The Pair Correlation Function of the Liquid-Vapour Interface: A Monte Carlo Calculation

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A Monte Carlo simulation of the liquid-vapour interface near the triple point is reported. A monotonic density profile is obtained. In the entire interface the pair correlation function $g(r)$ was found to be very close to the liquid bulk $g(r)$, except for the low density region ($\varrho(z)/\varrho_{\text{liq}} \leqq 0.25$) where information was inaccessible. The behaviour of the solution of the BGYB equation for the density profile is explored in the context of the new information concerning the pair correlation function in the interface.

1. Introduction

Ambiguities concerning the density profile at the liquid-vapour interface were recently overcome. Several results based on Molecular Dynamics [1, 2] and Monte Carlo [3–6] simulations, and calculations based on a numerical solution of the first member of the Born-Green-Yvon-Bogolyubov hierarchy of equations [7] gave a monotonic density profile. The computer simulation techniques have greater weight in comparison with the results of the BGYB equation, since it was shown [8] how the latter is sensitive to the details of the input quantities, such as pair potential and pair correlation function (pcf). Information about the pcf in the interface region is rather limited [9]. Usually the anisotropy of the pcf is not taken into account and dependence upon the coordinate perpendicular to the interface is overcome by some "ad hoc" approximation [8, 10, 11].

2. Results

In this paper we report a Monte Carlo calculation on a liquid slab, similar to the calculations reported by other authors [3, 5]. The system consisted of 128 argon atoms interacting with the Lennard-Jones potential ($\varepsilon/k = 119.4\,\text{K}$, $\sigma = 3.405 \times 10^{-10}\,\text{m}$). Periodic boundary conditions were used in the x and y directions in the plane of the interface. Initially, the atoms were placed on the sites of a cubic close-packed lattice. The atoms which evaporated from the two free surfaces were reflected by two rigid walls at $z = \pm 7$. (Throughout the paper we shall use dimensionless quantities such as length, density and temperature ($\varepsilon = 1$, $k_{\text{B}} = 1$, $\sigma = 1$)). The temperature was taken to be 0.7; this is in the vicinity of the triple point temperature. The side edge lengths in the x and y direction were $a_x = 5.52$, $a_y = 4.78$. The potential was truncated at $r = 2.4$.

After equilibration, a Markov chain of approximately 3×10^6 steps was generated. The information concerning the density profile (Fig. 1) was essentially the same as that obtained by other authors [1–6]. With increasing number of configurations in the averaging procedure, the density profile approaches a smooth curve. Special attention was paid to the investigation of the pcf. The positions of the atoms located in the layer ($-1 \leqq z \leqq 1$) were used to evaluate the liquid "bulk" correlation function (Figure 2). The results are in perfect agreement with the pcf obtained by Verlet

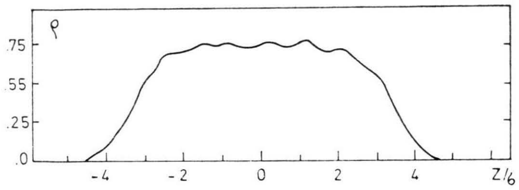

Fig. 1. The density profile as a function of the coordinate running perpendicular to the symmetry plane of the slab. The unit of density is (particles/σ^3).

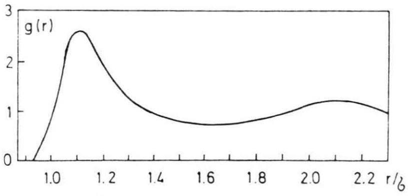

Fig. 2. The pair correlation function of the bulk liquid obtained from the positions of the particles at $-1 \leqq z \leqq 1$ (see Figure 1).

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by means of molecular dynamics calculations [12]. The anisotropic pcf at the liquid-vapor interface depends on three independent variables z_1, z_2 and r, where r is the distance between the atoms 1 and 2 located at z-coordinates z_1 and z_2. The pair correlation function $g(z_1, z_2, r)$ is related to the two particle distribution function $n^{(2)}(\boldsymbol{r}_1, \boldsymbol{r}_2)$ in the following way:

$$n^{(2)}(\boldsymbol{r}_1, \boldsymbol{r}_2) = \varrho(\boldsymbol{r}_1)\, \varrho(\boldsymbol{r}_2)\, g(z_1, z_2, r)\,. \tag{1}$$

The anisotropic pcf $g(z_1, z_2, r)$ can be calculated by counting the number of pairs $(\mathrm{d}^2 n(z_1, z_2, r))$ with one atom located in the volume element $\mathrm{d}V_1$ and the other in the volume element $\mathrm{d}V_2$, since by definition

$$g(z_1, z_2, r) = \frac{1}{\varrho(z_1)\, \varrho(z_2)} \frac{\mathrm{d}^2 n(z_1, z_2, r)}{\mathrm{d}V_1\, \mathrm{d}V_2}\,. \tag{2}$$

The calculation of the pcf as a function of three independent variables is inconvenient because the tabulation of such a function needs an enormous amount of space, and the information is not easy to extract. We were particularly interested in the dependence of the pcf along the coordinate perpendicular to the liquid-vapour interface. Therefore, we tried to evaluate the pcf as a function of interparticle distance r and of z^*, where $z^* = (z_1 + z_2)/2$ is the center of mass of the two particles. This means that it is necessary to average Eq. (2) over the variable z_{12} ($z_{12} = |z_1 - z_2|$):

$$g(z^*, r) = \frac{1}{r} \int_0^r \frac{\mathrm{d}z_{12}}{\varrho(z_1)\, \varrho(z_2)} \frac{\mathrm{d}^2 n(z_1, z_2, r)}{\mathrm{d}V_1\, \mathrm{d}V_2}\,. \tag{3}$$

Since during the MC run the density profile was not yet known the averaging procedure in (3) had to be performed at the end of the run. To evaluate this integral, the distribution of pairs had to be known as a function of all three variables z^*, z_{12}, and r. We did not follow the $\mathrm{d}^2 n(z_1, z_2, r)/\mathrm{d}V_1\, \mathrm{d}V_2$ dependence upon z_{12} by evaluating its values at discrete points, but we calculated the first few moments of the distribution:

$$M_k(z^*, r) = \int_0^r \frac{\mathrm{d}^2 n(z_1, z_2, r)}{\mathrm{d}V_1\, \mathrm{d}V_2} \cdot z_{12}^k\, \mathrm{d}z_{12}\,. \tag{4}$$

Using these moments and denoting $1/\varrho(z_1)\, \varrho(z_2)$ by $f(z^*, z_{12})$, the right hand side of (3) can be written as

$$g(z^*, r) = \frac{1}{r} \sum_{k=0}^{\infty} \frac{1}{k!} M(z^*, r) \left. \frac{\partial^k}{\partial z_{12}^k} f(z^*, z_{12}) \right|_{z_{12}=0}\,. \tag{5}$$

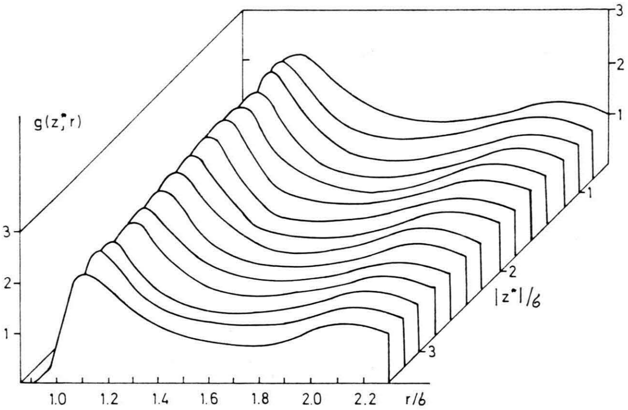

Fig. 3. The dependence of the pair correlation function for the liquid-vapour interface on the distance between the two particles and the z coordinate of their centre of mass ($z^* = (z_1 + z_2)/2$).

The partial derivatives were evaluated numerically at the end of the MC run. This series converges rapidly, so that the first three terms give the result with sufficient accuracy. In this way we obtained the pcf as a function of two variables z^* and r. The results are depicted in Figure 3.

3. Discussion

In order to interpret our results obtained by the MC simulation we observe in Fig. 3 that the height of the first maximum of the pcf does not exceed the corresponding value of the bulk liquid pcf for the interval of z values with densities between 0.75 and 0.2. Also, the second peak persists when going from bulk liquid towards lower densities, which further supports the resemblance between the liquid bulk pcf and the pcf in the interface region.

The results depicted in Fig. 3 are somewhat confusing because they do not show the transition of the pair correlation function from liquid appearance to the vapour phase pair correlation function $g_{\text{vap}}(r) = \exp\{-V(r)/kT\}$, which has one peak and then monotonously decays to the value 1. The curves in Fig. 3 exhibit the minimum ($0.75 \leqq g(1.5 \leqq r \leqq 1.8) \leqq 0.85$), and the second maximum at $r \approx 2$ even for densities as low as 0.2. Thus we can conclude that the transition from the liquid $g(r)$ to the vapour phase $g(r)$ is accomplished in the interval of densities below $\varrho = 0.2$. At temperatures close to the triple point the vapour phase pcf serves as a fair approximation only in a very limited density interval. Also the virial expansion of the equation of state supports the statement that

$g_{\text{vap}}(r)$ is acceptable only at low values of the density — below the coexistence curve and not in the liquid-vapour coexistence region. Close to the triple point the radius of the convergence of the virial series is of the order of magnitude of the vapour density which is a few orders of magnitude below the liquid density.

The question arises of how the results depicted in Fig. 3 relate to the solution of the first member of the Born-Green-Yvon-Bogolyubov hierarchy of equations for the liquid-vapour interface. If by the Monte Carlo or molecular dynamics method one would be able to generate a reliable pair correlation function over the whole range of densities through the liquid-vapour interface, the BGYB equation should be satisfied and should reproduce the density profile obtained by the same simulation. In our case the MC results do not give the pair correlation function for densities below $\varrho = 0.2$. At the triple point temperature, $g_{\text{vap}}(r)$ has a very high peak value (≈ 3.7) and thus differs significantly from the calculated values at higher densities in the liquid-vapour interface. This discontinuity in the pair correlation function produces an ill effect in the iterational procedure involved in the solution of the BGYB integro-differential equation.

Therefore special care must be devoted to the problem of how to connect $g_{\text{vap}}(r)$ and the liquid bulk pair correlation function. The algorithms [10, 11] that have been tried to solve this problem were inefficient [8]. It was mentioned previously that $g_{\text{vap}}(r)$ is applicable only over a narrow range of densities. The failure of the above mentioned algorithms is due to the extrapolation of $g_{\text{vap}}(r)$ into the region of high densities ($\varrho > 0.2$). Toxvaerd [1] overcomes this problem by using the pair correlation function of a metastable and unstable uniform macroscopic fluid. We also tried to solve the BGYB equation by inserting the calculated pair correlation function (the values depicted in Figure 3). When the transition from the MC pair correlation function to $g_{\text{vap}}(r)$ was taken to be smooth enough, a monotonic density profile was obtained. We observed that the results were strongly dependent upon the choice of the pair correlation function for the low density interval.

4. Conclusion

It can be concluded that the pair correlation function obtained by the Monte Carlo simulation is in agreement with the monotonic density profile at the liquid-vapour interface. It was found that the pair correlation function within the interface is very close to the liquid bulk correlation function for all the regions except those with densities below 0.2, where the MC method is inefficient. Since the coordination number of first neighbours is decreasing approximately as fast as the density is decreasing, the first peak of the pcf does not rise, which means that the pcf does not approach the vapour phase bulk pair correlation function. On the basis of this information, we conclude that the structure of the interface possesses a resemblance to the structure of the liquid bulk. Also long range order persists, which is manifested as the second peak in the pair correlation function.

Finally, the results must be subjected to a critical consideration concerning the conditions of the Monte Carlo calculation. The number of configurations (3×10^6) represents today the lower limit for treating unhomogeneous systems. Also the number of particles is rather low and may have ill effects on the results. However, the agreement of the density profile with the results of other works with larger numbers of particles encourage us to think that also the information concerning the pair correlation function is reliable.

Acknowledgements

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