Monte Carlo Simulation of the Interfaces Liquid-Crystal and Liquid-Rigid Wall

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The structure of liquids at liquid-crystal and liquid-rigid wall interfaces was studied by the Monte Carlo method on systems consisting of either 128 Lennard-Jones atoms or 128 hard spheres. The resulting density profile can serve as a reference for the approximative methods based on the BGYB hierarchy of integral equations. The pair correlation function close to the rigid wall is found to deviate appreciably from the bulk liquid pair correlation function. The maxima and minima of $g(r)$ are more pronounced in the first two "layers" of atoms close to the rigid wall.

1. Introduction

The structure of simple monoatomic liquids in the vicinity of interfaces such as liquid-vapour, liquid-crystal or liquid-rigid wall is not yet known in detail. In this work we report the results of Metropolis [1] Monte Carlo simulations of such systems, i. e. liquid-corresponding crystal and liquid-rigid wall. The results of the calculations of this kind [2, 3] can be compared with the results of statistical mechanics calculations based on the Born-Green-Yvon-Bogolyubov hierarchy of equations, which are quite numerous [4—9]. Besides the standard calculations of the density profile, we also calculated the pair correlation function in the inhomogeneous region. On the basis of its behaviour the appropriateness of the isotropic "ansatz" for the pair correlation function in the vicinity of the rigid wall, used in statistical mechanics theories, can be judged.

2. Description of the Calculation

Liquid-rigid wall systems were studied using 128 hard spheres or 128 atoms interacting with a Lennard-Jones potential:

$$V(r) = 4\varepsilon[(\sigma/r)^{12} - (\sigma/r)^6].$$

The particles were enclosed in a rectangular box with the longest edge parallel to the z axis. Periodic boundary conditions were applied in the x and y directions. The plane $z=0$ was taken to be rigid and impenetrable for the centre of the particles. At the other side of the box the particles whose z coordinate exceeded a certain value were exposed to a uniform external force in the negative z direction. The extension of this field along the z axis, and its strength, were chosen to obtain the desired "bulk" density. An alternative choice to the external field at the upper boundary would be a rigid wall of the same type as the one at $z=0$. In this case the influence of the rigid walls would interfere since the two walls are not enough separated. According to our experience the soft wall represented by a linear potential has influences of shorter range. The usual Metropolis [1] Monte Carlo (MC) method was used. For each calculation approximately 2×10^6 configurations were generated, without counting the equilibration moves. The "bulk" pair correlation function was calculated for the part of the system with approximately constant density. The position of the particles in the layer $0 \leqq z \leqq 3\sigma$ was used to determine the pair correlation function, depending upon three variables, z_{12}, z^* and r, where z_1 and z_2 are the z coordinates of the particles 1 and 2 and r the interparticle distance while $z_{12}=z_1-z_2$ and $z^*=(z_1+z_2)/2$. Dimensionless quantities are used henceforth ($k_B=1$, $\varepsilon=1$, $\sigma=1$).

The simulation of the liquid-crystal interface proceeded in a similar manner to that of the liquid-rigid wall system. Periodic boundary conditions were used in the x and y directions. Instead of a rigid wall at $z=0$, there were fixed atoms at $z=-0.928$. The atoms were located on the sites of the (1, 1, 1) plane of a face-centered cubic crystal and then randomly displaced by the amount of the average amplitudes of thermal vibrations at the corresponding temperature. At $z=10\sigma$ the system was closed by a rigid wall, but enough space was left for a free surface to be formed. This type of calculation was performed only with particles interacting with the Lennard-Jones potential.

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3. Results for the Liquid-Rigid Wall System

The liquid-rigid wall system was studied for hard spheres and for Lennard-Jones particles. The density profiles for hard spheres are depicted in Figure 1. The value $\varrho(0)$ is related to the pressure [10] p by the relation

$$\varrho(0) = p/T \tag{1}$$

and, using the Carnahan-Starling formula [11], to the bulk density ϱ_B:

$$\varrho(0)/\varrho_\mathrm{B} = [1 + \pi\,\varrho_\mathrm{B}/6 + (\pi\,\varrho_\mathrm{B}/6)^2 - (\pi\,\varrho_\mathrm{B}/6)^3]/[1 - (\pi\,\varrho_\mathrm{B}/6)]^3 \,. \tag{2}$$

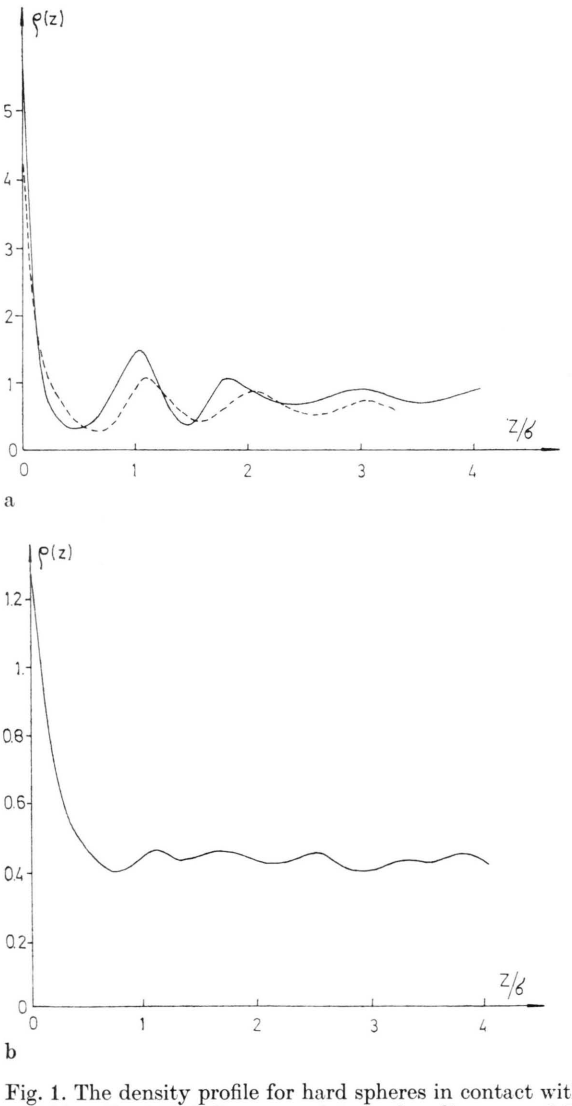

Fig. 1. The density profile for hard spheres in contact with a rigid wall. a) Full line $\varrho_\mathrm{B} = 0.8$; broken line $\varrho_\mathrm{B} = 0.7$; b) $\varrho_\mathrm{B} = 0.43$.

We also calculated the pair correlation function for the bulk which is connected with the pressure of the bulk by the pressure equation [12]. Therefore we were able to check the relation between the density at the wall and the value of the bulk pair correlation function g_B $(r = 1)$:

$$\varrho(0)/\varrho_\mathrm{B} = 1 + 2\pi\,g_\mathrm{B}(1)/3 \,. \tag{3}$$

The results of our calculations satisfy Eqs. (2) and (3) with deviations within a few percent. Our correlation function of the bulk was also in good agreement with the pair correlation function of Alder and Hecht [13].

Figure 1a shows that the profile at high bulk density is strongly layered. At low bulk density (Figure 1b), the influence of the rigid wall is weak and short ranged. The oscillations at $z > 1.5$ would vanish if the statistics were better. The two curves in Fig. 1a, corresponding to the densities 0.7 and 0.8, depict the effect of "compressing" the layers as a consequence of increasing density. It must also be pointed out that the two calculations were performed with different side egdes a_x and a_y. It could be that this is partly the reason for such a strong shift of the maxima in $\varrho(z)$. The density profiles can be compared with results obtained by the Percus-Yevick (PY) [4, 5], by the mean spherical (MSA) [6] and by superposition (SA) [7] approximations. The last two approximations give exact values for $\varrho(0)/\varrho_\mathrm{B}$. It seems [7] that the MSA method gives the best agreement with the Monte Carlo calculations. The density profiles at the bulk density $\varrho_\mathrm{B} = 0.8$, obtained by the other two methods, PY and SA, both show deviations from the MC results. The PY approximation exhibits oscillations that are too indistinct in comparison with the MC results, while the amplitudes of oscillations of $\varrho(z)$ obtained by the SA are approximately 30% too high. The loci of maxima and minima obtained by the PY approximation nearly coincide with those of the MC method, while the subsequent maxima of the SA are too much separated.

The study of the pair correlation function close to the interface shows that it deviates appreciably from the bulk pair correlation function. We were not able to calculate the complete dependence of the function $g(z_{12}, z^*, r)$ on all three coordinates since the statistics were not good enough. We calculated $g(z_i, r)$ within the first three layers of atoms ($z_i \approx 0, 1, 2$) which correspond to maxima of the subsequent peaks in $\varrho(z)$. From Table 1 we can

Table 1. The ratio of the values of the pair correlation function at the subsequent maximum of $\varrho(z)$ over the corresponding value of the bulk pair correlation function $g_B(r)$. The quantity $r_{\min}$ is the location of the first minimum in the pair correlation function. The figures in the table are the average values of the results obtained by studying two rigid wall-hard sphere liquid systems presented in Figure 1a.

	$z \approx 0$	$z \approx 1$	$z \approx 2$
$g(z, \sigma)/g_B(\sigma)$	1.2	1.06	1
$g(z, r_{\min})/(g_B(r_{\min})$	0.75	0.8	1

see that when approaching the well, the oscillatory character of the pair correlation function is more and more pronounced, which means that the layers of atoms have a more and more pronounced crystalline character. One can conclude that integral equation theories which do not take into account the variation of the pair correlation function in the vicinity of the rigid wall, can give reasonable results for the density profile only fortuitously.

The Monte Carlo results for the liquid-rigid wall system with the Lennard-Jones type of interaction are depicted in Figure 2. The high density profile corresponds to a temperature slightly above the triple point value. The oscillations of the density profile are not dumped, which means that the correlations induced by the rigid wall are long ranged. Since the system is close to the crystal-liquid coexistence line, it is probably in the metastable state. The low density profile in Figure 2 corresponds to a state above the critical temperature at $\varrho_B = 0.55$ nad $T = 2.5$. The density at the wall fits the p/T value [Eq. (1)] for the Lennard-Jones fluid. The density oscilllations are not pronounced.

4. Results for the Liquid-Cystal Interface

The liquid-rigid wall system with the temperature and the density close to the triple point may be considered as an approximation to the liquid-crystal system. We studied a liquid-crystal system of Lennard-Jones particles, directly, as stated in Section 2. The calculation was performed at the triple point where the boundaries between the three phases are not necessarily stationary. In our case, the system was constrained by the plane of fixed atoms at $z = -0.928$. On the other hand, the cohesion forces and the periodic boundary conditions stimulate the system to form interfaces parallel to the $z = 0$ plane. The result is presented in Fig. 3, where the density profile of the liquid-crystal interface corresponding to the triple point temperature is depicted. One can see a gradual transition from the oscillatory density profile of crystalline structure to the more or less monotonic density profile of "liquid phase". Then the density decays to the vapour density of practically zero value.

Recently Ladd and Woodcock [14] reported the results for the three coexisting phases (crystal-liquid-vapour) of the Lennard-Jones system. They performed molecular dynamics calculation on the system consisting of 1500 particles with the (1, 0, 0) crystal plane being parallel to the interfaces. For

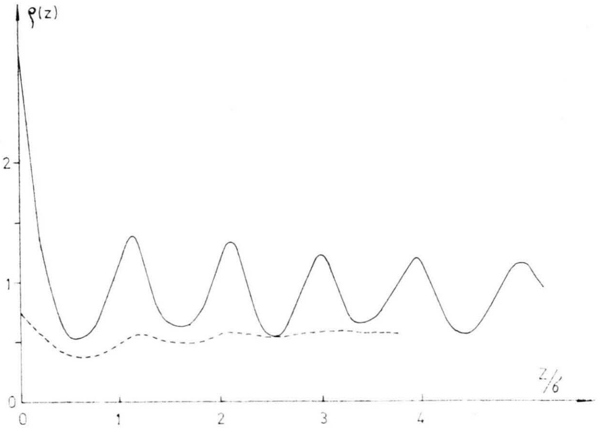

Fig. 2. The density profile for Lennard-Jones particles in contact with a rigid wall. Full line $\varrho_B = 0.87$, $T = 0.71$, broken line $\varrho_B = 0.55$, $T = 2.5$.

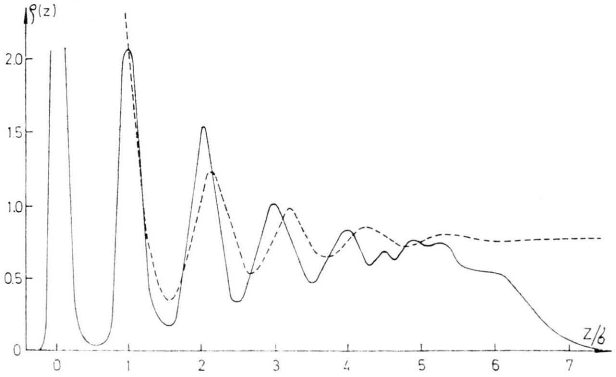

Fig. 3. The density profile for the liquid-crystal interface at the triple point of a Lennard-Jones system. The density profile obtained by the superposition approximation for $\varrho_B = 0.8$, $T = 1.4$ is shown for comparison (broken line).

such a geometry the subsequent maxima in the density profile are by a factor $\sqrt{3}/2$ more densely spaced than in our case. It is interesting to point out that the density oscillations predicted by the integral equation theories fit better to the sequence of (1, 1, 1) planes than to the sequence of (1, 0, 0) planes. Because of the insufficient number of particles we were not able to find out whether the large range for the liquid-crystal interface depends upon the orientation of the interface with respect to the orientation of the crystal axes.

The pair correlation function of the liquid-vapour interface was studied by the present authors and the results will be published elsewhere [15]. The pair correlations at the liquid-crystal interface are in agreement with the information provided by the density profile. According to the pair correlations of hard spheres close to the rigid wall (see Table 1), we also found that the pair correlation in the subsequent maxima is more and more liquid-like when going from crystal to liquid phase.

The liquid-crystal interface can not be studied by the integral equation theories. These theories can not deal with the three body correlations which are of crucial importance in the crystal phase. In the case of the liquid-rigid wall system the computer simulation and the integral equation theories can compete. When integral equation theories are applied to the liquid-rigid wall system, with cohesive interparticle interactions one must be careful, since Eq. (1) tells us that at the triple point temperature the density at the wall is approximately zero. If we would like to treat the liquid-rigid wall system, we are essentially treating a vapour-liquid system since the density at the wall must be approximately zero, which indicates the existence of the vapour phase. In this case the vapour phase pair correlation function would also have to be taken into account. This means that integral equation theories are more adequate for the study of the liquid-crystal interface for higher (p, T) values at the liquid-crystal coexistence line. This was done previously using the superposition approximation [16], and it was found that close to the liquid-crystal coexistence line, the solution of the integral equation diverges by amplifying oscillations. At the point ($\varrho_B = 0.8$, $T = 1.4$), which is rather deep in the liquid region, the iterations are convergent. The result of this calculation is given in Fig. 3 for comparison with MC results. The maxima in $\varrho(z)$ obtained by the SA are too sparse — a feature which is also encountered in [7].

5. Conclusion

In this paper we presented Monte Carlo results for the density profile of a liquid close to a rigid wall and at the liquid-crystal interface. The results are reliable, especially for the case of the hard sphere fluid in contact with the rigid wall. The study of systems close to the crystal-liquid coexistence line is tricky because of the existence of metastable states. The pair correlation function close to the rigid wall shows considerable deviation from the corresponding bulk pair correlation function. This is not a stimulating circumstance for the statistical mechanical theories based on the BGYB hierarchy of integral equations, where the variation of $g(r)$ is not taken into account. The efficiency of the integral equation theories, if applied to the liquid-rigid wall system, depends upon the degree of their self-consistency. The only calculation of liquid-rigid wall density profiles for hard spheres that does not involve quantities obtained by some other method, are the Percus-Yevick calculations. The mean spherical approximation and the superposition approximation both accept the best available $g(r = \sigma)$ value for a hard sphere fluid. This enables them to obtain the correct density at the wall.

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