Two-body contribution to the density fluctuations in a dilute gas from molecular-dynamics simulations

Ubaldo Bafile
Istituto di Elettronica Quantistica, Consiglio Nazionale delle Ricerche, via Panciatichi 56/30, I-50127 Firenze, Italy

Fabrizio Barocchi
Dipartimento di Fisica, Università di Firenze, largo Enrico Fermi 2, I-50125 Firenze, Italy

Martin Neumann
Institut für Experimentalphysik der Universität Wien, Strudlhofgasse 4, A-1090 Wien, Austria
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We have performed molecular-dynamics simulations of the intermediate scattering function $F(k,t)$ of a Lennard-Jones gas at room temperature, low densities, and very low k values in order to study the density dependence of the deviations from the free-gas dynamics. We have extracted the linear term in the density expansion of these deviations as a function of time, which provides information on the two-body interaction potential. We compare these results with those obtained recently from a neutron inelastic scattering experiment on ^{36}Ar, performed in the same range of thermodynamical states and with a theoretical calculation for hard spheres. The comparison confirms the experimental results and shows unambiguously that the linear term in a density expansion of $F(k,t)$ and of the dynamic structure factor $S(k,\omega)$ is a sensitive probe of the details of the pair interaction.

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From recent inelastic neutron scattering measurements of the dynamic structure factor $S(k,\omega)$ of low-density gaseous ^{36}Ar at very low momentum transfer, a correction to the free-gas behavior has been obtained [1]. In Ref. [1] it was experimentally shown that for a real gas the concept of virial (i.e., density) expansion, already applied to the study of static properties [2], is also valid for $S(k,\omega)$ in the appropriate (k,ω) range, which is outside the region of the (k,ω) space where collective modes are present in the spectra of density fluctuations. Then, either condition $kl_0 \gg 1$ or $\omega t_0 \gg 1$ must be satisfied, where l_0 and t_0 are the Boltzmann mean free path and mean free time, respectively, of a corresponding hard-sphere (HS) system.

A general theoretical support to this approach has been also given recently [3]. Thus one can write for the normalized dynamic structure factor

$$\frac{S(k,\omega)}{S(k)} = S^{(0)}(k,\omega) + nS^{(1)}(k,\omega) + O(n^2) , \qquad (1)$$

where n is the number density, $S(k)$ is the static structure factor, and $S^{(0)}(k,\omega)$ is the free-gas term which equals the dynamic structure factor of a system of noninteracting particles. The first-order term $S^{(1)}(k,\omega)$ is directly related to the two-body dynamics and therefore to the details of the pair interaction in the system.

Although HS theory [4] correctly predicts some spectral features of $S^{(1)}(k,\omega)$, nevertheless important differences exist, in this respect, between the model HS system and a real gas [1], which have been attributed to the fact that the characteristics of the real potential must determine precisely the dynamics of an isolated pair. However, only HS calculations are available [4] for a comparison between experimental results and theory. The evaluation of the density correction to the free-gas limit of $S(k,\omega)$ for a realistic pair potential is therefore essential in order to have a more meaningful comparison with the experimental results and also to assess the difference from HS theory.

An exact, either quantum mechanical or classical, calculation of $S^{(1)}(k,\omega)$ is possible but quite difficult. An easier approach is, in principle, the one based on classical calculations performed by means of molecular-dynamics (MD) computer simulation. A classical approach is appropriate for argon at room temperature, while MD gives the possibility of studying a large range of densities so that the onset of higher-order terms in (1) can be investigated. In the MD case one evaluates, for a given pair interaction potential, the Fourier transform of $S(k,\omega)$, i.e., the so-called intermediate scattering function

$$F(k,t) = \frac{1}{N} \sum_{a,b} \langle \exp[-i\mathbf{k}\cdot\mathbf{R}_a(0)] \exp[i\mathbf{k}\cdot\mathbf{R}_b(t)] \rangle , \qquad (2)$$

where N is the number of particles, $\mathbf{R}_a(t)$ is the position of atom a at time t, and the brackets denote an ensemble average. A density expansion equivalent to (1) can then be written as

$$\frac{F(k,t)}{F(k,0)} = \int_{-\infty}^{+\infty} d\omega \exp(i\omega t) \frac{S(k,\omega)}{S(k)} = F^{(0)}(k,t) + nF^{(1)}(k,t) + O(n^2) , \qquad (3)$$

where $F^{(0)}(k,t)$ and $F^{(1)}(k,t)$ are the Fourier transforms of $S^{(0)}(k,\omega)$ and $S^{(1)}(k,\omega)$, respectively. The free-particle term is a simple Gaussian given by $F^{(0)}(k,t) = \exp(-k_B T k^2 t^2 / 2M)$, where k_B, T, and M are the Boltzmann constant, the temperature, and the atomic

mass, respectively. The excess correlation $\Delta F(k,t) = F(k,t)/F(k,0) - F^{(0)}(k,t)$ contains the density dependence and its leading term is connected to the two-body dynamics.

At the very low densities required for the higher-order terms in (3) to be negligible and either condition $kl_0 \gg 1$ or $\omega t_0 \gg 1$ to be fulfilled, MD simulation is an unusual technique because collisions are very rare. Therefore, very long calculations are necessary to produce $\Delta F(k,t)$ data suitable for a density expansion with a statistical error small enough to obtain $F^{(1)}(k,t)$ with sufficient precision, since at low density $F^{(0)}(k,t)$ is the dominant term in (3). Moreover, $F^{(1)}(k,t) \approx \Delta F(k,t)/n$ is appreciably different from zero only at very low k, so that a rather large box is required, which implies a large N even at low densities.

MD simulations of $F(k,t)$ for continuous pair potentials at larger n and k values have been reported quite a few years ago [5]. Here we briefly describe the present MD calculations and the density analysis of $F(k,t)$ at low k values and low density, from which $F^{(1)}(k,t)$ can be determined and compared with experimental data. The Lennard-Jones (LJ) pair potential has been chosen because it is the simplest functional form for a realistic pair potential for a MD simulation and permits a meaningful comparison with both the experimental results and HS theory.

The MD simulations have been performed at room temperature with the Verlet algorithm [6] for six densities in a cubic box of fixed size L such that the minimum k value ($k_{\min} = 2\pi/L = 0.5$ nm^{-1}) is in the range where a linear density dependence has been found experimentally [1]. The density was varied, by changing N, in the range $0.25 \le n \le 2.00$ nm^{-3} ($0.0099 \le n^* \le 0.0790$). The box length was $L^* = 36.9$ and the time step $\Delta t^* = 0.002$. We denote by asterisks dimensionless quantities reduced by means of appropriate combinations of the LJ parameters σ and ε, and of the atomic mass M, given for ^{36}Ar by $\sigma = 0.3405$ nm, $\varepsilon/k_B = 119.8$ K, and $M = 59.726 \times 10^{-27}$ kg. In particular, the reduced time unit equals 2.05 ps. Some parameters of the various runs are listed in Table I. It can be seen that even at the lowest density the box length is larger than the mean free path l_0, while t_0 is of the order of 10^3 time steps. We have truncated the interaction at 3σ and, since the average number N_c of particles in the cutoff sphere, also given in Table I, is extremely small, we have used neighbor tables (which were updated using the link-cell method [6]) to make the calculation as efficient as possible.

TABLE I. Parameters of the simulation runs. The temperature is $T = 300.0$ K ($T^* = 2.504$), except for the last state where $T = 301.5$ K ($T^* = 2.517$).

N	n (nm^{-3})	p (MPa)	l_0^*	t_0^*	N_c
496	0.25	1.03	22.81	9.03	1.12
992	0.50	2.05	11.41	4.52	2.23
1488	0.75	3.05	7.60	3.01	3.35
1984	1.00	4.05	5.70	2.26	4.46
2977	1.50	6.01	3.80	1.50	6.70
3969	2.00	8.00	2.85	1.13	8.93

We first evaluated the normalized correlation functions $F(\mathbf{k},t)/F(\mathbf{k},0)$ for the discrete set of wave vectors $\mathbf{k}$ compatible with the shape of the box with $0.5 \le k \le 1.5$ nm^{-1}. Then, the excess correlation $\Delta F(k,t)$ was obtained by averaging over all directions of $\mathbf{k}$ with fixed k, which are statistically equivalent, and subtracting $F^{(0)}(k,t)$. An estimate of the statistical uncertainties was also obtained from the averaging procedure.

The simulation runs were extended up to 10^8 time steps for the first four densities and to 10^7 for the two higher ones. The need for very long runs is essentially due to the fact that in a low-density gas, statistical averaging is a very slow process because of the large ratio $t_0^*/\Delta t^*$. This is apparent when $\Delta F(k,t)$ is compared with intermediate results obtained with a lower number of time steps. An example of this comparison is displayed in Fig. 1, which shows that the final run lengths provide a sufficient convergence of the calculations. In particular, it appears that $\Delta F(k,t)$ converges to zero at times of the order of twice the position of the pronounced minimum. The convergence rate is faster at higher densities, where $t_0^*/\Delta t^*$ is lower.

Another source of error, especially at low k, may be artifacts due to the finite system size and the recurrence time (which is the time it takes a sound wave to travel through the box). In order to estimate these effects at least qualitatively, we have repeated the simulation at $n = 0.50$ nm^{-3} with a box size of exactly $2L$ (which is 8 times the number of particles) and 5×10^7 time steps. The results are also shown in Fig. 1. Given the difficulty of the calculation, the agreement between systems of different size is very good. A possible overall systematic error of the order of the statistical one has been taken into account.

$\Delta F(k,t)/n$ is plotted in Fig. 2 for three values of k. At the lower k values the most prominent features are a negative broad peak followed in time by a positive one, while another positive peak emerges at lower times as k increases. The peak abscissas are at approximately constant values of kt and are all much larger than the half width of $F^{(0)}(k,t)$, i.e., the significant deviations from $F^{(0)}(k,t)$ are confined to the tail of the correlation function $F(k,t)/F(k,0)$.

In Fig. 2 a linear density dependence of $\Delta F(k,t)$ would show up as a flat surface along the n axis. This is indeed the case for the largest k value and $n \le 1.25$ nm^{-3}. In contrast, at the lowest k value the range of linearity, if any, is much smaller.

The analysis in terms of a density expansion has been carried out following the same procedure applied to the experimental results [1], but working in the time domain instead of the frequency domain. At each (k,t) point we performed a linear least-squares fit with zero intercept (i.e., a one-parameter fit) to the data for $\Delta F(k,t)$ as a function of density, using the data at a number of densities varying from two to six.

As an overall criterion for assessing the linear density dependence we use, for each k value and for each number of densities used in the fits, the mean square deviation δ^2 of the weighted least-squares fit divided by the number of

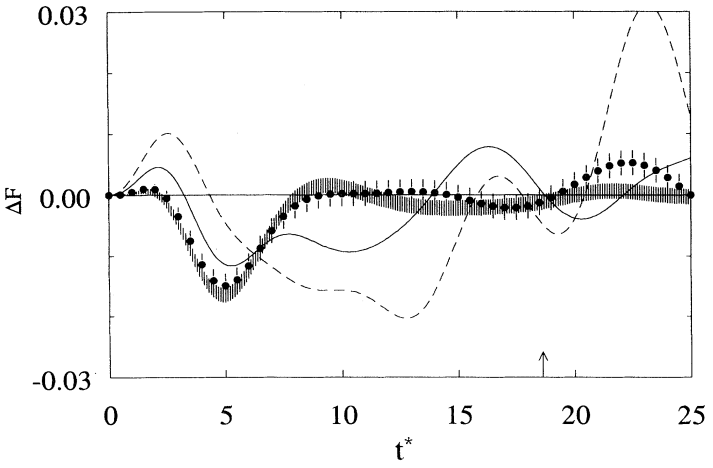

FIG. 1. $\Delta F(k,t)$ at $n=0.50$ nm^{-3} and $k=1.00$ nm^{-1} for three lengths of the simulation run: 10^6 time steps (dashed line), 10^7 time steps (solid line), and 10^8 time steps (error bars). The error bars for the simulations with 10^6 and 10^7 time steps are much larger than those reported for the case of the longest run. Dots with error bars are the results of the simulation performed in a box of length $2L$. The estimated recurrence time for an ideal gas in the smaller system is indicated by an arrow.

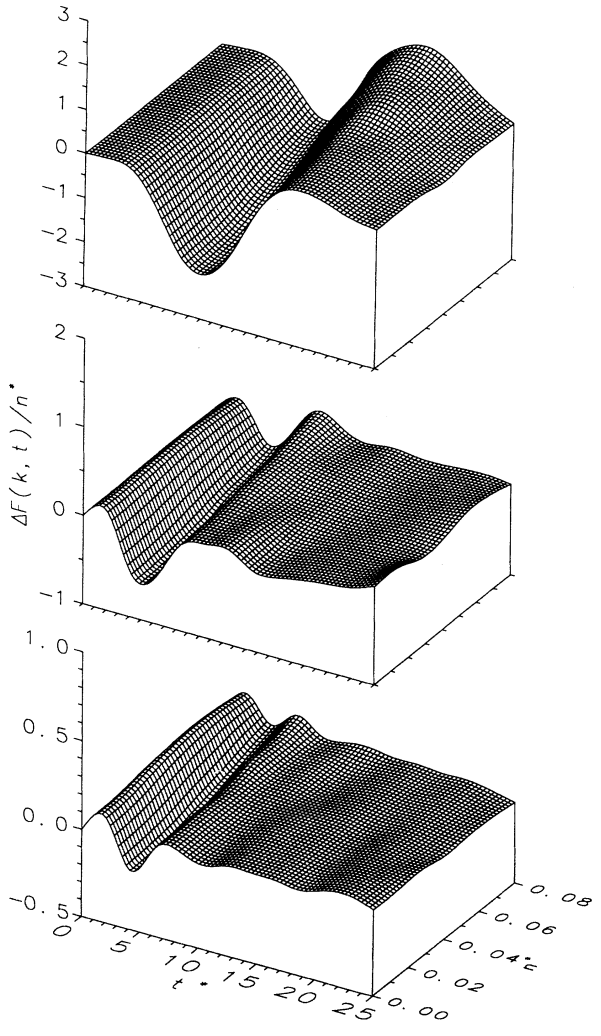

FIG. 2. $\Delta F(k,t)/n^*$ as a function of time and density at three values of k: (a) $k=0.50$ nm^{-1}, (b) $k=0.71$ nm^{-1}, and (c) $k=1.00$ nm^{-1}.

degrees of freedom and averaged over t for times up to the second positive peak included. The results are reported in Table II. Apart for the unexplained exception at $k=1.00$ nm^{-1}, the inclusion in the fit of higher densities data produces an increase of δ^2 that is larger for smaller k, thus showing that the region of linear behavior in n expands with k. In particular, δ^2 increases clearly when the third density is included in the fit at $k=0.50$ nm^{-1} and the fourth one is included in the fit at $k=0.71$ nm^{-1}. For $k\geq 0.87$ nm^{-1}, the quality of fit is not too much changed by the inclusion of densities up to $n\leq 1.50$ nm^{-3}. These results are in agreement with the experimental ones [1] for $S^{(1)}(k,\omega)$, although the analysis of the experiment suggested that also the data at $n=2.00$ nm^{-3} could be used for linear fits for $k\geq 1.00$ nm^{-1}.

According to the previous results, we have determined $F^{(1)}(k,t)$ as the linear fit parameters, using data with $0.25\leq n\leq 0.50$ nm^{-3} at $k=0.50$ nm^{-1}, with $0.25\leq n\leq 0.75$ nm^{-3} at $k=0.71$ nm^{-1}, and with $0.25\leq n\leq 1.50$ nm^{-3} at $k\geq 0.87$ nm^{-1}. The results for $F^{(1)}(k,t)$ are plotted in Fig. 3, where they are compared with HS theory [4] and with the experimental data for ^{36}Ar [1], after Fourier transformation of the respective $S^{(1)}(k,\omega)$ to the t space. We note that the main results of Ref. [1] are clearly confirmed when the comparison between experimental and HS data is extended to include MD simulation. In particular, the following features

TABLE II. δ^2 of the weighted least-square fits of $F^{(1)}(k,t)$ with a number of densities varying from two to six.

k (nm^{-1})	Two	Three	Four	Five	Six
0.50	0.32	3.34	4.88	10.55	11.19
0.71	0.97	1.36	3.09	5.29	7.90
0.87	1.04	0.85	1.10	1.10	3.31
1.00	0.51	3.57	2.96	2.64	2.93
1.12	0.56	2.02	3.23	4.68	6.58
1.22	2.07	1.14	2.15	4.29	7.82
1.41	0.07	0.57	1.16	1.58	2.91
1.50	0.40	1.45	2.35	2.58	4.02

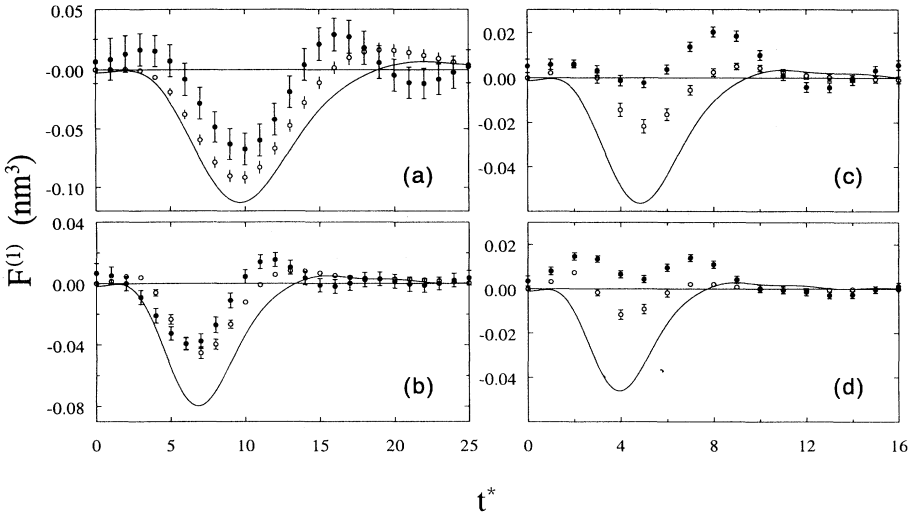

FIG. 3. Linear term of the density expansion of $\Delta F(k,t)$ obtained from the simulation data (open circles) at (a) $k=0.50$ nm^{-1}, $n\leq 0.50$ nm^{-3}; (b) $k=0.71$ nm^{-1}, $n\leq 0.75$ nm^{-3}; (c) $k=1.00$ nm^{-1}, $n\leq 1.50$ nm^{-3}; and (d) $k=1.22$ nm^{-1}, $n\leq 1.50$ nm^{-3}. The black dots are the experimental results in ^{36}Ar [1] and the solid line is the hard-sphere theory [4].

emerge from Fig. 3.

(1) The HS model correctly predicts the time range where deviations of $F(k,t)$ from the free-gas limit are significant also for real potentials, but the time dependence of these deviations is different for HS compared to the real pair potential, the difference increasing with increasing k.

(2) The possibility of extracting quantitative information on the two-body dynamics even in the presence of the dominant free-gas contribution is evident, in the investigated k range, from both the experiment and the computer simulation.

(3) The simulation data lie between the experimental and the HS theoretical ones. In particular, at the lowest k the three curves are in good qualitative agreement, while at high k the simulation is at least qualitatively similar to the experimental results.

We can therefore conclude that MD simulations produce meaningful results also in a very low density regime and strongly support the experimental finding of a quite good sensitivity of $S^{(1)}(k,\omega)$ or $F^{(1)}(k,t)$ to the details of the pair potential. In particular, the remarkable qualitative agreement of the three sets of data at the lowest k, contrasted with the large difference between HS and continuous potentials at higher k, suggests that $F^{(1)}(k,t)$, or equivalently $S^{(1)}(k,\omega)$, when studied in the appropriate k range, may be a sensitive probe of the intermediate- and the short-range part of the pair interaction. Surprisingly, these differences already show up at k values corresponding to wavelengths that are of the order of 20 molecular diameters.

[1] P. Verkerk, U. Bafile, F. Barocchi, L. A. de Graaf, J.-B. Suck, and H. Mutka, Phys. Rev. Lett. **67**, 1262 (1991).

[2] For instance, the density expansion of the static structure factor has been used for the direct experimental determination of the pair potential in H. Fredrikze, J. B. van Tricht, A. A. van Well, R. Magli, P. Chieux, and F. Barocchi, Phys. Rev. Lett. **62**, 2612 (1989).

[3] M. Moraldi, M. Celli, and F. Barocchi, Phys. Rev. A **46**, 7561 (1992).

[4] B. Kamgar-Parsi, E. G. D. Cohen, and I. M. de Schepper, Phys. Rev. A **35**, 4781 (1987).

[5] See references quoted in J. P. Hansen and I. R. McDonald, *Theory of Simple Liquids* (Academic, London, 1986), Sec. 3.3.

[6] M. P. Allen and D. J. Tildesley, *Computer Simulation of Liquids* (Clarendon, Oxford, 1987).