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Born-Green-Yvon approach to the local densities of a fluid at interfaces

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The local density of a nonuniform fluid is calculated from the first equation of the Born-Green-Yvon hierarchy by modeling the pair correlation function. For that purpose, the mean force term is divided into two parts, corresponding to the mutual repulsion of the fluid atoms and the their mutual attraction, respectively. In the repulsive force term the interaction is approximated by a hard-sphere interaction and the pair correlation function is taken locally as that of a homogeneous hard-sphere fluid at some average density determined by spatial coarse graining. In the attractive force term the particles are taken to be uncorrelated. The formalism is applied to (a) the free-liquid surface, (b) gas adsorption on a wall at low temperatures, and (c) a liquid in contact with a wall. In all cases good agreement with existing computer simulations is obtained. An interesting feature arises for the free-liquid surface, where the equation turns out to be an eigenvalue equation for the coexisting liquid density. For this case the surface tension is also calculated.

I. INTRODUCTION

The local density of a fluid in equilibrium at an interface is of considerable practical interest. It is the purpose of this paper to show that the Born-Green–Yvon equation is an excellent starting point for a theoretical approach if physically reasonable approximations for the pair correlation function are made. Within the same approximations results for such different situations as (a) the free-liquid surface, (b) gas adsorption on a wall at low temperatures, and (c) a liquid in contact with a wall, will be obtained. The agreement with computer simulations is nearly within the accuracy of the latter.

Most of the theories start either from the Born-Green–Yvon equation,[1,2] or use a closure for the Ornstein-Zernike equation,[3–5] or start from an expression for the free-energy of the system.[6–8] The references given here refer only to recent works which are thought to be representative in their field. A more complete list of theoretical works and computer simulations can be found elsewhere.[9] We begin by shortly reviewing the approximations and the results of the different theoretical approaches.

Among the free-energy approaches the density-functional theory[6] has received much attention. The basic idea is that there exists a functional Ω of the local number density $n(\vec{r})$, such that the equilibrium $n(\vec{r})$ minimizes Ω. This concept has been applied with success to the electron gas and to liquid helium. For classical fluids an exact expression for the function Ω could also be constructed.[10] The actual calculations[6,11] for three-dimensional classical fluids, however, start from an approximate functional. There, an approximation for the Helmholtz free-energy F is used, where F is expressed as functional of the local free-energy density $f(\vec{r})$, the local number density $n(\vec{r})$, and the direct correlation function $c(\vec{r}_1, \vec{r}_2)$,

$$F = F(f(\vec{r}), n(\vec{r}), c(\vec{r}_1, \vec{r}_2)) \ .$$

In the further treatment additional approximations have to be used. The direct correlation function was taken to be that of a homogeneous fluid at some intermediate local density $c(\vec{r}_1, \vec{r}_2) = c_{\text{hom}}(\vec{r}_1, \vec{r}_2; n_\alpha)$ with $n_\alpha = [n(\vec{r}_1) + n(\vec{r}_2)]/2$. The local free-energy density, a not very well defined quantity, was assumed to be the free-energy density of a homogeneous fluid at the local density $f(\vec{r}) = f(n(\vec{r}))$. The free-energy of the homogeneous fluid was calculated consistently with the direct correlation function. Pointing out this consistency, Ebner *et al.*[6] believed their approach to be superior to other existing theories, a view which seems open to discussion. In any case, the assumptions that c and f depend on a local density become dangerous if the local density is in the liquid-vapor coexistence region or if it can become higher than any bulk liquid density, which happens in the case of low-temperature adsorption. In the next step, the more rigorous concept then required the calculation of $c(\vec{r})$ for a homogeneous fluid from the Percus-Yevick equation for a variety of densities. In a simpler version additional approximations for c were made. Finally a prescribed form of the local density containing several parameters was used, and by minimizing the approximate functional these parameters were determined. In discussing the results we will restrict ourselves to two cases. For the free-liquid surface reasonable density profiles and surface tensions were obtained. It must, however, be noted that the coexisting liquid and vapor densities could only be obtained by a double tangent construction with respect to the free-energy of the uniform states. This requires another evaluation of the Percus-Yevick equation for a variety of states or a free-energy expression from outside the theory. The other result concerns the film formation of a gas adsorbed on a solid surface.[11] Simulations[12] have shown that the density-functional result is quite unlikely to be correct. Explanations for that could be a bad choice of the trial density function[12] or that the fluid is already in the liquid-gas coexistence region (for arguments see Sec. III), so that the results describe some metastable state. Summarizing, we want to say that the approximate density-functional theory as described above has increased our understanding of nonuniform fluids. While several approximations have to be made, they seem to be physically reasonable for many cases. In those cases, however, where incorrect results are predicted, it is difficult to locate the source of error.

Within the framework of the density-functional theory an exact relation, Eq. (12) of Ref. 10, has been derived also, which relates the local density to the direct correlation function in a similar form, as does the Born-Green–Yvon equation with the local density and the pair correlation function.[33] That equation, however, does not yet seem to have been evaluated for three-dimensional cases. Moreover we will not call it a free-energy approach.

Other free-energy approaches are the modified van der Waals theory of Davis *et al.*[7] and the Singh-Abraham theory.[8] The former is similar to the approximate density-functional theory in concept, the main difference lying in the fact that the approximate expression for the free-energy contains the pair correlation function instead of the direct correlation function. Furthermore, a recent paper[13] shows that the results obtained from both theories for the free-liquid surface are quite similar. The Singh-Abraham theory is somewhat different in that it uses several perturbation schemes. An essential shortcoming of this approach is that the resulting equations are so complicated that they can hardly be evaluated. To the author's knowledge only the density profile for a free-liquid surface has been determined. This was done under the restriction of using a prescribed function with only one free-parameter. Keeping in mind the long-lasting quarrel whether a free-liquid surface shows a layered structure or not, a one-parameter ansatz, however, anticipates the result.

The use of the Ornstein-Zernike equation for interface problems seems to be of limited success, as till now no closure could be found that would yield reasonable results for rather different physical situations. The case of hard spheres in contact with a hard wall was investigated for different closure relations.[2–4,14,15] The Percus-Yevick and hypernetted-chain closures yield density profiles which are in considerable error close to the wall. While for a hard wall this failure can be remedied by using the generalized mean spherical closure[14] this cannot be done so easily for more realistic wall-particle interactions. For the case of wall-particle and particle-particle interactions of the Lennard-Jones type a recent investigation[5] has shown that the Percus-Yevick and the hypernetted-chain closure predict density profiles with a much too high first peak, if solutions can be obtained at all. A more basic objection against using the Ornstein-Zernike approach for fluid-wall problems is the fact that the wall must be plane and cannot be allowed to show any atomic structure. Finally it should be mentioned that in an investigation of the free-liquid surface,[3] the Percus-Yevick closure led to a strongly layered density profile, which contradicts the simulation results.[16]

The Born-Green–Yvon (BGY) equation, which for the case of a wall-particle potential $u^s(\vec{r})$ and a particle-particle potential $u(\vec{r})$ is written as[17]

$$\vec{\nabla}_1 \ln n(\vec{r}_1) = -\beta\vec{\nabla}_1 u^s(\vec{r}_1) + \int n(\vec{r}_2) g(\vec{r}_1, \vec{r}_2)[-\beta\vec{\nabla}_1 u(r_{12})]\, d\vec{r}_2 , \tag{1}$$

represents the condition of mechanical equilibrium for the system and constitutes an exact relation between the local number density $n(\vec{r})$ and the pair correlation function $g(\vec{r}_1, \vec{r}_2)$. The first term on the right-hand side of Eq. (1) is the external force and the second one is the mean intermolecular force exerted on particle 1. In order to obtain an equation for $n(\vec{r})$ one has to approximate the pair correlation function. This, however, is the only approximation needed and in this respect the Born-Green–Yvon approach is superior to the free-energy theories. Previous works have applied this approach to the free-liquid surface[1,18,19] and to fluids in contact with a wall.[2,20,21]

By using the BGY equation for the free-liquid surface, in Refs. 18 and 19 an oscillating density profile was found, while that obtained by Toxvaerd[1] in monotonic. First, it is the present authors' view that the approximations for the pair correlation function in all three papers are rather artificial constructions. Second, a special feature of the free-liquid surface should be pointed out. At a given temperature a free-liquid surface can exist only for one definite pair of coexisting densities, which depend on the approximation used for the pair correlation function. As in all three cases the liquid density was prescribed from the very beginning, the suspicion arises that in Refs. 18 and

19 the BGY equation should have only the trivial solution $n = \text{const}$ and that the given density profiles are some artefacts. Toxvaerd circumvented this problem by using a model pair correlation function containing one free-parameter. Then by prescribing the coexisting liquid density, a solution for the density profile could only be found for one value of that free-parameter. An alternative way would be to use a model for the pair correlation function without free-parameters and to look for those coexisting densities for which a solution of the BGY equation can be found. This procedure will be adopted in the present paper.

Considering the question of how to approximate the pair correlation function g something can be learned from simulation results[22,23] and Fischer's work on fluids in contact with a wall.[2,21] For the case of the hard-sphere fluid in contact with a hard wall the BGY equation was solved in Ref. 2 by approximating the pair correlation function everywhere by its bulk form. The calculated density profile was in reasonably good agreement with computer simulations.[22] On the other hand, Snoek and Henderson[22] have investigated the pair correlation function very thoroughly by simulations. Roughly speaking it can be said that g is similar to its bulk form for any pairs $(\vec{r}_1, \vec{r}_2)$. Approximating g by its limiting form far away from the interface, is, however, not possible in the case of the liquid-gas interface and highly questionable for a low-density gas adsorbed on a wall. For these cases it was thought[21] that the pair correlation function could be taken locally as that of a homogeneous fluid at some intermediate density $n_\beta = n(\frac{1}{2}(\vec{r}_1 + \vec{r}_2))$. Such an assumption, however, contradicts strongly the findings of Refs. 22 and 23, where the pair correlation function in all planes parallel to the surface was found to be nearly the same, irrespective of whether the local density there is high or not. Similarly, taking g locally at the density $n_\alpha = \frac{1}{2}(n(\vec{r}_1) + n(\vec{r}_2))$, which is used in the free-energy approaches, is not much better. Contrary to the statement of Davis,[13] the assumption about the density at which g should be taken plays an important role. As an example, we mention that continuing the calculations of Ref. 21 to higher densities, yields only one distinct peak in the density profile which is inconsistent with the simulation results of Ref. 23. Another objection is the fact that the densities n_α or n_β can become much higher than any bulk densities.

In this paper we propose to take the pair correlation function g locally as the pair correlation function of a homogeneous fluid at an average density $\bar{n} = (1/v)\int n(\vec{r})dr$, where the averaging is done over a volume v of molecular size. Such an averaged density $\bar{n}$, which can be viewed as resulting from spatial coarse graining, is a smoothly varying function that is likely to remain bounded to physically possible bulk densities. For a dense liquid in contact with a wall, $\bar{n}$ will everywhere be close to the bulk fluid density, so that the approximation is reasonable in this case. In any case, limiting values of the density are obtained properly.

A direct use of the approximation $g = g(\bar{n})$ is, however, advisable only for a hard-sphere fluid, where merely the value of g for two spheres in contact is required. For a realistic interaction between the fluid particles the computational effort would become prohibitively large and, moreover, it may happen that $\bar{n}$ lies in the liquid-gas coexistence region. To overcome this problem we take into account that realistic intermolecular interactions consist of strong short-ranging repulsive forces and weak long-ranging attractive forces. Already van der Waals argued that the structure of a uniform liquid should essentially be determined by the repulsive forces while the attractive forces merely form a uniform background potential. For nonuniform fluids it cannot be assumed that such a simple approximation holds, but it is rather plausible that the pair correlation function will be less important in the mean attractive force exerted on one particle, than in the mean repulsive force because of the long-ranging nature of the attractive forces. In this sense we split the intermolecular potential u into a repulsive part u^0 and an attractive part u^1, which by insertion into Eq. (1) yields the mean repulsive and the mean attractive force on particle 1. Then, the attractive forces are treated in the most simple way by neglecting any correlations. In the mean repulsive force, the pair correlation function is assumed to be that of a reference system of particles interacting through the soft repulsive potential u^0. Finally, the repulsive interactions are replaced by hard-sphere interactions and the pair correlation function is related locally to that of a homogeneous hard-sphere fluid at the average density $\bar{n}$.

II. MATHEMATICAL FORMULATION OF THE APPROXIMATIONS

We consider a fluid of spherical particles in equilibrium at temperature T, $\beta = 1/kT$. The interaction between two fluid particles i and k shall be $u(r_{ik}) = u_{ik}$ with $r_{ik} = |\vec{r}_i - \vec{r}_k|$, and the external potential is taken as $u^s(\vec{r}_i)$; the total potential energy U is assumed to be

$$U = \sum_i u^s(\vec{r}_i) + \sum_{i<k} u(r_{ik}) .$$

The Born-Green–Yvon equation for that system was given in Eq. (1).

For a realistic intermolecular potential u with repulsive and attractive forces we start by splitting the potential according to the prescription of Weeks, Chandler, and Andersen,[24]

$$u(r) = u^0(r) + u^1(r)\,, \tag{2}$$

with

$$u^0(r) = \begin{cases} u(r) - u_{\min}, & \text{for } r \leq r_{\min} \\ 0, & \text{for } r > r_{\min} \end{cases} \tag{3}$$

where $r_{\min}$ is the distance of $u_{\min}$, the minimum of the potential. Insertion of Eq. (2) into the mean force term of Eq. (1) yields trivially,

$$\int ng(-\beta\vec{\nabla}_1 u)\,d\vec{r}_2 = \int ng(-\beta\vec{\nabla}_1 u^0)\,d\vec{r}_2 + \int ng(-\beta\vec{\nabla}_1 u^1)\,d\vec{r}_2\,, \tag{4}$$

where the first term on the right-hand side is the mean repulsive force and the second term constitutes the mean attractive force.

According to the arguments of Sec. I, the correlation in the mean attractive force will be neglected, which means $g=1$. Hence, in this approximation we have

$$\int n(\vec{r}_2)g(\vec{r}_1,\vec{r}_2)[-\beta\vec{\nabla}_1 u^1(r_{12})]\,d\vec{r}_2 = -\beta\vec{\nabla}_1\int n(\vec{r}_2)u^1(r_{12})\,d\vec{r}_2\,. \tag{5}$$

For the treatment of the mean repulsive force we first introduce a reference system that consists of soft repulsive spheres interacting with the potential u^0 and that additionally has the same local density $n(\vec{r})$ as the original system, which can be achieved by some external potential. The first approximation is to replace g by the pair correlation function g^0 of the reference system,

$$\int ng(-\beta\vec{\nabla}_1 u^0)\,d\vec{r}_2 = \int ng^0(-\beta\vec{\nabla}_1 u^0)\,d\vec{r}_2\,. \tag{6}$$

This approximation, taken for itself, is thought to be good at high average densities and to become worse for the low-density low-temperature region; there, however, a certain compensation with the approximation of Eq. (5) may occur. At this stage it is useful to introduce the background correlation function y^0 of the reference system, which is defined by

$$g^0(\vec{r}_1,\vec{r}_2) = \exp[-\beta u^0(\vec{r}_1,\vec{r}_2)]\,y^0(\vec{r}_1,\vec{r}_2)\,.$$

By using y^0 we can write

$$\int ng^0(-\beta\vec{\nabla}_1 u^0)\,d\vec{r}_2 = \int ny^0(\vec{\nabla}_1 e^{-\beta u^0})\,d\vec{r}_2\,. \tag{7}$$

In a second step we replace the soft repulsive spheres by hard spheres, denoting that potential by u^{HS}. A temperature-dependent hard-sphere diameter d is determined according to the prescription of Barker and Henderson[25]

$$\int (e^{-\beta u^0} - e^{-\beta u^{\mathrm{HS}}})\,dr = 0\,, \tag{8}$$

and the background correlation function y^0 is approximated in the sense of the blip expansion[24] by y^{HS}. Thus we get

$$\int ny^0(\vec{\nabla}_1 e^{-\beta u^0})\,d\vec{r}_2 = \int ny^{\mathrm{HS}}(\vec{\nabla}_1 e^{-\beta u^{\mathrm{HS}}})\,d\vec{r}_2\,. \tag{9}$$

Using the fact that the derivative of the hard-sphere Boltzmann factor is the Dirac δ function[2]

$$\frac{d}{dr_{12}}\,e^{-\beta u^{\mathrm{HS}}} = \delta(r_{12} - d)\,,$$

we obtain from Eq. (9):

$$\int ny^{\mathrm{HS}}(\vec{\nabla}_1 e^{-\beta u^{\mathrm{HS}}})\,d\vec{r}_2 = \int n(\vec{r}_2)g^{\mathrm{HS}}(\vec{r}_1,\vec{r}_2\,;\,r_{12}=d) \times\left(\frac{-\vec{r}_{12}}{r_{12}}\right)\delta(r_{12}-d)\,d\vec{r}_2\,. \tag{10}$$

In this expression $g^{\mathrm{HS}}(\vec{r}_1,\vec{r}_2;r_{12}=d)$ denotes the pair correlation function for hard spheres in contact. One observes that this is the only value of the pair correlation function needed.

The final approximation concerns the value of the pair correlation function for hard spheres in contact. Following the suggestion of Sec. I, we take this value locally as that of a homogeneous fluid at an average density $\bar{n}$,

$$g^{\mathrm{HS}}(\vec{r}_1,\vec{r}_2;r_{12}=d) = g^{\mathrm{HS}}_{\mathrm{hom}}(r_{12}=d\,;\bar{n}(\vec{r}_1,\vec{r}_2))\,. \tag{11}$$

The average density $\bar{n}$ is determined by

$$\bar{n}(\vec{r}_1,\vec{r}_2) = \frac{1}{v}\int n(\vec{r}+\vec{r}_c)\,d\vec{r}\,, \tag{12}$$

where the averaging is done over a sphere of diameter d centered at the point of contact $\vec{r}_c = \frac{1}{2}(\vec{r}_1+\vec{r}_2)$.

Putting together all the approximations yields the equation

$$\vec{\nabla}_1 \ln n(\vec{r}_1) = -\beta\vec{\nabla}_1 u^s(\vec{r}_1) - \beta\vec{\nabla}_1\int n(\vec{r}_2)u^1(r_{12})\,d\vec{r}_2 + \int n(\vec{r}_2)g^{\mathrm{HS}}_{\mathrm{hom}}(d;\bar{n})\left(\frac{-\vec{r}_{12}}{r_{12}}\right)\delta(r_{12}-d)\,d\vec{r}_2\,, \tag{13}$$

where $\bar{n}$ is defined by Eq. (12) and $g^{\mathrm{HS}}_{\mathrm{hom}}(d;\bar{n})$ can readily be obtained from the Carnahan-Starling equation.[26] In this approximation to the BGY equation the only unknown function now is the local density $n(\vec{r})$. So far, the equation is still quite general and could also be used for the case of a nonplanar wall or for the investigation of the surface of a droplet, to give only two examples.

In the situations to be studied in this paper the density will vary only in the z direction. In this case only the z component of Eq. (13) survives. Then it is convenient to introduce coordinates as shown in Fig. 1. Now the second integral in Eq. (13) can be written as[2]

$$-2\pi\int_{-d}^{+d} n(z_2)\,g_{\text{hom}}^{\text{HS}}(d;\bar{n}(z_1,z_2))\,z_{12}\,dz_{12}\,.$$

Finally, by prescribing a boundary value n_b for the local density at $z=\infty$, Eq. (13) can be integrated from $z=\infty$ to a value $z=z_0$ to give

$$n(z_0)=n_b\exp\left(-\beta u^s(z_0)-\int\beta u^1(r_{02})[n(z_2)-n_b]\,d\vec{r}_2+2\pi\int_{z_0}^{\infty}dz_1\int_{-d}^{+d}dz_{12}\,n(z_2)\,g_{\text{hom}}^{\text{HS}}[d,\bar{n}(z_1,z_2)]\,z_{12}\right). \qquad (14)$$

This integral equation, which contains the external potential u_s, the limiting density n_b, and the temperature T as parameters can be solved numerically by iteration.

III. RESULTS AND DISCUSSION

A. Free-liquid surface

We have investigated the plane liquid-gas surface for a Lennard-Jones fluid

$$u(r)=4\epsilon[(\sigma/r)^{12}-(\sigma/r)^6]\,, \qquad (15)$$

neglecting any external forces $u^s\equiv 0$. The coexisting liquid and gas densities are denoted by n_l and n_g. The density n_l is taken as the boundary value in Eq. (14); to agree with the literature we assume that in this case the boundary value is prescribed at $z=-\infty$. The plane $z=0$ is defined as the Gibbs dividing surface

$$\int_{-\infty}^{0}dz[n(z)-n_l]+\int_{0}^{+\infty}dz[n(z)-n_g]=0\,. \qquad (16)$$

For solving Eq. (14) at a fixed temperature T, we start with a guessed value of n_l, an arbitrary coordinate ζ in the z direction and a guessed density profile $n_{\text{in}}^1(\zeta)$, fulfilling the conditions $n_{\text{in}}^1(\zeta)\to\text{const}$ for $\zeta\to\infty$. As a first step we determine the coordinate ζ_g of the Gibbs dividing surface of n_{in}^1 and introduce $z=\zeta-\zeta_g$. Now we insert n_{in}^1, rescaled to the z coordinate, into the right-hand side of Eq. (14) and thus obtain a profile n_{out}^1 from the left-hand side. In general, these two profiles will be different and in the usual way we construct another input profile by mixing $n_{\text{in}}^{i+1}=(1-x)n_{\text{in}}^i+xn_{\text{out}}^i$. Before inserting the new profile into Eq. (14) we again have to determine the Gibbs dividing surface and to rescale the profile. For an arbitrarily prescribed liquid density n_l, however, the best agreement which can be achieved between the input and the output profile is of the kind

$$n_{\text{out}}^i(z+\Delta)=n_{\text{in}}^i(z)\,, \qquad (17)$$

which means that the density profile is shifted either to higher- or lower-z values. Thus, for an arbitrary value of n_l no solution of the BGY equation besides the trivial one $n(z)=n_l$, can be found. By varying the liquid density we observe that the shift Δ is a monotonically increasing function of n_l. In this way it was possible to find exactly one density n_l for which $\Delta=0$. Hence, the integrated BGY equation, Eq. (14), in its homogeneous form $u^s\equiv 0$, is an eigenvalue equation in the sense that at a given temperature T only for one value of $n_b=n_l$ a nontrivial solution exists. The coexisting gas density n_g is the limiting value of the eigensolution for $z\to\infty$.

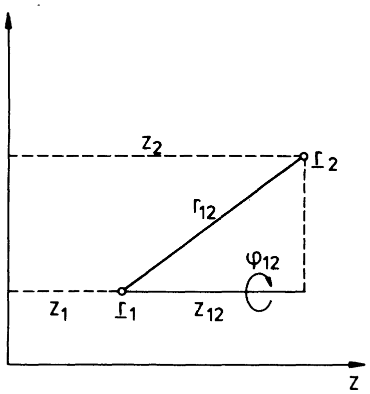

FIG. 1. The coordinates used for the case of plane interfaces. The density varies along the z direction.

Once having obtained the density profile, it is also possible to calculate the surface tension γ from[17]

$$\beta\gamma=\tfrac{1}{4}\int dz_1\int d\vec{r}_2\,n(\vec{r}_1)n(\vec{r}_2)g(\vec{r}_1,\vec{r}_2)\beta\frac{du}{dr_{12}}\frac{r_{12}^2-3z_{12}^2}{r_{12}}\,, \qquad (18)$$

if the pair correlation function $g(\vec{r}_1,\vec{r}_2)$ is approximated in the same way as in Sec. II.

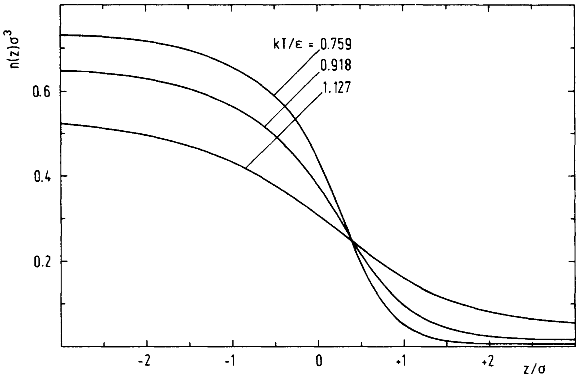

FIG. 2. Density profiles for the free-liquid surface of a Lennard-Jones fluid obtained at different temperatures as eigensolutions of Eq. (14) with $u^s \equiv 0$. The profiles can be compared with simulation results of Ref. 16.

The numerical integrations in Eq. (14) were performed over an interval which was symmetric to the Gibbs dividing surface and extended over 12 to 16 molecular diameters, such that at its boundaries the density profile practically had achieved the limiting values n_l and n . Because of long-ranging contributions the intervals for numerical integration in Eq. (18) have to be even larger. In any case, analytical corrections for long-ranging interactions were added where necessary.

Calculations were performed at the reduced temperatures $kT/\epsilon = 0.759$, 0.918, 1.002, and 1.127. Figure 2 shows the density profiles for the three temperatures for which computer simulations[16] are also available. Table I contains our results for the coexisting densities, the surface tension, and the surface thickness L, which is defined as[16]

$$L = -(n_l - n_g)\left(\frac{dn(z)}{dz}\right)^{-1}_{z=z_0}, \tag{19}$$

where z_0 is given by

$$n(z_0) = \tfrac{1}{2}(n_l + n_g).$$

A discussion of our results should start with the coexisting densities. At $kT/\epsilon = 0.759$ our liquid density agrees approximately with that of Ref. 16, but both these values are inconsistent with that given by Hansen and Verlet.[27] At $kT/\epsilon = 1.127$ the liquid densities of Refs. 16 and 27 agree approximately, but ours is somewhat lower. Therefore, when comparing our surface tension and thickness with the results of Ref. 16 we expect better agreement at lower temperatures. This is true for the surface tension, where the difference increases from 7% at the lowest temperature to 20% at the highest temperature. This agreement is remarkably good regarding the fact that the scattering between different simulation results[16,28] is considerably higher. The surface thickness obtained by simulations depends on the number of particles,[16] a fact which was explained by postulating surface capillary waves.[29] At $kT/\epsilon = 0.759$ our value $L/\sigma = 1.41$ could be a lower bound to the simulation results, thus giving the intrinsic surface thickness. At $kT/\epsilon = 1.127$ our result is somewhat higher than the simulation result for 255 particles, which may be caused by the different liquid densities.

TABLE I. The free-surface of a Lennard-Jones liquid. The table gives as functions of the temperature, the coexisting liquid and gas densities, the surface tension, and the surface thickness.

kT/ϵ	$n_l\sigma^3$	$n_g\sigma^3$	$\gamma\sigma^2/\epsilon$	L/σ
0.759	0.740	0.003	0.84	1.41
0.918	0.662	0.012	0.57	1.99
1.002	0.619	0.021	0.45	2.37
1.127	0.548	0.041	0.27	3.20

B. A gas in contact with a wall

Adsorption at low temperatures belongs to the most challenging interface problems for the theoretician. Below the critical temperature even a gas of low bulk density is expected to form at the solid surface several densely packed layers. The questions are, how many layers are formed, how densely are these layers packed and how does the transition from the layered structure to the bulk density behave. Approaching the coexisting bulk gas density, these questions become increasingly interesting.

For this type of problem only a few simulations have been performed. We decided to make a comparison with the results of Rowley *et al.*,[30] who did sampling in the grand canonical ensemble for the case of a Lennard-Jones gas in contact with a plane 9-3 wall:

$$u^s(z) = \tfrac{1}{2}3^{3/2}\epsilon_{gs}[(\sigma_{gs}/z)^9 - (\sigma_{gs}/z)^3], \tag{20}$$

taking $\epsilon_{gs}/\epsilon = 9.24$ and $\sigma_{gs}/\sigma = 0.5621$. At the temperature $kT/\epsilon = 1.002$ density profiles for the gas were given at bulk densities up to $n\sigma^3 = 0.025\,73$, which is supposed to be close to the coexisting density of the Lennard-Jones fluid. It shall be mentioned that we obtained the bulk gas densities from the activities of Ref. 30 by using the series representation of the density in powers of the activity.

We had to solve now the inhomogeneous form of Eq. (14), $u^s = u^s(z)$, for a prescribed limiting density n_b. In order to ensure that our limiting density n_b does not lie in the liquid-gas coexistence region, we performed a calculation for the free-liquid surface at $kT/\epsilon = 1.002$, which gave an eigensolution with the coexisting density $n_g\sigma^3 = 0.0207$, a value which is likely to be smaller than the exact value of the Lennard-Jones fluid.[27] Within the framework of our approximations for $g(r)$, however, this is the coexisting gas density and no higher bulk gas densities should be possible. Actually we were able, again by using iteration algorithms, to find solutions for Eq. (14) for limiting densities up to $n_b\sigma^3 = 0.0200$. The convergence of the iteration always became slower with increasing bulk density but the difference between the input and the output density profile could be made arbitrarily small, so that we can be sure to have obtained the solution. The numerical integrations were performed in intervals up to 10 molecular diameters extending from the wall into the gas. We failed in finding a solution for $n_b\sigma^3 = 0.02573$, as with any iteration step the transition zone between the layers and the bulk gas was shifted away from the wall and the number of layers increased steadily. It is from this experience that we believe that the density profiles found by the approximate density-functional approach in Ref. 11 could describe some metastable states.

Our density profiles for $n_b\sigma^3 = 0.01919$ and 0.02000 are shown in Fig. 3. The lower density corresponds to run 6 at $kT/\epsilon = 1.002$ of Ref. 30. We observe nearly quantitative agreement between the simulation and our theory, the main difference lying in the fact that our second and third peak are somewhat smaller but broader. For a quantitative comparison we calculated the excess number coverage θ^e and the layer coverages θ^i according to the prescriptions of Ref. 30. We obtained $\theta^e = 2.26$, $\theta^1 = 0.86$, and $\theta^2 = 0.72$, while the corresponding numbers of Ref. 30 are 1.960, 0.898, and 0.675. Figure 3 is also interesting because the profiles there belong to bulk densities which are close to the coexisting gas density. With increasing bulk density the first two layers adjacent to the wall remain unchanged while the transition zone between the third layer and the bulk gas obviously tends to form a plateau, which gives a certain insight into the onset of bulk condensation. Our theoretical results are also in reasonable agreement with recent experimental findings[31] which showed three to four adsorbed gas layers at the beginning of bulk condensation. Perhaps we should still mention, that we do not yet have final results for bulk densities $n_b\sigma^3$ between 0.0200 and 0.0207 as the numerical treatment in that region is tough.

C. A liquid in contact with a wall

Recently it was pointed out by simulation workers[32,23] that the attractive forces between the fluid atoms play an important role for the structure of a fluid in contact with a wall. In the framework of our approximations this can be readily understood, as in Eq. (13) the contribution of the attractive forces can alternatively be regarded as that of an additional external potential.

First we studied a Lennard-Jones and a hard-sphere fluid in contact with a 9-3 wall under the same conditions as it was done in the simulations of Abraham and Singh.[32] Thus, we used the temperature $kT/\epsilon = 1$, the bulk density $n_b\sigma^3 = 0.65$, and the wall potential of Eq. (20) with $\epsilon_{gs}/\epsilon = 1.877$ and $\sigma_{gs}/\sigma = 0.7148$; the hard-sphere diameter was chosen to be σ. The iterative solution of Eq. (14)

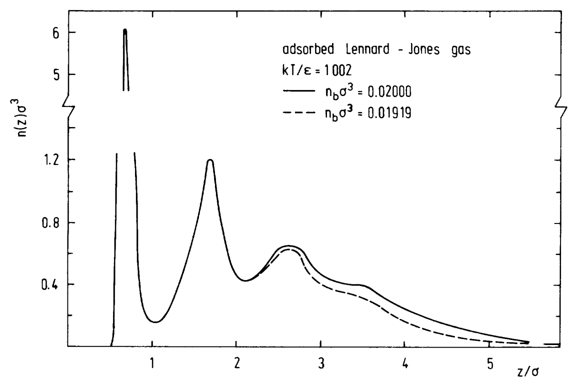

FIG. 3. Density profiles for a Lennard-Jones gas adsorbed on a plane wall. The bulk gas densities are close to the coexisting gas density, which in the framework of our approximations was found to be $n_g\sigma^3 = 0.0207$. The lower density corresponds to the simulation run 6 at $kT/\epsilon = 1.002$ of Ref. 30.

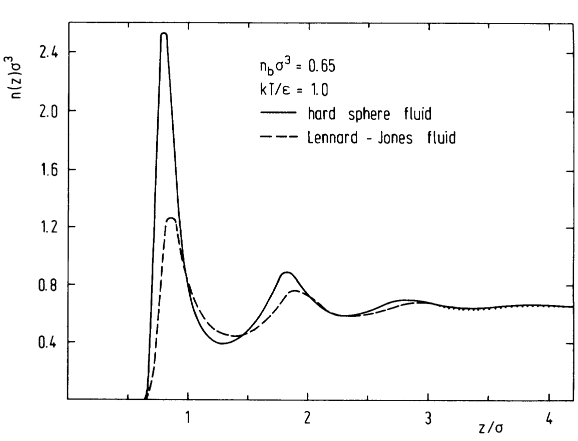

FIG. 4. Density profiles for a hard sphere and a Lennard-Jones fluid in contact with a 9-3 wall. The profiles can be compared with simulation results in Ref. 32.

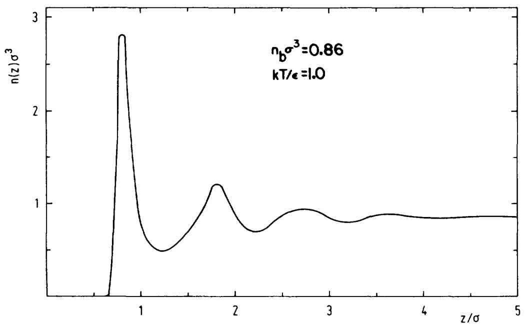

FIG. 5. Density profile for a Lennard-Jones liquid at a rather high liquid density in contact with a 9-3 wall. The conditions here are the same as for one simulation result shown in Fig. 9 of Ref. 23.

converged quickly for the hard spheres, but much slower for the Lennard-Jones liquid, which may be due to the fact that the bulk liquid density is close to the coexisting liquid density. Our resulting density profiles are given in Fig. 4 and show the expected difference between the hard-sphere and the Lennard-Jones fluid. They are in rather good agreement with the simulation results,[32] much better than any of the solutions obtained by closing the Ornstein-Zernike equation.[5]

In order to check the reliability of our approach also at the highest liquid densities, we performed a calculation for a Lennard-Jones liquid in contact with a 9-3 wall at the bulk liquid density $n_b\sigma^3 = 0.86$. The wall potential was given again by Eq. (20) with $\epsilon_{gs}/\epsilon = 2.208$ and $\sigma_{gs}/\sigma = 0.7148$, the temperature was $kT/\epsilon = 1$. Our density profile is shown in Fig. 5 and is again in good agreement with that in Fig. 9 of Ref. 23, which was obtained by simulations for the same case.

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[33] By comparing Eq. (12) of Ref. 10 with Eq. (13) of R. Lovett, C. Y. Mou, and F. P. Buff, J. Chem. Phys. 65, 570 (1976), one has the impression that the first equation is nothing other than an integrated form of the second one. Following the arguments of the latter paper a close relation between the exact density-functional theory and the Born-Green-Yvon approach is evident.