Computer simulation of dense krypton gas: Effect of long-range three-body interactions

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Using molecular-dynamics simulations, we show that long-range three-body interactions have a negligible effect on the static and dynamical structure factors and on the transport properties of Kr gas.

I. INTRODUCTION

In a recent paper[1] we investigated, by computer simulations, the role of the three-body Axilrod-Teller (AT) potential (leading term of the long-range many-body interactions) on the static and dynamical properties of Xe near the triple point. Our main conclusions were that though the AT potential had a marked effect on the thermodynamic properties (internal energy, pressure, compressibility), it had very little effect on structural (static and dynamical) or transport properties.

On the other hand, Egelstaff and collaborators[2] performed neutron-scattering measurements of the static and dynamical structure factors of dense Kr gas at room temperature (297 K) (densities up to 14 atoms/nm^3). By comparing these measurements with corresponding computer-simulation results based on the best available *pair* potential, they found quantitatively significant differences for the static structure factor $S(k)$ for wave vectors $k \leq 1$ Å^{-1} (Refs. 2 and 3) and for the dynamical structure factor $S(k,\omega)$ (Ref. 4) in the wave vector range $0.60 \leq k \leq 1.30$ Å^{-1} (at density $\rho = 1.38$ atoms/nm^3). These differences were attributed to many-body effects.[5] Similar discrepancies have also been reported[6] to occur in Kr at $T = 200$–220 K.

The purpose of this article is to show that the conclusions reached for Xe near the triple point also apply to room-temperature Kr, namely that the effect of the AT potential on the static and dynamical structure factors is extremely small (at least for the wave vectors $k \geq 0.30$ Å^{-1} accessible in our computations) and cannot explain the above mentioned differences. Towards this end we performed two sets of molecular-dynamics (MD) simulations, one with an accurate pair potential, the Hartree-Fock-dispersion-type potential proposed by Aziz[7], also used in the MD simulations by Salacuse, Schommers, and Egelstaff[4] and one with an added three-body AT potential with strength $\nu = 220.4 \times 10^{-84}$ erg cm^9 (Ref. 8).

For brevity of notation we will refer to both systems as two-body and three-body systems. After giving some details on the MD simulations in Sec. II, we present in Sec. III our results for the structure factors and transport properties.

II. MOLECULAR-DYNAMICS SIMULATIONS

The MD simulations were carried out in the same way as in our previous study of Xe and we refer the reader to Ref. 1 for technical details. We only mention that we used 108 particles. This rather small number of particles was forced upon us by the relatively large amount of computer time which is required, in the presence of three-body forces, to produce dynamical properties with reasonable statistical error. A complete study of size effects on these quantities is still lacking, but from recent simulation studies of the transport coefficients of the Lennard-Jones system[9–11] it would appear that only the shear viscosity is affected by a 108-particle system.[9] Moreover, in the present study, we are primarily interested in the differences between the properties of the two- and three-body systems. In using for both systems the same number of particles it is likely that finite-size effects will be nearly identical with and without three-body interactions, especially for the dynamical properties for

TABLE I. Effect of the Axilrod-Teller potential on internal energy U and compressibility factor Z. Two body and three body denote the systems interacting with the pair potential (Ref. 7) and pair plus Axilrod-Teller potential, respectively. $U^{(2)}$ ($Z^{(2)}$) is the pairwise additive and $U^{(3)}$ ($Z^{(3)}$) the nonadditive contribution to U (Z). Correction terms have been included for truncation of the pair and triplet potentials (cf. Ref. 1). These are -0.244, -0.294, 0.0033, and 0.004 for $U^{(2)}$, $Z^{(2)}$, $U^{(3)}$, and $Z^{(3)}$, respectively.

System	T (K)	U	$U^{(2)}$ (kJ/mol)	$U^{(3)}$	Z	$Z^{(2)}$	$Z^{(3)}$
Two body	295.6±0.4	−5.978±0.002			1.315±0.004		
Three body	296.2±1.4	−5.684±0.002	−5.981±0.002	+0.298±0.0004	1.650±0.008	1.287±0.007	0.363±0.0004
Expt.[a]	297	−5.62			1.66		

[a]Reference 12.

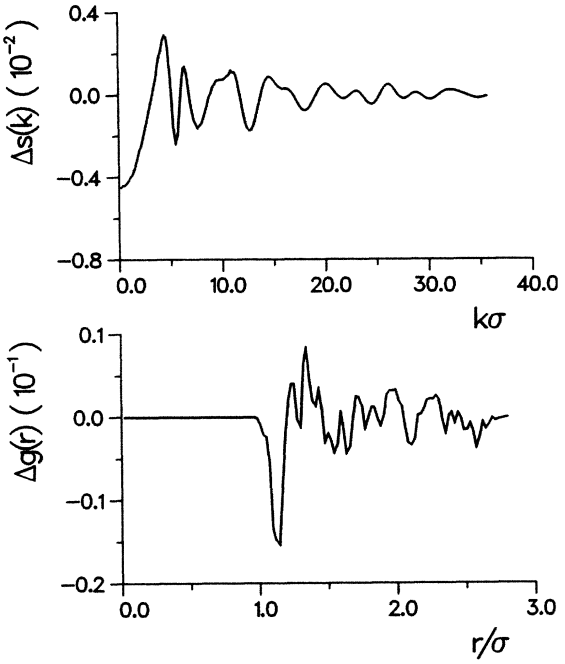

FIG. 1. Differences between the pair distribution functions $\Delta g(r)=g$(two body)-g(three body) and the structure factors $\Delta S(k)=S$(two body)-S(three body) of the two-body (Aziz potential) (Ref. 7) and the three-body (Aziz + AT potential) systems. [$\sigma=3.579$ Å is the distance where the Aziz potential (Ref. 7) is zero.]

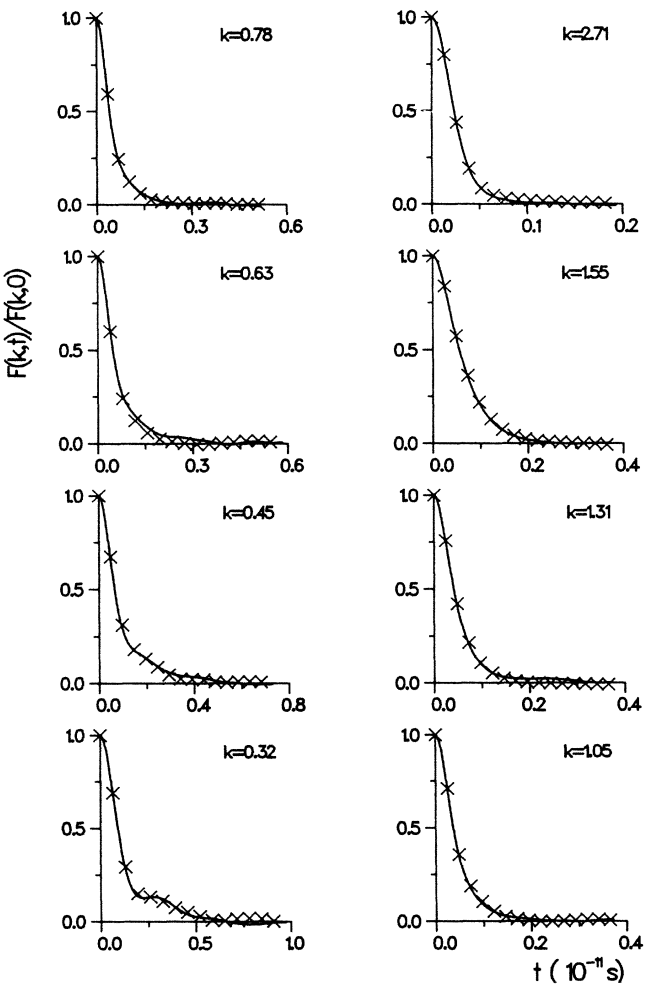

FIG. 2. Normalized intermediate scattering function $F(k,t)/F(k,0)$. Solid line: three-body system (Aziz + AT potential); crosses: two-body system (Aziz potential). The wave vectors k are in units of Å^{-1}.

which the contribution of the latter turns out to be rather small.

The thermodynamic state we consider has temperature $T=297$ K and density $\rho=13.8$ atoms/nm^3. For this density the box (cubic) length is $L=19.84$ Å. The time for a sound wave to travel across the box is 3.2 ps [using the experimental sound velocity 625 m/s (Ref. 12)]. The results presented in the following section are averages over 10 independent runs of 10 000 time steps each ($\Delta t=0.81\times10^{-14}$ s). The quoted statistical error represents one standard deviation.

III. RESULTS

A. Thermodynamic properties and static structure

The values for the internal energy U and compressibility factor $Z=p/\rho k_B T$ (p pressure, k_B Boltzmann's constant) are given in Table I together with separate contributions from the two- and three-body potentials. For the thermodynamic state considered the contribution of the AT potential to the internal energy is $\sim5\%$ and to the pressure 30%. The total values are in good agreement with experiment,[12] in accord with previous findings by Barker.[13]

On the contrary, the effect on the pair distribution function $g(r)$ and the structure factor

$$S(k)=1+\rho\int[g(r)-1]e^{i\mathbf{k}\cdot\mathbf{r}}d\mathbf{r} \tag{1}$$

is extremely small, as illustrated in Fig. 1 which shows the differences of these quantities for the two- and three-body systems. Statistically significant differences (though quite small) occur in Δg only in the region of the main peak and of the first minimum. For larger r ($r>5$ Å) the oscillations in Δg merely reflect the statistical error on the $g(r)$'s (estimated to be ±0.005). No effect of the three-body potential on the peak positions in $g(r)$ is observed.

In order to obtain $S(k)$ from the Fourier transform (1), $g(r)$, calculated in the MD simulations only up to $r=L/2=9.9$ Å, had first to be extrapolated to infinity. This was done in the way described in Ref. 14 by assuming (for both systems) that the two-body direct correlation function $c(r)=0$ for $r>L/2$. Differences in $S(k)$ are very small for all values of k. The lowering of $S(k)$ in the small-k region for the three-body system is in agreement with the depletion of the main peak in $g(r)$.

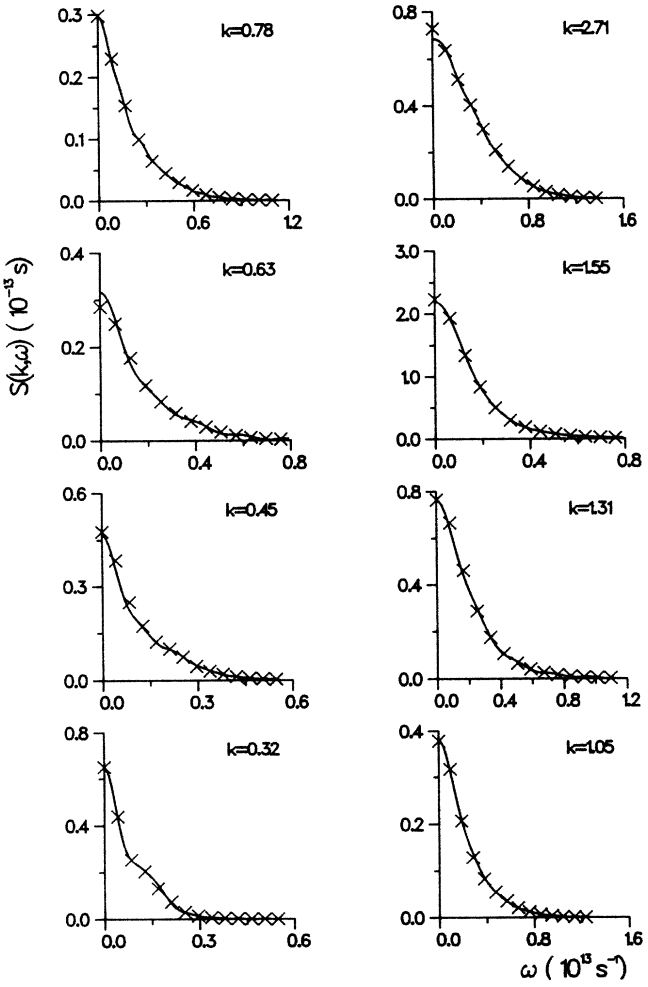

FIG. 3. Dynamical structure factor $S(k,\omega)$. The symbols are as in Fig. 2.

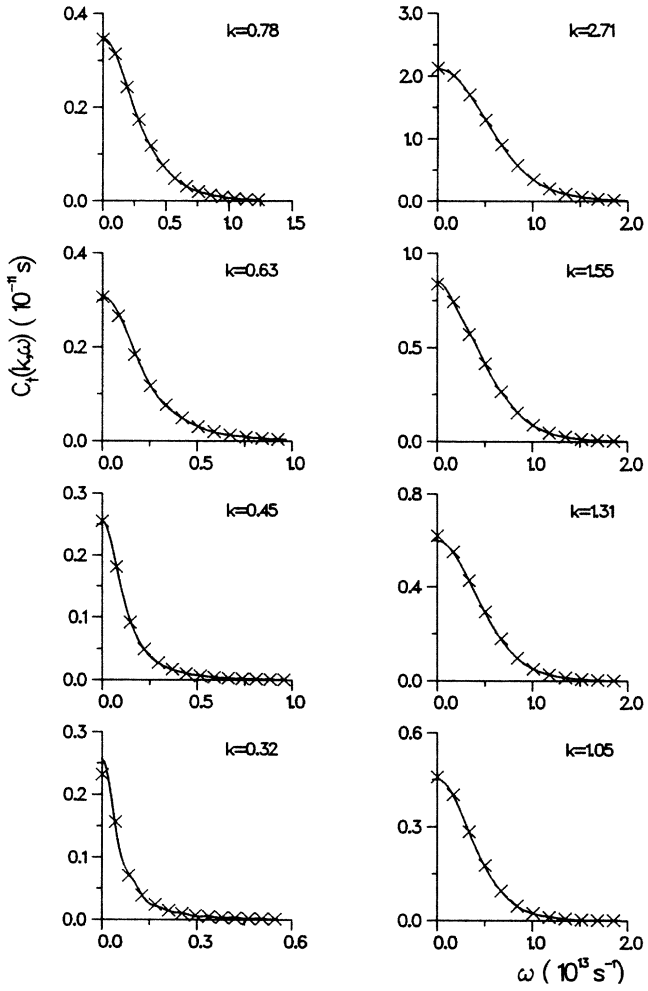

FIG. 4. Transverse current autocorrelation function $C_t(k,\omega)$. The symbols are as in Fig. 2.

B. Dynamical structure factor and transverse current autocorrelation function

Among the collective properties we calculated the intermediate scattering function

$$F(k,t)=\frac{1}{N}\left\langle \sum_{i,j} e^{i\mathbf{k}\cdot[\mathbf{r}_i(0)-\mathbf{r}_j(t)]} \right\rangle , \tag{2}$$

the transverse current autocorrelation function

$$C_t(k,t)=\frac{1}{N}\left\langle \sum_{i,j} v_i^{\perp} v_j^{\perp} e^{i\mathbf{k}\cdot[\mathbf{r}_i(0)-\mathbf{r}_j(t)]} \right\rangle \tag{3}$$

TABLE II. Initial values of the intermediate scattering function $F(k,t=0)$. $S(k)$ denotes the structure factor obtained by Fourier transform (1) of $g(r)$ extrapolated to all r in the way described in the text.

	Two body		Three body	
k (Å^{-1})	$F(k,t=0)$	$S(k)$	$F(k,t=0)$	$S(k)$
0.317	0.155±0.004	0.137	0.156±0.005	0.131
0.448	0.153±0.002	0.144	0.147±0.003	0.140
0.634	0.148±0.003	0.157	0.150±0.003	0.155
0.776	0.169±0.002	1.175	0.168±0.001	1.173
1.051	0.249±0.002	0.251	0.252±0.002	0.252
1.306	0.470±0.004	0.466	0.462±0.005	0.470
1.552	1.029±0.009	1.029	1.032±0.01	1.029
2.707	0.795±0.003	0.800	0.793±0.003	0.801

TABLE III. Values of the transport coefficients and initial values of the associated time correlation functions. Two body and three body denote the systems interacting with pair potential (Ref. 7) and pair plus Axilrod-Teller potential, respectively. The experimental value of $\eta_s = 0.142$ (Ref. 15).

	$C_{\eta_s}(0)$ (10^{12} mPa)	$C_{\eta_v}(0)$ (10^{12} mPa)	$C_\lambda(0)$ (10^{16} erg K^{-1} cm^{-1})	η_s (mPa s)	η_v (mPa s)	λ (W K^{-1} m^{-1})
Two body	0.78±0.02	0.65±0.02	2.09±0.06	0.132±0.003	0.087±0.002	0.053±0.003
Three body	0.77±0.02	0.66±0.03	2.08±0.06	0.129±0.004	0.092±0.005	0.054±0.002

($v_i^\perp$ velocity component of the ith particle perpendicular to $\mathbf{k}$), and their Fourier transforms $S(k,\omega)$ and $C_t(k,\omega)$, where

$$S(k,\omega)=\frac{1}{2\pi}\int_{-\infty}^{+\infty}F(k,t)e^{i\omega t}dt \tag{4}$$

and a similar relation holds for $C_t(k,\omega)$. The simulation results for $F(k,t)$ (normalized), $S(k,\omega)$, and $C_t(k,\omega)$ are shown in Figs. 2–4, respectively, for wave vectors $k = 0.31, 0.45, 0.63, 0.78, 1.05, 1.31, 1.55, 2.71$ Å^{-1} compatible with the periodic boundary conditions of our system. We first can remark that the present results for $F(k,t)$ using the pair potential alone are in close agreement with those of Salacuse, Schommers, and Egelstaff[4] using 256 and 500 particles. This is true, in particular, for the values of $F(k,t)$ at time $t=0$ listed in Table II. These values agree well with those obtained by Fourier transform of the pair correlation function [Eq. (1)], except for the lowest k vectors, where the extension procedure on the simulated $g(r)$ corrects to some extent the finite-size effects.

The main observation of this work is, however, that the effect of the AT potential on $F(k,t)$ and $C_t(k,t)$ and consequently on $S(k,\omega)$ and $C_t(k,\omega)$ is extremely small at all wave vectors considered. This is quite similar to what we found for Xe near triple point.[1] As a corrollary, it follows that the differences between the experimental $S(k,\omega)$ and the simulation results (based on pair potential only) in the wave vector range 0.60 Å$^{-1} \le k \le 1.30$ Å^{-1}—a higher first peak and a faster decay of the experimental $S(k,\omega)$ at low frequency—cannot be explained by the long-range three-body AT potential.

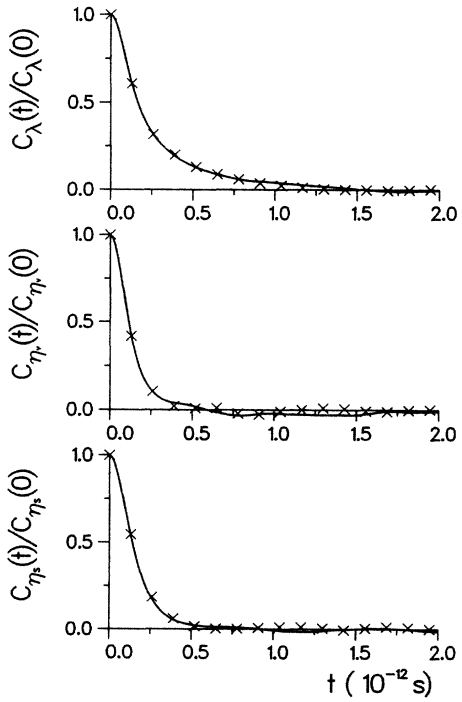

FIG. 5. Normalized time correlation functions $C_\alpha(t)/C_\alpha(0)$. ($\alpha=\eta_s,\eta_v,\lambda$) associated with the shear viscosity η_s, the bulk viscosity η_v, and the thermal conductivity λ. The symbols are as in Fig. 2.

C. Transport coefficients

The hydrodynamic transport coefficients, shear viscosity η_s, bulk viscosity η_v, and thermal conductivity λ were calculated from the time correlation functions of the off-diagonal and diagonal parts of the stress tensor and of the heat flux (Green-Kubo relations):

$$\alpha=\int_0^\infty C_\alpha(t)dt \quad (\alpha=\eta_s,\eta_v,\lambda)\ . \tag{5}$$

Explicit expressions for $C_\alpha(t)$ were given in Ref. 1. The MD results for $C_\alpha(t)/C_\alpha(0)$ are shown in Fig. 5 for the two- and three-body systems. Table III compares the initial values of C_α and the transport coefficients. In calculating the latter from Eq. (5) a cutoff was introduced in the time integration when the magnitude of the (average) correlation function was equal to the noise level assumed to be one standard deviation. The error (one standard deviation) on the transport coefficients was estimated by averaging over the ten independent runs. As for the other time-dependent properties considered in this work, the transport coefficients are not affected by the AT potential. Experimental results are available for the shear viscosity.[15] Its value is about 10% higher than the calculated value. Part of this discrepancy may be due to the small size of our system. At high density and low temperature (triple-point conditions) the finite-size effect on the shear viscosity has been estimated to be about 10% (Ref. 9). Experimental values for the bulk viscosity and thermal conductivity seem unfortunately not available for the thermodynamic conditions considered in our simulations.

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