Theory of static correlations in rare gases for realistic model-interactions: Triple-point region and critical point

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The crossover modified-hypernetted-chain equation, extended to take into account three-body forces, is tested against recent simulation results for realistic models of krypton and xenon which include also the three-body Axilrod-Teller interaction $v_{AT}^{(3)}$. The effect of $v_{AT}^{(3)}$ on $g(r)$ is reproduced so well that this equation can also be used in the framework of inversion of structural data to separate the true two-body contribution out of the extracted effective potential. We also study the way $v_{AT}^{(3)}$ influences the critical point of the liquid-vapor phase transition for Ar, Kr, and Xe. We find that both ρ_c and T_c are lowered by $v_{AT}^{(3)}$ and that the small deviations from the law of corresponding states are as much due to $v_{AT}^{(3)}$ as to the different shape of the pair interaction.

I. INTRODUCTION AND SUMMARY

The crossover modified-hypernetted-chain equation[1] (MHNC-CRS) has been recently extended[2] to take into account the presence of a three-body interaction (triplet MHNC-CRS). A serious quantitative test of this equation is now possible against accurate simulation results[3,4] obtained by using realistic pair interactions for rare gases with and without the Axilrod-Teller (AT) triple-dipole interaction $v_{AT}^{(3)}$. We find that there is satisfactory agreement between theory and simulation and that the largest source of error in the triplet MHNC-CRS is due to the treatment of the *pair* interaction. We also show that three-body forces are treated accurately enough to deal with the problem of inversion of structural data and that the extracted effective pair potential can be decomposed into a true two-body part plus the contribution of a given three-body term.

We extend our study to the critical region of Ar, Kr, and Xe. ρ_c and T_c are lowered by $v_{AT}^{(3)}$ and the small deviations from the law of corresponding states are due as much to the different intensity of the three-body term as to the different shape of the pair interaction.

In Sec. II we compare results from simulation and from triplet MHNC-CRS in the triple point region and we analyze our model in the framework of inversion of structural data. In Sec. III the critical point of Ar, Kr, and Xe is determined.

II. TRIPLE-POINT REGION

The following exact relation holds[5] for a system described by a two-body interaction $\phi(r)$ plus a three-body interaction $v^{(3)}$:

$$g(r)=\exp[-\beta\phi(r)+h(r)-c(r)+C(r)+E^{(2)}(r)+E^{(3)}(r)] , \quad (1)$$

where $\beta=(k_B T)^{-1}$, $h(r)=g(r)-1$ and $c(r)$ are the total and direct correlation function, respectively, and $C(r)$ is the dressed three-particle vertex:

$$C(r_{12})=\rho\int d^3r_3 g(r_{13})g(r_{23})\times\{\exp[-\beta v^{(3)}(\mathbf{r}_1,\mathbf{r}_2,\mathbf{r}_3)]-1\} . \quad (2)$$

The bridge function has been split in two parts. $E^{(2)}(r)$ is the same functional of h as in the two-body case and $E^{(3)}(r)$ is formally given as the sum of an infinite series of bridge diagrams which have at least three vertices connected by the three-body Mayer function. As in Ref. 2, we neglect $E^{(3)}$ and approximate $E^{(2)}$ by a MHNC-CRS bridge function. A simpler approximation was studied earlier[6,7] where the low-density limit for $g(r)$ is used in (2).

The MHNC-CRS depends on three parameters, the hard sphere diameter d, and the two crossover parameters R and w which characterize the length scale over which the bridge crosses over from a hard-sphere type to a mean spherical form. The values of R and w are not chosen empirically as in Refs. 1 and 2, but they are determined on the basis of an extended[8] Lado's criterion.[9] The three parameters are computed without $v_{AT}^{(3)}$. The computations have been performed for Xe and Kr under the same conditions as Refs. 3 and 4. The pair potentials used are those of Refs. 10 and 11, respectively, truncated as in the simulation. The value of the intensity of $v_{AT}^{(3)}$ is

$\nu_3 = 2.204 \times 10^{-82}$ erg cm^9 for Kr and $\nu_3 = 7.950 \times 10^{-82}$ erg cm^9 for Xe.

In Fig. 1 $g(r)$ of Xe is compared with the simulation and we also show the difference $\Delta g = g^{(3)} - g^{(2)}$ between the two $g(r)$ with and without $v_{AT}^{(3)}$. In Fig. 2 the same difference is shown for $S(k)$. The effect of $v_{AT}^{(3)}$ is very small in both cases and well reproduced by our equation. The main effect on $g(r)$ is a depression for distances up to the first maximum, followed by some small oscillations. The effect on $S(k)$ is significant only at small k and it is less than 1% at the main peak. Similar results hold for Kr. The deviation between theory and simulation is smaller for Δg than for $g(r)$ itself. We conclude that the main error of the triplet MHNC-CRS is due to the way the two-body interaction is treated. On the other hand, the low-density approximation[6,7] for $C(r)$ strongly overestimates the effect of $v_{AT}^{(3)}$ on $g(r)$ at high density. The integral equation result for $S(0)$ is higher than the result of simulation by about 6% for Xe and 4.5% for Kr. For the latter the experimental equation of state[12] is in good agreement with the triplet MHNC-CRS result and with the virial pressure given by simulation.[4] Hence the simulation $S(0)$ is at fault due to either the extension algorithm[13] of $g(r)$ or the finite-size correction to $g(r)$ of order $1/N$ associated with the canonical ensemble.

The structure factor $S(k)$ uniquely determines a pair interaction, but when many-body forces are present, the extracted potential ϕ_{eff} is an effective one showing density and temperature dependence. Its difference from the bare two-body interaction ϕ_0 is a measure of many-body forces.

Assuming that the most important many-body forces are the three-body ones, in the present approximation the effective interaction is given by

$$\phi_{\text{eff}}(r) = \phi_0(r) - k_B T C(r) \ . \tag{3}$$

Suppose that ϕ_{eff} has been obtained from $S(k)$ and the related $g(r)$ by a suitable inversion scheme, the predictor-corrector method,[14] for instance. For an assumed form of $v^{(3)}$ the computation of $C(r)$ with the experimental $g(r)$ is straightforward and from (3) ϕ_0 can be obtained directly. If the choice of $v^{(3)}$ is appropriate, the extracted ϕ_0 should show no state dependence. It is then possible to test models of $v^{(3)}$.

Neglecting $E^{(3)}$ is justified in the direct problem, as we have seen earlier in this section. This, however, should be explicitly verified in the much more delicate inversion problem. We have tested it with the simulation results already discussed for the xenon model at the triple point, the most difficult thermodynamic state from this point of view. Indices 2 and 3 denote correlation functions of the system without and with three-body forces, respectively. It is known[14] that a MHNC approximation for $E^{(2)}$ is not good enough in the inversion problem. We can obtain, however, the exact bridge function of the system with just two-body forces from

$$E(r,h_2) = \beta\phi(r) - h_2(r) + c_2(r) + \ln g_2(r) \tag{4}$$

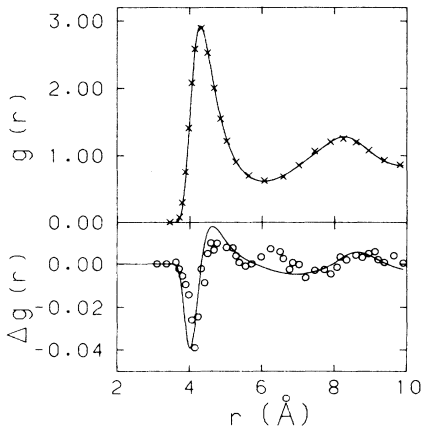

FIG. 1. $g(r)$ for xenon with three-body AT interaction for a triple-point state ($k_B T/\varepsilon = 0.622, \rho\sigma^3 = 0.777$): simulation (Ref. 3) (×) and triplet MHNC-CRS (——). Difference $\Delta g(r) = g^{(3)} - g^{(2)}$ of $g(r)$ with and without $v_{AT}^{(3)}$: simulation (○), MHNC-CRS (——).

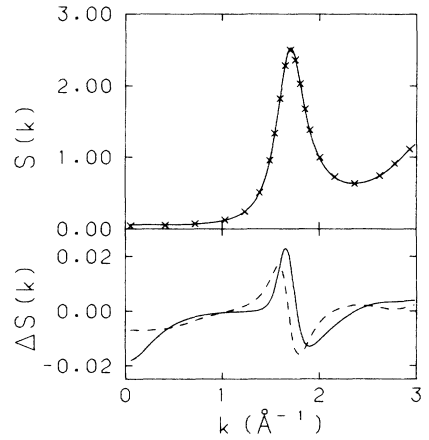

FIG. 2. Same as in Fig. 1 for $S(k)$ (×, simulation; ——, triplet MHNC-CRS) and $\Delta S(k) = S^{(3)} - S^{(2)}$ (— — —, simulation; ——, MHNC-CRS).

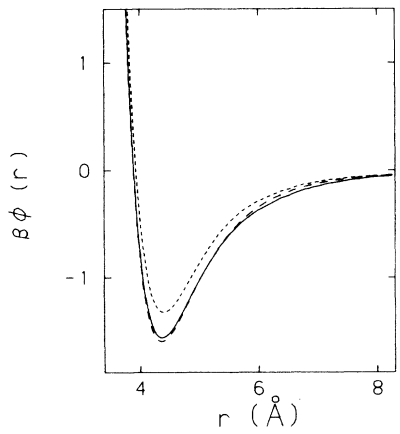

FIG. 3. Test of the inversion scheme for Xe in the presence of $v_{AT}^{(3)}$: true pair interaction in units of $k_B T$ (— — —), effective pair interaction as given by (5) (---), and extracted pair interaction from (3) (——).

TABLE I. Temperature and density of the critical point. First column: experimental critical temperature (Ref. 17). Second column: reduced values. Third and fourth columns: our results without and with AT triple-dipole interaction. Last four columns: analogous values for the density.

	T_c (K)	T_c^*	$T_c^*(0)$	$T_c^*(V_3)$	ρ_c (nm^{-3})	ρ_c^*	$\rho_c^*(0)$	$\rho_c^*(V_3)$
Ar	150.7	1.052	1.065	0.990	8.06	0.304	0.302	0.290
Kr	209.3	1.047	1.077	0.987	6.52	0.299	0.302	0.288
Xe	289.7	1.026	1.047	0.944	5.09	0.300	0.302	0.286

by using $g_2(r)$ and $c_2(r)$ obtained by simulation [to compute $c_2(r)$, $g_2(r)$ is extended according to Verlet's algorithm[13]]. If we approximate the two-body part $E^{(2)}(r,h_3)$ of the bridge function by $E(r,h_2)$, the effective two-body potential is

$$\phi_{\text{eff}}(r)=h_3(r)-c_3(r)-\ln g_3(r)+E(r,h_2) \tag{5}$$

and from (3) we obtain $\phi_0(r)$. If our approximation is good, ϕ_0 should be very close to Aziz's potential $\phi(r)$ and this is indeed the case as shown in Fig. 3. For comparison, ϕ_{eff} is also plotted. It is clear that the term $C(r)$ gives the major contribution to $\beta(\phi_{\text{eff}}-\phi)$ and that the remainder, which is $E^{(3)}(r)+E^{(2)}(r,h_3)-E(r,h_2)$, is small. In a real inversion procedure Eq. (5) cannot be used because $E(r,h_2)$ is unknown and one only has the bridge function for ϕ_{eff}, i.e., $E^{(2)}(r,h_3)$. However, once $\phi_0(r)$ has been obtained from (3) by using $E^{(2)}(r,h_3)$ in (5), a simulation with $\phi_0(r)$ makes it possible to compute the exact bridge function of ϕ_0 and from this an improved estimate of ϕ_0 can be obtained. We conclude that it is possible to test models of $v^{(3)}$ and to extract the true two-body interaction by doing computations with two-body forces only, thus avoiding the much more costly simulation with three-body forces.

III. CRITICAL POINT

We have determined the critical point of Ar, Kr, and Xe on the basis of the triplet MHNC-CRS equation. This equation does not give an accurate description of critical phenomena but shows a genuine critical point with diverging isothermal compressibility and correlation length.[15] The hard-sphere diameter is determined according to Lado's criterion for every different density and kept fixed along an isochore since it depends weakly on temperature. The optimized crossover parameters in the critical region are $w=0.575$ and $R=1.375$. The range $R_{\max}$ of the r interaction is such that $R_{\max}\gtrsim 8\xi$ where ξ is the correlation length, and the maximum value of $R_{\max}$ is 100σ. The cutoff for $\phi(r)$ is at $R_{\max}$.

We have performed the computation with and without the AT $v^{(3)}$. As pair interaction for Kr and Xe we use the same potentials as in Sec. II. For argon we use the potential in Ref. 16 and $\nu_3=0.734\times10^{-82}$ erg cm^9. The critical point is obtained as the maximum of the spinodal curve. We estimate a maximum absolute error of 0.005 both in T_c^* and ρ_c^* and a much smaller relative error between the different models (reduced units for T and ρ are in terms of ε and σ^3, respectively, ε being the well depth and σ of the position of the zero of the pair interaction.

In Table I the experimental[17] and the computed ρ_c and T_c are given. The experimental values of ρ_c^* and T_c^* show small deviations from the law of corresponding states. The presence of $v_{\text{AT}}^{(3)}$ lowers both T_c and ρ_c, in agreement with previous computations[2] and this effect is very well approximated by a linear dependence in terms of $V_3=\nu_3/\varepsilon\sigma^9$: $T_c^*(V_3)=(1-aV_3)T_c^*(0)$, $\rho_c^*(V_3)=(1-bV_3)\rho_c^*(0)$ with $a=1.0$ and $b=0.56$. Within the accuracy of our computation we find the same value of $\rho_c^*(0)$ for the three rare gases when $V_3=0$ while there are small variations of $T_c^*(0)$, of order of 3% between Kr and Xe. These variations are in agreement with a random-phase calculation, the strengths of the attractive wells [integral of $r^2\phi(r)$ starting from σ] of Ar, Kr, and Xe being in the ratios 1:0.99:1.02. This effect is of the same order as the change of T_c^* induced by the different value of the intensity ν_3 for the three rare gases. Hence, on the basis of the present best representation of the interatomic forces, the deviations from the law of corresponding states for Ar, Kr, and Xe are due in equal parts to the different shape of $\phi(r)$ and to the difference in $v_{\text{AT}}^{(3)}$.

Considering absolute values for the critical point, the best agreement with experiment is shown by data in Table I obtained *without* three-body forces. However, it is known that outside the critical region many-body forces are needed in order to get agreement with the equation of state of the heavy rare gases, and actually good quantitative agreement is found in this case in Refs. 3 and 4 when $v_{\text{AT}}^{(3)}$ is used. This suggests that MHNC-CRS underestimates both T_c and ρ_c by about 5%, and that the agreement with experiment found in Ref. 18 with a two-body potential is fortuitous.

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