PHYSICAL REVIEW E VOLUME 55, NUMBER 3 MARCH 1997

Influence of three-body forces on the gas-liquid coexistence of simple fluids: The phase equilibrium of argon

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(Received 3 October 1996)

The effect of three-body classical dispersion forces on the gas-liquid coexistence of argon is explored by means of a reference hypernetted-chain integral equation and Gibbs ensemble Monte Carlo simulations. We find that the combination of Aziz's [J. Chem. Phys. **99**, 4518 (1993)] pair interaction with the standard Axilrod-Teller [J. Chem. Phys. **11**, 299 (1943)] triple dipole potential leads to the best prediction of the experimental coexistence curve. By contrast, when the Lennard-Jones potential is used in conjunction with the Axilrod-Teller interaction the calculated curve deviates appreciably from the experimental data, far from improving the reasonable plain Lennard-Jones results. Additionally, the integral equation approach with an effective state-dependent pair potential to account for the three-body interactions leads to very accurate results for the thermodynamic and coexistence properties of the fluid. This feature comes to prove that the theory can be an invaluable tool for studying systems with three-body interactions of the Axilrod-Teller type. [S1063-651X(97)00103-7]

PACS number(s): 61.20.Gy, 64.70.Fx, 05.20.−y

I. INTRODUCTION

It is a well-known fact that three-body forces should be taken into account to fairly describe some experimental properties of dense simple fluids [1–5]. Furthermore, Barker *et al.* [2] showed unequivocally that a realistic pair potential, obtained from spectroscopic data in the *gas* phase, plus a three-body interaction of the Axilrod-Teller (AT) type [6], is sufficient to reproduce accurately the thermodynamics of argon, krypton, and xenon throughout a wide range of temperatures and densities. These authors also indicated that the use of pair potentials based on condensed phase data could lead to errors in the determination of the thermodynamic properties. Only for krypton [4,5] further three-body contributions seem to be needed in the evaluation of the neutron-diffraction structure factor.

Nonetheless, a comprehensive study of the influence of the AT interaction on the coexistence properties of rare gases remains to be done. In this paper we intend to fill this gap relying on two powerful techniques: the Gibbs ensemble Monte Carlo (GEMC) method [7] and a reference hypernetted-chain (RHNC) integral equation [8]. In this connection, a work on the gas-liquid coexistence of argon has recently been published [9], in which the effect of three-body forces is partially incorporated, though completely neglected in the GEMC calculations. This obviously leads to a coexistence curve that agrees with the pure Lennard-Jones (LJ) results of Panagiotopoulos [7]. Also, in a previous work the authors studied the gas-liquid coexistence of argon by means of the RHNC equation [10] plus an effective state-dependent pair potential that is introduced in order to deal with the AT triplet interactions [11]. This effective pair potential approach has been widely used in the literature in connection with RHNC theory [12,13] and has proven to perform well for calculating bulk properties of rare gases. The apparent improvement achieved in the coexistence curve presented in Ref. [10] when the LJ is combined with the AT potential must be treated with reserve, since RHNC predictions for the compressibility factor are found to lay somewhat far from simulation results [10]. This failure is especially notorious when the integral equation approach is compared with perturbation theory [14], suggesting that the evaluation of the three-body contributions to the thermodynamic properties might be inaccurate. However, we will see that the explicit formula to calculate the triplet pressure used so far [10,11] contains an error that results in Euler's theorem not being fulfilled for the triplet contributions to energy and pressure. By correctly recalculating this latter quantity we will show that the RHNC approach plus superposition approximation yields thermodynamic properties more accurate than presently believed.

In this work we have revisited the original RHNC approach to assess the influence of three-body interactions on the gas-liquid coexistence of argon. In our calculations we have used the fact that the AT potential is a homogeneous function of the interparticle separation to check the evaluation of the three-body term in the virial equation. It will be seen that now the RHNC approach is even more accurate than Barker's perturbation theory [14] in this sort of system.

In view of the good performance of the RHNC approximation we have tackled the problem of the phase coexistence in order to ascertain unambiguously the role of the three-body AT interaction in the gas-liquid equilibrium. In addition to the theoretical approach, we have carried out extensive GEMC simulations in which the three-body potential is *explicitly* considered in the acceptance criteria, so that the

TABLE I. Pressure and internal energy of a fluid whose particles interact through a 6-12 LJ potential ($\epsilon/k = 120$ K, $\sigma = 3.405$ Å) and the Axilrod-Teller triple-dipole potential ($\nu/\epsilon\sigma^9 = 0.072$), from Monte Carlo simulations and RHNC and perturbation theories.

	$kT/\epsilon = 1.033$, $\rho\sigma^3 = 0.65$		$kT/\epsilon = 0.746$, $\rho\sigma^3 = 0.817$	
	U/NkT	$P/\rho kT$	U/NkT	$P/\rho kT$
MC[a]	$-4.227(2)$	0.15(1)	$-7.566(7)$	0.56(4)
MD[b]	-4.221	0.10	-7.560	0.38
MC[c]	$-4.229(10)$	0.180(30)	$-7.534(40)$	0.802(90)
perturbation[d]	-4.224	0.138	-7.555	0.62
RHNC	-4.221	0.184	-7.531	0.792

[a] Taken from Ref. [18].

[b] Taken from Ref. [27].

[c] Results obtained using 250 particles and three-body cutoff $r_{3c} = 2.5\sigma$.

[d] Taken from Ref. [14].

evaluated coexisting densities reflect the effect of triple interactions. Based on the short-range features of the three-body forces [10], we have defined a reasonable small cutoff for the three-body interactions, and thus the GEMC simulations, although cumbersome, are computationally feasible. We will see that the agreement between theory and simulation is very encouraging for the two models studied in this work.

As already mentioned, we have focused on two choices for the pair potential to be used in addition to the AT triple interaction. First we have dealt with the standard LJ potential, whose parameters are obtained from second virial coefficient measurements [15]. On the other hand, we have used the most accurate pair potential for argon available to date, which has recently been proposed by Aziz [16]. This interaction was parametrized in order to fit a complete set of spectroscopic properties of argon in the *gas* phase, and therefore it is expected to be a pure and very accurate pairwise interaction. In both cases we will see that the introduction of the AT potential lowers the critical temperature and the liquid-side equilibrium densities with respect to the two-body results, as in Ref. [10]. Whereas this feature results in a misrepresentation of the coexistence properties in the LJ plus AT case, the AT potential added to the Aziz's pair interaction is found to bring the curve obtained using only Aziz's pair potential into perfect agreement with the experimental coexistence curve of argon. We will see how these results provide interesting information about the crucial role of three-body forces in the gas-liquid equilibrium.

We have organized this paper as follows. Section II is devoted to a brief summary of the RHNC theory in systems modeled via pair interactions plus three-body interactions. Also in this section we give details of the GEMC method utilized to simulate these systems. Results for the thermodynamics of the LJ plus AT system for two states are reported also in Sec. II. The prediction of the gas-liquid coexistence curve of argon using both the LJ and the Aziz's potentials plus the AT interaction can be found in Sec. III. We report results from RHNC theory and GEMC simulations for both cases. Section III also includes an in-depth discussion on the role of the AT potential in the phase coexistence. Finally, in Sec. IV, we present the main conclusions that can be drawn from this work.

II. RHNC THEORY AND GEMC METHOD FOR SYSTEMS WITH AXILROD-TELLER THREE-BODY FORCES

A. Interaction model

The total potential energy of a system made up of N spherical particles can be expressed as an infinite sum of increasing n-body contributions

$$U_N = \sum_{i<j}^{N} u_2(r_{ij}) + \sum_{i<j<k}^{N} u_3(\mathbf{r}_i, \mathbf{r}_j, \mathbf{r}_k) + \cdots, \tag{1}$$

where u_n is the n-body interaction potential. In most cases terms with $n > 4$ are neglected and therefore only u_2 and u_3 are sufficient for an adequate description of the system.

As regards the pair interactions, here we have dealt with the well-known Lennard-Jones potential

$$u_2(r) = 4\epsilon\left[\left(\frac{\sigma}{r}\right)^{12} - \left(\frac{\sigma}{r}\right)^{6}\right], \tag{2}$$

where σ and ϵ stand for the particle size and the well depth of the potential. It is recalled that these parameters are typically obtained from experimental second virial coefficient measurements. With this prescription the LJ potential is known to give reasonable results for gas-liquid coexistence properties, although sometimes a rescaling to the critical properties is also desirable.

Now if one wants to go beyond the accuracy of the simple LJ interaction, one has to resort to properties other than the second virial coefficient, and on this connection one has a good number of two-particle spectroscopic (ultraviolet vibration-rotation spectrum), scattering, and transport properties. Within the class of potentials that give a correct account of the these types of properties falls the potential model proposed by Aziz [16]. It has the functional form

$$u_2(r) = Ae^{(-\alpha r + \beta r^2)} - \left[\sum_{n=3}^{7} C_{2n} r^{-2n} g_{2n}(\rho r)\right] f(\rho r), \tag{3}$$

where the parameters A, α, β, C_n, and ρ can be found in Table I of Ref. [16]. The functions $f(R)$ and $g_n(R)$ are in turn given by

$$g_n(R)=[1-e^{-2.1R/n-0.109R^2/n^{1/2}}]^n, \tag{4}$$

$$f(R)=1-R^{1.68}e^{-0.78R}, \tag{5}$$

with R in atomic units.

Use of Aziz's interaction will guarantee that one will have the most accurate representation of the low-density system. When the density increases three-body forces come into play, which we have incorporated by means of the Axilrod-Teller triple dipole potential [6]

$$u_3(\mathbf{r}_1,\mathbf{r}_2,\mathbf{r}_3)=\nu\frac{r_{12}^2r_{13}^2r_{23}^2+3(\mathbf{r}_{12}\cdot\mathbf{r}_{13})(\mathbf{r}_{21}\cdot\mathbf{r}_{23})(\mathbf{r}_{31}\cdot\mathbf{r}_{32})}{r_{12}^5r_{13}^5r_{23}^5}, \tag{6}$$

where $\mathbf{r}_{ij}$ is the vector joining particles i and j and $\nu=7.32\times10^{-108}$ J m^9 for argon.

When treating systems where three-body potentials are present, the main problem with integral equation theories arises from the assumption of the principle of pairwise additivity [17], i.e.,

$$U_N=\sum_{i<j}^{N}u_2(r_{ij}). \tag{7}$$

Nonetheless, this shortcoming can be bypassed by means of the definition of an effective pair potential that accounts for the triplet interactions. In this context Attard derived the following form for the effective potential [11]:

$$\beta u^{\rm eff}(r_{12})=-\rho\int[e^{-\beta u_3(\mathbf{r}_1,\mathbf{r}_2,\mathbf{r}_3)}-1]g(r_{13})g(r_{32})d\mathbf{r}_3, \tag{8}$$

with $\beta=1/kT$ as usual and $g(r)$ the pair distribution function of the fluid. Equation (8) is formally equivalent to the *three-body vertex* used by Reatto and Tau [12]. This way of treating three-body forces has proven to be efficient for the typical triple potentials used for rare gases [4,5,12,18], including the standard AT potential, but it is found to perform poorly in systems with very strong angular correlations stemming from three-body forces, as is the case on liquid silicon [19,20].

B. RHNC theory

The RHNC integral equation for homogeneous simple fluids consists of the combination of the Ornstein-Zernike relation [17]

$$\gamma(r_{12})=\rho\int c(r_{32})[\gamma(r_{13})+c(r_{13})]d\mathbf{r}_{13}, \tag{9}$$

with the closure

$$c(r_{12})=e^{-\beta u_2(r_{12})+\gamma(r_{12})-B_0(r_{12})}-\gamma(r_{12})-1, \tag{10}$$

where c is the direct correlation function, $\gamma=g-c-1$ is the series function [8,17], and B is the bridge function. Provided B_0 is known, Eqs. (9) and (10) form a closed system of equations for the variables c and γ. The natural choice for B_0 is the use of the hard-sphere fluid as reference system, so that we take

$$B(r_{12})=B_{\rm HS}(r_{12};d), \tag{11}$$

with $B_{\rm HS}$ the hard-sphere bridge function, which depends on the hard-sphere diameter d. This parameter may be adjusted by requiring that the free energy of the fluid reaches a minimum. Lado, Foiles, and Ashcroft [8] showed that this condition is equivalent to the relation

$$4\pi\int_0^\infty[g(r)-g_{\rm HS}(r)]\frac{\partial B_{\rm HS}(r;d)}{\partial d}r^2dr=0, \tag{12}$$

where $g_{\rm HS}$ is the hard-sphere pair distribution function.

Equations (9)–(11), complemented with Eq. (12) to fix the value of d, are found to describe correctly the structure and thermodynamics of systems with pairwise additive forces [8] and also have been successfully employed to evaluate the gas-liquid coexistence of LJ fluids [21]. When three-body interactions are present, Eq. (10) should be modified so that now

$$c(r_{12})=e^{-\beta u_2(r_{12})-\beta u_2^{\rm eff}(r_{12})+\gamma(r_{12})-B_{\rm HS}(r_{12};d)}-\gamma(r_{12})-1, \tag{13}$$

where $u_2^{\rm eff}$ is the effective pair potential given by Eq. (8). Equations (8)–(10) represent a more involved system of equations that has to be solved iteratively for each value of d. It was shown elsewhere [10] that the presence of the three-body term does not significantly alter the validity of Eq. (12) as a criterion to find the minimum in the free energy. The iterative method of solution has been also described in Ref. [10] in addition to details to evaluate the integral involved in Eq. (8).

Once a converged solution for $g(r)$ has been obtained the internal energy and the pressure of the fluid can be evaluated by means of [22]

$$\begin{aligned}U&=U_2+U_3\\&=\frac{1}{2!}\rho^2\int u_2(r_{12})g(r_{12})d\mathbf{r}_1d\mathbf{r}_2\\&\quad+\frac{1}{3!}\rho^3\int u_3(r_{12},r_{13},r_{23})g_3(r_{12},r_{13},r_{23})d\mathbf{r}_1d\mathbf{r}_2d\mathbf{r}_3,\end{aligned} \tag{14}$$

$$\begin{aligned}P&=P_2+P_3\\&=\frac{NkT}{V}-\frac{1}{V2!3}\rho^2\int r_{12}\frac{\partial u_2(r_{12})}{\partial r_{12}}g(r_{12})d\mathbf{r}_1d\mathbf{r}_2\\&\quad-\frac{1}{V3!3}\rho^3\int(r_{12}\partial/\partial r_{12}+r_{13}\partial/\partial r_{13}+r_{23}\partial/\partial r_{23})\\&\quad\times u_3(r_{12},r_{13},r_{23})g_3(r_{12},r_{13},r_{23})d\mathbf{r}_1d\mathbf{r}_2d\mathbf{r}_3.\end{aligned} \tag{15}$$

In expressions (14) and (15), g_3 refers to the triple correlation function, which is, in principle, unknown. Nonetheless, it can be estimated by means of a natural extension of Kirkwood's superposition approximation [11,23]

$$g_3(r_{12},r_{13},r_{23})=g(r_{12})g(r_{13})g(r_{23})e^{-\beta u_3(r_{12},r_{13},r_{23})}. \tag{16}$$

TABLE II. Experimental phase coexistence properties of argon [26].

T (K)	ρ_g g cm^{-3}	ρ_l g cm^{-3}	P (kbar)
91	0.00813	1.372	1.47
100	0.01686	1.314	3.24
120	0.06014	1.163	12.13
140	0.17885	0.943	31.68

By performing the change of variables

$$r'_{12}=r_{12}, \quad r'_{13}=r_{13}, \quad x=\frac{r_{12}^2+r_{13}^2-r_{23}^2}{2r_{12}r_{13}}, \tag{17}$$

the virial operator now reads

$$\begin{aligned}(r_{12}\partial/\partial r_{12}+r_{13}\partial/\partial r_{13}+r_{23}\partial/\partial r_{23})u_3(r_{12},r_{13},r_{23})\\ =(r'_{12}\partial/\partial r'_{12}+r'_{13}\partial/\partial r'_{13})u_3(r'_{12},r'_{13},x).\end{aligned} \tag{18}$$

One then finds that the internal energy and the pressure of the fluid can be rewritten in terms of the new variables as

$$\begin{aligned}\frac{\beta U^{\mathrm{ex}}}{N}=&2\pi\rho\int_0^\infty u^{(2)}(r_{12})g(r_{12})r_{12}^2dr_{12}\\ &+\frac{4\pi^2\rho^2}{3}\int_0^\infty\int_0^\infty\int_{-1}^1\beta u^{(3)}(r_{12},r_{13},x)g^{(3)}\\ &\times(r_{12},r_{13},x)r_{12}^2r_{13}^2dr_{12}dr_{13}dx,\end{aligned} \tag{19}$$

$$\begin{aligned}\frac{\beta P}{\rho}=&1-\frac{2\pi\rho}{3}\int_0^\infty\beta r_{12}^3\frac{\partial u^{(2)}(r_{12})}{\partial r_{12}}g(r_{12})dr_{12}\\ &-\frac{8\pi^2\rho^2}{9}\int_0^\infty\int_0^\infty\int_{-1}^1\beta r_{12}^3\frac{\partial u^{(3)}(r_{12},r_{13},x)}{\partial r_{12}}g^{(3)}\\ &\times(r_{12},r_{13},x)r_{13}^2dr_{12}dr_{13}dx.\end{aligned} \tag{20}$$

In expressions (19) and (20) we have dropped the primes from the new variables for simplicity. In Eq. (20) it is understood that the two integrals arising from the two terms in Eq. (18) are identical by symmetry considerations. This leads to an extra factor of 2 in the triplet contribution to the pressure that is missing in the corresponding expression in Ref. [10] and, consequently, the results for the triplet pressure presented therein are also affected by this error. On the other hand, since the AT potential is a homogeneous function of the variables r_{12}, r_{13}, and r_{23}, Euler's theorem applied to Eqs. (14) and (15) leads to

$$P_3V=3\,U_3. \tag{21}$$

Equations (19) and (20) are easily shown to fulfill this relation, which can actually be used as a check of the numerical accuracy of the integrations and the internal consistency of the results. In Table I we can compare the present RHNC estimates for the pressure (together with those for the energy) with simulation and perturbation theory data. We see that the energy and now the pressure as well are in good agreement with both Monte Carlo (MC) and molecular-dynamics (MD) results. Also it should be pointed out that the RHNC approach turns out to be more accurate than perturbation theory [14] if a comparison is made with MC results performed with 250 particles and a three-body cutoff of 3σ. This evidences that the effective potential and superposition approximations are adequate approaches to deal with AT three-body forces.

C. GEMC method

We have simulated the gas-liquid coexistence of argon with the LJ potential and Aziz's potential plus the AT triple dipole potential using the GEMC method [7]. The major shortcoming when simulating systems with three-body forces is the large amount of CPU time required to perform the runs. Nonetheless, computational times can be brought down to reasonable values by using an adequate cutoff for the three-body forces. From the effective pair potential approach one learns that the AT triple potential has little effect for intermolecular distances beyond 2.5σ [10]. We have taken this value as an appropriate cutoff and, therefore, only triplets of particles for which $r_{12},r_{13},r_{23}<2.5\sigma$ are considered to evaluate three-body energies. Increasing the cutoff to 3.0σ did not result in appreciable changes in the thermodynamics and consequently no long-range corrections were used for the triple potential.

GEMC simulations were organized in steps, each one consisting of one translational attempt per particle, one attempt of changing the volume of the boxes, and N_i insertion attempts. N_i was tuned to ensure an acceptance ratio of particle interchanges that allows for a reasonable rapid equilibration. Due to the small probability of accepting interchanges at high densities, N_i was set to 500 at low temperatures. By contrast, only 10 insertion attempts were required at near critical temperatures. Simulations were per-

TABLE III. Phase coexistence results for argon modeled via LJ potential ($\epsilon/k=120$ K, $\sigma=3.405$ Å) plus AT three-body potential ($\nu/\epsilon\sigma^9=0.072$) from GEMC and RHNC theories.

	GEMC				RHNC		
T K	ρ_g g cm^{-3}	ρ_l g cm^{-3}	P_g (kbar)	P_l (kbar)	ρ_g g cm^{-3}	ρ_l g cm^{-3}	P (kbar)
90	0.0131(15)	1.306(12)	2.3(3)	−4.6(10.5)	0.0074	1.304	2.3
108	0.052(3)	1.188(3)	9.7(4)	5.0(2.0)	0.032	1.183	7.1
120	0.102(5)	1.092(3)	17.6(4)	13.4(1.7)	0.059	1.089	13.4
132	0.170(13)	0.983(12)	27.3(1.3)	25.6(5.0)	0.102	0.971	18.9
138					0.123	0.887	21.8

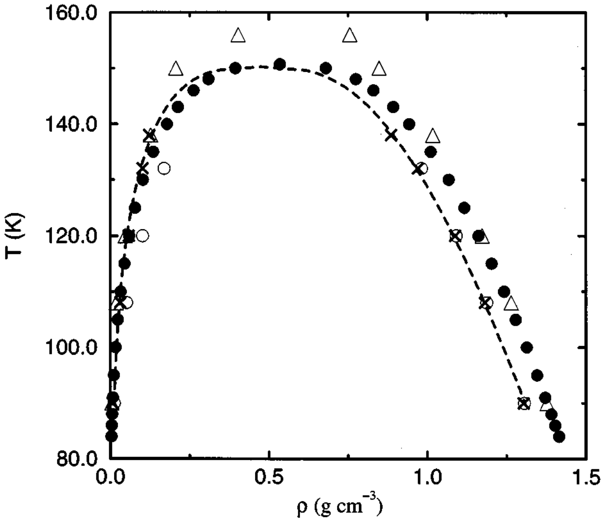

FIG. 1. Gas-liquid coexistence curve of argon from experiment [26] (black circles), GEMC data with the pure LJ potential [7] (open triangles), GEMC data with the LJ plus AT triple potential (open circles) and the RHNC data with the same pair of triple potentials (times). The dashed line stands for a scaling law fit of the RHNC data.

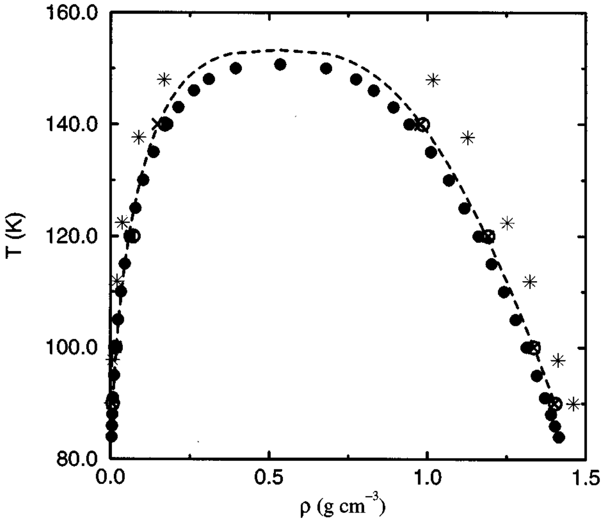

FIG. 2. Gas-liquid coexistence curve of argon from experiment [26] (black circles), GEMC data with Aziz's potential plus the AT interaction (open circles), and RHNC data with Aziz's potential only (asterisks) and with Aziz's potential plus the AT triple potential (times). The dashed line has the same meaning as in Fig. 1.

formed with 300 and 500 particle samples at low and high temperatures, respectively. The number of steps needed to equilibrate the system ranged from 2000 to 30 000, increasing with temperature. Once the system was thermalized, 10 000–90 000 further steps were generated to obtain the coexisting densities and vapor pressures. Typical CPU times required ranged from 9 to 90 h in a DEC ALPHA 600 5/300.

III. THE GAS-LIQUID COEXISTENCE CURVE OF ARGON

Using the RHNC approach outlined in the preceding section, we have evaluated the gas-liquid coexistence properties of argon (experimental data are collected in Table II) modeled via LJ and Aziz's pair potentials plus the AT triple interaction. We have calculated the pressure along gas and liquid isotherms by making use of Eq. (15) with the relation (21) to determine the three-body contribution. The chemical potential was calculated from the excess Helmholtz free energy A^{ex},

$$\beta\mu/N = \ln\rho + A^{\mathrm{ex}}/NkT + P_v/\rho kT, \tag{22}$$

which in turn is evaluated from thermodynamic integration of the pressure and the internal energy [24]. Once pressure and chemical potential are computed along gas and liquid isotherms, it is possible to find densities for which the conditions of chemical equilibrium are fulfilled:

$$\beta\mu(\rho_l,T) = \beta\mu(\rho_g,T),$$

$$\beta P(\rho_l,T)\sigma^3 = \beta P(\rho_g,T)\sigma^3. \tag{23}$$

The RHNC gas-liquid coexistence curve can be fitted to the usual scaling laws [10] in order to estimate the critical temperature and density. The results for the LJ plus AT case are displayed in Table III and Fig. 1, while those for Aziz's potential plus the AT interaction are shown in Table IV and Fig. 2. In both cases RHNC estimates can be compared with the corresponding GEMC calculations. The most striking feature that can be drawn from this comparison is that the RHNC theory is virtually exact in predicting the liquid branch of the phase diagram. Vapor pressures are similarly well reproduced. On the contrary, the RHNC equation somehow fails in the gas branch of the diagram at temperatures near the critical point. Nonetheless, the estimation is almost perfect throughout the whole coexistence curve when Aziz's potential is utilized as a pairwise interaction instead of the LJ potential. In short, the RHNC approach applied here proves to be very accurate for the two cases considered.

By comparing with the experiment, we can also explore the adequacy of the present models to describe argon. It is a

TABLE IV. Phase coexistence results for argon modeled via Aziz's pairwise potential [16] ($\epsilon/k = 143.25$, $\sigma = 3.350$ Å) plus AT three-body potential ($\nu/\epsilon\sigma^9 = 0.0698$) from GEMC and RHNC theories.

	GEMC				RHNC		
T (K)	ρ_g (g cm^{-3})	ρ_l (g cm^{-3})	P_g (kbar)	P_l (kbar)	ρ_g (g cm^{-3})	ρ_l (g cm^{-3})	P (kbar)
90	0.0076(28)	1.405(12)	1.6(5)	52.6(1.6)	0.0064	1.401	1.2
100	0.0161(16)	1.337(9)	3.1(3)	36.8(7.4)	0.0159	1.337	3.0
120	0.0723(35)	1.193(7)	13.7(5)	70.5(8.4)	0.0653	1.193	12.9
140	0.171(46)	0.986(35)	32.6(7.4)	44.7(12.6)	0.149	0.978	29.5

well-known issue (which can be readily confirmed by inspection of Fig. 1) that the LJ pair potential, implemented as a unique interaction in theory or simulation, reproduces reasonably well the coexisting liquid densities of argon at low and intermediate temperatures [25]. However, it seems inadequate as far as the equilibrium gas densities and critical properties are concerned. This clearly suggest that some improvement in the microscopic model is needed. In this respect, the addition of the AT triple interaction decreases both critical temperature and density, as well as the coexisting liquid densities. This was already made apparent in previous RHNC calculations [10] and can be unequivocally confirmed by Figs. 1 and 2.

When the LJ potential is used as a pair interaction, the introduction of the three-body forces corrects, to a certain degree, the location of the critical point, but fails to reproduce the liquid branch of the phase diagram. This implies that either the LJ model is a poor pair interaction or it somehow includes three-body effects. However, this latter hypothesis seems to contradict the fact that LJ parameters are obtained from *second* virial coefficient measures at low densities [15] and therefore there is no reason to think that LJ parameters are affected by triple correlations.

On the other hand, if Aziz's interaction is used instead of the simpler LJ potential, the prediction of the coexistence curve performs its best. Aziz's potential is a very accurate *pairwise* model that fits spectroscopic properties of argon in the gas phase. Since this potential is a plain and accurate pairwise interaction, it is unable to reproduce the coexistence curve by itself, as can be seen in Fig. 2. When Aziz's potential is added to three-body forces the critical temperature and density are lowered to the point that the experimental values are reproduced. Thus RHNC estimates for the critical temperature and density are 153.3 K and 0.530 $\mathrm{g\,cm^{-3}}$, which compare favorably with the experimental values 150.6 K and 0.536 $\mathrm{g\,cm^{-3}}$ [26]. Moreover, both the gas and liquid branches of the coexistence curve are well reproduced by both GEMC and RHNC predictions when argon is modeled in this way.

IV. CONCLUSION

Two main conclusions can be derived from this work. First of all, it is shown that the effective potential approach plus the use of the superposition approximation to evaluate the triplet energy and pressure constitute a very accurate tool to deal with three-body AT forces in the context of the RHNC theory. In this connection, deviations of the RHNC equation reported in previous papers [10] are due to an incorrect calculation of the three-body contribution to the pressure and not to a shortcoming of the effective potential approach. Second, our results for the gas-liquid coexistence curve of argon confirm the assumption [2,3] that an adequate description of rare gases should include a combination of an accurate pair potential with the AT three-body interaction. In this respect, it is not definitively ruled out that further triple interactions are needed to get an even more realistic description of all thermodynamic properties, but such interactions must be necessarily small.

ACKNOWLEDGMENTS

This work has been financed by Spanish Dirección General de Investigación Científica y Técnica under Grant No. PB94-0112.

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