Densities profiles and adsorption isotherms are calculated, by means of the mean spherical approximation, for hard spheres near a uniform hard surface when there is an exponentially decaying attractive interaction between the wall and hard spheres.

I. INTRODUCTION

Recently, Henderson, Abraham, and Barker (1) have suggested that the problem of a fluid in contact with a wall can be regarded as the limiting case of a mixture in which one of the components becomes infinitely dilute and then infinitely large. In particular, they obtained the appropriate form of the Ornstein-Zernike equation,

\[ h_{12} = c_{12} + \rho h_{11} \ast c_{11} \]

where the asterisk denotes a convolution, \( \rho = N/V \) is the bulk density of the fluid in contact with the wall, \( h_{11}(r) + 1 = h_{11}(r) + 1 g_{11}(r) \) are the radial distribution functions (RDFs), i.e., \( g_{11}(r) \) is the density of molecules of species 1 at distance \( r \) from the center of a molecule of species 1 and \( c_{11}(r) = c_{11}(r) \) are the direct correlation functions. In equation (1), the particle of species 2 is the particle which is assumed to be infinite in size.

The Ornstein-Zernike equations are just the definition of the \( c_{11}(r) \) and become useful when supplemented by some approximate equations for the \( c_{11}(r) \). One of the most useful approximations is the mean spherical approximation (MSA) of Lebowitz and Percus (2). For systems for which the intermolecular potential is

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\[ u_{ij}(r) = \begin{cases} = & \text{, } r < \sigma_{ij}, \\ = \phi_{ij}(r) & \text{, } r > \sigma_{ij}, \end{cases} \tag{2} \]

where \( \sigma_{ij} = (\sigma_{i} + \sigma_{j})/2 \) and \( \sigma_{ij} \) is the molecular diameter, the MSA is

\[ \sigma_{ij} = -\frac{\delta \phi_{ij}(r)}{\delta \phi_r} , \text{, } r > \sigma_{ij} \tag{3} \]

which together with the exact condition, \( \phi_{ij}(c) = 1, c < \sigma_{ij} \) permits a solution of [1]. When \( \delta = 0 \) \( \text{[i.e., infinite temperatures]} \), equation \( [3] \) becomes the Percus-Yevick (3) approximation for hard spheres.

Henderson, Abraham, and Barker (HAB) have obtained the Percus-Yevick (PY) results for the density profile \( \rho(\alpha) = \rho_{ij}(\alpha + \delta) \) from [1] and the analytic expressions of Lebowitz (4) for \( c_{ij}(\alpha) \). Similar results have been reported by Percus (5).

Subsequently, we (6) have obtained the solution of the MSA when \( \omega_{ij}(r) = 0 \) and \( \omega_{ij}(r) \) is a Yukawa function, i.e.,

\[ \omega_{ij}(r) = e^{-x}\sigma_{ij} \text{, } r > \sigma_{ij} \tag{4} \]

In the limit \( \delta_{ij} \rightarrow \infty \), equation \( [5] \) becomes

\[ \omega_{ij}(\delta_{ij}c) = e^{-x\sigma_{ij}} \text{, } \delta > 0 \tag{5} \]

where \( x = r - \sigma_{ij} \) and \( c = \sigma_{ij} \). Thus, the exponential function is the limit of the Yukawa potential which is appropriate to the wall-molecule interaction. Interestingly, if the wall is assumed to consist of individual molecules which interact with the fluid by Yukawa intermolecular potentials and if the interaction of a fluid molecule is computed by integrating the interactions with all the molecules in the wall, the wall-molecule interaction is an exponential function with the same decay constant \( x \) as that of the individual wall-molecule fluid-molecule interactions. Thus, in both senses the exponential function is the natural extension of the Yukawa potential to wall-molecule interactions.

We have used (6) this solution to obtain the density profile of hard spheres near a hard wall by regarding \( \delta c \) not as a thermodynamic variable, but as an adjustable parameter which can be chosen by thermodynamic considerations. In this work we apply our results to the case where \( \omega_{ij}(\alpha) \) is the attractive interaction between the molecules and the wall.

II. DENSITY PROFILE

As we have mentioned, the solution of (1) gives $h_{12}(r)$. The density profile of the molecules near the wall is just $\rho(x) = \rho[h(0,\rho(x)) + 1]$. We have plotted $\rho(x)$ in Fig. 1 for three thermodynamic states.

![Graph showing density profiles for $\beta\epsilon = 2, \rho = 0.8$; $\beta\epsilon = 0, \rho = 0.8$; and $\beta\epsilon = 0, \rho = 0.2$.]

Fig. 1. Density profiles of gas near a wall.
At low densities, the density profile is strongly affected by the attractive potential \( w(r) \). However, at high densities, the density profile at \( \beta \epsilon / k = 2 \) is nearly equal to that at \( \beta \epsilon = 0 \). This means that structure of the fluid near the wall is dominated by the structure of hard spheres near a hard wall. This should mean that a perturbation treatment of fluids near a wall will be as successful as for bulk fluids.

III. ABSORPTION

The number of molecules per unit area absorbed by the wall is

\[
N_a = \int_0^m (\rho(s) - \rho) ds,
\]

where \( \rho(s) \) and \( \rho \) are the densities inside the fluid and at the wall, respectively. For the case when \( w(s) \) is given by equation [5], we have shown [6] that this integral may be obtained analytically. Our result is

\[
N_a = \rho \left[ \frac{3n}{2(1+2n)} + \frac{\beta \epsilon}{2} \frac{(1-n)^6}{(1+2n)^2} \right],
\]

where \( n = n_0^{3/11} \) and

\[
C = \frac{L(s) + S(s)e^8}{S(s)e^8},
\]

\[
L(s) = 12n \left( \frac{14n}{2} + 1 + 2n \right),
\]

\[
S(s) = (1-n)^2 s^3 + 6n(1-n)^2 s^2 + 12n s - 12n(1+2n).
\]

If \( s = \infty \), equation [7] becomes

\[
N_a = \rho \left[ \frac{3n}{2(1+2n)} + \frac{\beta \epsilon}{2} (1-n)^2 \right].
\]

The van der Waals limit, \( s = 0 \), is of more interest. For this case

\[
N_a = \rho \left[ \frac{3n}{2(1+2n)} + \frac{\beta \epsilon}{2} \frac{(1-n)^6}{(1+2n)^2} \right].
\]

The second term in equation [12] gives the contribution of the attractive forces. It is of interest to note that it is damped at high densities because of the term \( (1-n)^2/(1+2n)^2 \) which is just the PY or NSA approximation for \( \beta T \), for hard spheres. Thus as the bulk hard sphere fluid becomes incompressible, the contribution of the attractive forces becomes small. This is similar to the perturbation theory concepts of Barker and Henderson [8] for bulk fluids.
The adsorption, $N_a$, is plotted in Fig. 2

![Graph showing adsorption vs. pressure for different values of $\beta_e/z$.]

**Fig. 2** Adsorption of gas for various values of $z$ at $\beta_e/z = 2$.

for $z = 0$ and $\infty$ and for $z = 2$ which is a value appropriate for argon. The pressure of the bulk hard-sphere fluid is, in the PT (or HSA) approximation,

$$\frac{p}{p} = \frac{\ln n}{(1-n)}$$

(13)

It is seen that $z = 2$ is still close to the van der Waals limit.
In Fig. 3 we have plotted $N_a$ for $z = 2$ for $\beta e/z = 0, 1,$ and 2. There is adsorption even when there are no attractive forces ($\beta e = 0$) because of the hard core.

**Fig. 3.** Adsorption of gas for $z = 2$

repulsions of the gas. Similar results have been obtained.
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by Ferrera and Smith (unpublished work) using a less realistic potential.

Fig. 4. Excess energy of adsorption for \( z = 2 \)
The excess energy of adsorption/unit area is given by

$$BE_a = \frac{3}{2} k_B + \int_0^\infty \nu_{12}(x) \delta(x) dx. \quad [14]$$

This integral may also be obtained analytically. The result is

$$BE_a = \frac{3}{2} h \int \frac{Rc}{n} C(1+n) - \frac{(Rc)^2}{2n} C^2 (1-n)^4 \sigma. \quad [15]$$

The first term gives the contribution of the kinetic energy. The excess energy of adsorption is plotted, for $z = 2$, for three temperatures in Fig. 4.

A comparison with experiment is not appropriate here as the case of liquid adsorption is excluded because $\nu_{12}(x) = 0$. However, these calculations do indicate the utility of applying theories which have proven useful in the theory of bulk fluids to fluids near a wall.

Blum and Stell (9) have also solved [1] when attractive forces are present.

IV. ACKNOWLEDGEMENT

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V. REFERENCES


