data (open circles: Ar-Ar; triangles: Ar-N; filled circles: N-N).

number of Monte Carlo simulations that serve as a reference. In Fig. 5 we show the results obtained for the internal energy and compressibility factor. Our RHNC-VM approach for this mixture case again tends to reproduce exactly the simulation results. Explicit data together with HNC calculations are collected in Table II. This latter approximation behaves poorly as far as the pressure is concerned as is characteristic in other systems as well.

As to the structure, in Fig. 6 we present the atom-atom distribution functions calculated from the projections of the molecular pair distribution function using Eqs. (13)–(14) from Ref. 6. In consonance with the good performance of the theory for the thermodynamics here we also see that the fluid structure is reproduced accurately when compared with MC simulation data.

In summary, we can conclude that being the VM equation an excellent approximation for mixtures of hard-core systems, the RHNC-VM scheme can now also successfully deal with mixtures of atomic and molecular fluids, opening a new path to deal with the problems of demixing in systems which might easily involve organic solvents, both polar and non-polar.

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