Quantum-corrected pair distribution function of liquid neon

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By means of computer simulation we have calculated the quantum-corrected pair distribution function $g(r)$ of liquid neon up to the term $\hbar^6$ of the Wigner-Kirkwood series expansion. The agreement between calculation and the experimental data at $T \simeq 35$ K of De Graaf and Mozer is now, for the first time, satisfactory.

Classical statistical mechanics is the usual framework in which the properties of high-density fluids are calculated by means of computer simulation techniques. Exceptions to this approach are the well known cases of the helium isotopes.

However, in the case in which either the temperature is low enough, or the mass of the elementary constituents is low enough, or the property under examination is studied at high enough frequency (which implies short correlation time), the quantum behavior of the many-body system cannot be neglected and consequently calculations must be performed with a theoretical approach which correctly takes into account quantum effects.

A rigorous quantum-mechanical calculation of the properties of a many-body system is presently not possible. However, there are two different approximate methods with which this problem can be approached for particles following the Boltzmann statistics.

One is based on the Wigner-Kirkwood expansion[1-4] and the other is based on the Feynman path-integral method.[5]

Recently we have shown how the Wigner-Kirkwood method can be applied for the calculation of spectral properties[4,6] and how various quantum corrections can be calculated for a many-body system by means of classical molecular-dynamics computer simulation techniques.[6,7] The quantum corrections to the pair-correlation function in a Lennard-Jones fluid have been also calculated in various thermodynamic conditions up to the order $\hbar^6$,[7,8] showing the effect of the particles diffraction on the short-range behavior of the static pair correlation function.[7] Calculations of $g(r)$, based on the Feynman path-integral method, have been performed by Pollock and Ceperly[9] for a Lennard-Jones fluid at various temperatures.

Liquid neon is a system of particular interest; its behavior is almost classical and therefore the Wigner-Kirkwood approach can be successfully used to calculate its properties. In fact, liquid neon (temperatures of the order of 35 K) is a system which can be considered in the framework of Boltzmann statistics and nevertheless shows a not negligible

quantum behavior in some of its properties. Calculations of the free energy[10] and of the collision-induced light scattering spectral moments of Ne^6 in the vicinity of the triple point, have already been performed and demonstrate the necessity of including quantum effects.

Here we report the result of a calculation of the pair distribution function $g(r)$ of liquid neon at reduced density $\rho_0^* = \rho_0 \sigma^3 = 0.694$ and reduced temperature $T^* = k_B T/\epsilon = 0.98$, where ρ, T, and k_B are the number density, the absolute temperature, and the Boltzmann constant, respectively, while σ and ϵ are the parameters of the Lennard-Jones potential used in the calculation.

Moreover, we will compare our calculations with the experimental values derived from the neutron scattering data by De Graaf and Mozer.[11] This comparison is of particular interest since the experimental results for the neutron structure factor $S(k)$ of De Graaf and Mozer are very precise and extend to unusually high k vectors, therefore permitting a reliable derivation of an experimental $g(r)$ by Fourier transformation.

Recently Powles and Abascal[12] have tried to reconcile the discrepancy between the classically calculated $g(r)$ of neon and the one which is extracted from the neutron scattering data. However, the disagreement between their calculation and the experimental values remains of the same order of magnitude as the one between the classical calculation and the experimental values. This could be attributed to the fact that Powles and Abascal used, in their calculation, the Mayer and Band[13] effective "quantum" potential which gives an incorrect account of the terms of order higher than $\hbar^2$, as it can be easily seen by comparing the $\hbar$ expansion for $g(r)$, which is derived in terms of the Mayer and Band effective potential, with the rigorous one which is given by the Wigner-Kirkwood expansion.[7]

We will show that the calculation of the terms up to $\hbar^6$ in the expansion of $g(r)$ is important for liquid Ne; therefore they must be correctly included.

The $\hbar$-series expansion of $g(r)$ as a function of the reduced variable $x = r/\sigma$ can be written up to $\hbar^6$ in the

form[7,8]

$$g(x) = g_c(x) + \left[\frac{\Lambda^*}{2\pi}\right]^2 g_1(x) + \left[\frac{\Lambda^*}{2\pi}\right]^4 g_2(x) + \left[\frac{\Lambda^*}{2\pi}\right]^6 g_3(x) \quad,$$

(1)

where $\Lambda^* = h/\sigma\sqrt{\epsilon m}$, m is the mass of the atoms, and

$$g_c(x) = \frac{1}{N\rho_0^*}\left\langle \sum_{\substack{l,j \\ l\neq j}} \delta(\mathbf{x} + \mathbf{x}_l - \mathbf{x}_j)\right\rangle \quad,$$

(2)

$$g_1(x) = \frac{1}{N\rho_0^*}\left\langle \sum_{\substack{l,j \\ l\neq j}} \delta(\mathbf{x} + \mathbf{x}_l - \mathbf{x}_j)\chi_1\right\rangle - g_c(x)\langle\chi_1\rangle \quad,$$

(3)

$$g_2(x) = \frac{1}{N\rho_0^*}\left\langle \sum_{\substack{l,j \\ l=j}} \delta(\mathbf{x} + \mathbf{x}_l - \mathbf{x}_j)\chi_2\right\rangle$$

$$- g_c(x)\langle\chi_2\rangle - g_1(x)\langle\chi_1\rangle \quad,$$

(4)

$$g_3(x) = \frac{1}{N\rho_0^*}\left\langle \sum_{\substack{l,j \\ l\neq j}} \delta(\mathbf{x} + \mathbf{x}_l - \mathbf{x}_j)\chi_3\right\rangle$$

$$- g_c(x)\langle\chi_3\rangle - g_1(x)\langle\chi_2\rangle - g_2(x)\langle\chi_1\rangle \quad.$$

(5)

In the Eqs. (2)–(5) the averages are performed over the classical phase space while the explicit expressions of the functions χ_1, χ_2, and χ_3 are given in Refs. 4 and 8.

As in a previous paper[7] the averages which appear in the various quantum corrections of $g(r)$ have been calculated, for neon at $\rho^* = 0.694$ and $T^* = 0.98$, by means of the molecular-dynamics computer simulation technique. Two independent computer experiments were carried out with two Digital Equipment Corporation VAX-11/750 minicomputers, one at the Prozessrechenanlage Physik of the University of Vienna and the other at the Institute of Astronomy of the University of Florence. In order to generate sufficient statistics, particularly for the calculation of the $\hbar^6$ correction, five independent computer runs with a number of time steps ranging between 25 000 and 100 000 for a total of 300 000 were performed on a 64 particles system interacting with a (12-6) Lennard-Jones (LJ) potential and contained in a dodecahedral box with periodic boundary conditions.

The dodecahedral shape was chosen, instead of the cubic one, in order to reduce the volume and hence the number of particles N. This was a very decisive step in our simulation since the calculation of the correction $g_3(x)$ is proportional to N^3.[8] $N = 64$ turned out as the minimum number of particles which was able to simulate the fluid once the reduced density was set to 0.694 and the force cut off radius was chosen equal to 2.5σ. The configurations were generated with a reduced time step of 0.005 by means of the Verlet algorithm. The independence of the results of the computer calculations from the number of particles used in the configuration was verified by comparing the $g_c(r)$, $g_1(r)$, and $g_2(r)$ obtained with 64 particles and a dodecahedral box shape with the ones obtained with 108 atoms and a cubic box at the same thermodynamic point.[8]

Figure 1 shows the results of our calculation for the four different parts which appear in the $g(r)$ given by Eq. (1) for liquid Ne at $\rho^* = 0.694$ and $T^* = 0.98$. From this figure one can notice the convergent character of the series (1) and the relative importance of the various terms, in particular, the importance of retaining and calculating all the terms
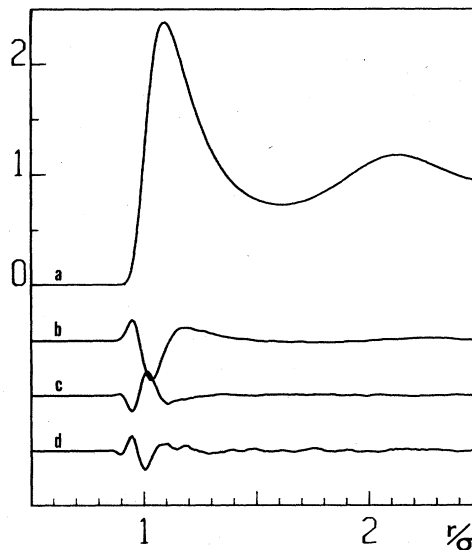

FIG. 1. Behavior of the parts of the quantum-corrected $g(r)$ of neon at $T^* = 0.98$, $\rho_0^* = 0.69$. The curves a, b, c, d represent g_c, $(\Lambda^*/2\pi)^2 g_1$, $(\Lambda^*/2\pi)^4 g_2$, $(\Lambda^*/2\pi)^6 g_3$, respectively.

up to $\hbar^6$ because of the strong cancellation among the various contributions.

The comparison between the quantum-corrected calculation $g(r)$ and the one derived from neutron diffraction experiment can now be performed. However, in order to do this first we must choose the (LJ) parameters σ and ϵ which will relate our calculated $g(r)$ (at a fixed ρ^* and T^*) to the one which can be derived from a set of experimental data for $S(k)$.

There are two sets of possible parameters which can be used. One is a set derived from gas phase properties, i.e., $\epsilon/k_B = 35.8$ K and $\sigma = 2.75$ Å,[14] and the other derived from the properties of the solid, i.e., $\epsilon/k_B = 36.76$ K and $\sigma = 2.786$ Å,[15] which also gives the correct thermodynamic

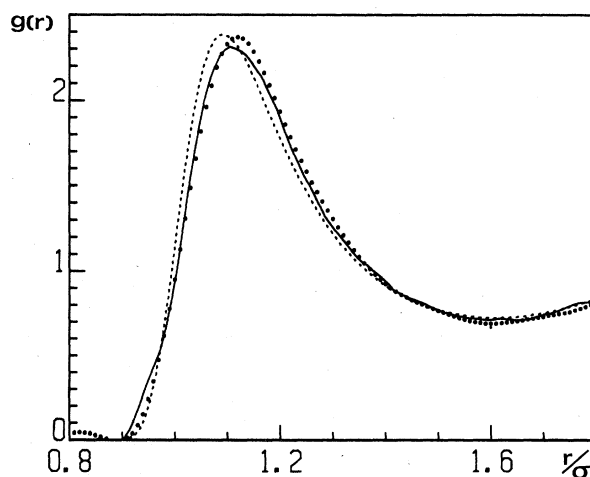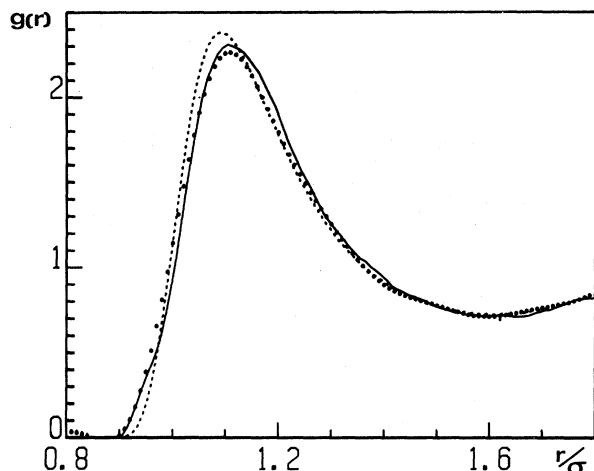
FIG. 2. Comparison between the calculated and experimental $g(r)$ for neon at $T^* = 0.98$ and $\rho_0^* = 0.69$. The dashed curve is the classical $g_c(r)$, the continuous is the quantum-corrected $g(r)$, and the dots are the experimental points for $T = 35.05$ K and $\rho_0 = 0.033\,38$ Å^{-3}. Here the LJ parameters are $\epsilon/k_B = 35.8$ K, $\sigma = 2.75$ Å.

FIG. 3. Comparison between the calculated and experimental $g(r)$ for neon at $T^* = 0.98$ and $\rho_0^* = 0.69$. The dashed curve is the classical $g_c(r)$, the continuous is the quantum-corrected $g(r)$ and the dots are the experimental points for $T = 36.02$ K and $\rho_0 = 0.03191$ Å^{-3}. Here the LJ parameters are $\epsilon/k_B = 36.76$ K, $\sigma = 2.786$ Å.
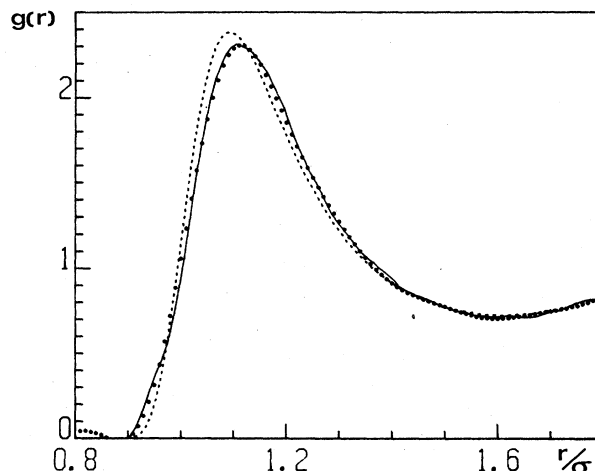

FIG. 4. Comparison between the calculated and experimental $g(r)$ for neon at $T^* = 0.98$ and $\rho_0^* = 0.69$. The dashed curve is the classical $g_c(r)$, the continuous is the quantum-corrected $g(r)$, and the dots are the experimental points for $T = 35.67$ K and $\rho_0 = 0.0320$ Å^{-3}. Here the LJ parameters are $\epsilon/k_B = 36.4$ K, $\sigma = 2.77$ Å.

properties of liquid Ne including quantum corrections as demonstrated by Hansen and Weis.[10]

If the gas phase values are taken for ϵ and σ, the comparison between our calculation and the experimental $g(r)$ can be readily done by a simple Fourier transformation of the experimental $S(k)$ of De Graaf and Mozer at $T = 35.05$ K and $\rho_0 = 0.03338$ Å^{-3}. On the other hand, if the solid phase ϵ and σ are taken, our reduced temperature $T^* = 0.98$ and density $\rho_0^* = 0.694$ correspond to a temperature $T = 36.02$ K and to a density $\rho_0 = 0.03191$ Å^{-3}; therefore, in order to compare our calculation with the experimental results we must interpolate, to this thermodynamic point, the values which are derived for $g(r)$ from the three $S(k)$ of De Graaf and Mozer. This interpolation is easily done from the three $g(r)$ which we have derived by Fourier transforming the three $S(k)$ of De Graaf and Mozer, since measurements have been done at three different densities and, moreover, the required density change is only 0.6% from $\rho_0 = 0.03169$ Å^{-3} to $\rho_0 = 0.03191$ Å^{-3}. The required temperature change, from $T = 35.05$ K to $T = 36.02$ K is a little higher and amounts to 2.7%. We have performed the density interpolation of $g(r)$ with a quadratic function while the temperature dependence was extrapolated by means of an exponential behavior of the type $\exp[-\phi(r)/k_B T]$, i.e., considering the effective potential which gives $g(r)$ as temperature independent within this small temperature range.

The result of the comparison between the quantum-corrected calculation and experimental $g(r)$ for the gas phase values of ϵ and σ is given in Fig. 2, while for the case of solid phase ϵ and σ is given in Fig. 3.

In both cases the quantum-corrected $g(r)$ gives a much better account of the experimental results than the classical one.

A small discrepancy of the order of 3% and 1.5% still remains in the region of the peak of $g(r)$ for the case of the gas phase ϵ, σ and the case of the solid phase ϵ, σ, respectively. It is not possible to attribute this remaining difference to the fact that the calculation neglects the contributions of quantum corrections of order higher than $\hbar^6$, because these would contribute at distances shorter than $x = r/\sigma \lesssim 1.1$ as Fig. 1 shows. Therefore the difference should be attributed to the insufficient refinement of the two pair potential used.

Finally, if different values of ϵ and σ are used the agreement between experiment and calculation can be improved as shown in Fig. 4 where the comparison has been done proceeding similarly to the case of Fig. 3, assuming $\epsilon/k_B = 36.4$ K and $\sigma = 2.77$ Å, which are intermediate compared with the ones used before.

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