

The mean spherical approximation for a Yukawa fluid interacting with a hard planar wall with an exponential tail

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Results, which supplement those of Thompson *et al.* (preceding paper), are given for a Yukawa fluid interacting with a hard planar wall with an exponential tail. It is argued that density profiles calculated in a mean spherical approximation treatment of this system are only qualitatively reliable.

1. INTRODUCTION

In previous papers [1, 2] we investigated the density profile of a fluid near a planar wall. We did this by combining an exact relation for the wall (situated at $x=0$) and fluid (in semi-infinite space $x>0$) correlation function

$$h_{21}(x) = -1, \quad x < 0, \quad (1 a)$$

with an approximate relation for the corresponding direct correlation function

$$c_{21}(x) = K_{21} \exp\{-\varepsilon_{21}x\}, \quad x > 0. \quad (1 b)$$

The functions $h_{21}(x)$ and $c_{21}(x)$ are connected by the Ornstein-Zernike relation

$$h_{21} = c_{21} + \rho h_{21} * c. \quad (2)$$

Here ρ is the density of molecules of the bulk fluid, $\rho = \lim_{x \rightarrow \infty} \rho(x)$, $h_{21}(x) = [\rho(x) - \rho]/\rho$ is the desired profile function, and $c(r)$ is the direct correlation function of the bulk fluid.

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The parameters K_{21} and z_{21} in equation (1 *b*) may be thought of either as determined by the fluid-wall interaction $W_{21}(x)$ [$c_{21}(x) = -\beta W_{21}(x)$ being the mean spherical approximation (MSA)] or as 'open' parameters to be determined by some criteria such as self consistency (generalized mean spherical approximation (GMSA)). In either case, a knowledge of $c(r)$ which specifies the nature of the bulk fluid is necessary and sufficient for making (1) and (2) a closed set of equations for $h_{21}(x)$.

In references [1] and [2] we dealt with a fluid of hard spheres of diameter σ and further assumed that the bulk fluid correlations are given by the Percus-Yevick approximation for this system. Hence

$$h(r) = -1, \quad r < \sigma, \quad (3 \text{ a})$$

$$c(r) = 0, \quad r > \sigma, \quad (3 \text{ b})$$

where $h(r)$ is the total correlation function of the bulk fluid which is related to $c(r)$ by the Ornstein-Zernike relation

$$h = c + \rho h^* c. \quad (4)$$

It is the purpose of this note to present results obtained from the solution of (1) and (2) for a more general bulk fluid, i.e. for the case where (3 *b*) is replaced by a Yukawa function :

$$c(r) = K \exp \{-z(r-\sigma)\}/r, \quad r > \sigma. \quad (5)$$

Recently, Thompson *et al.* [3] have independently considered this case and obtained profiles numerically. Therefore, we describe here only results not found in that paper. These results are, whenever possible given in terms of the parameters or properties of the bulk Yukawa fluid which are readily available [4-8].

As is the case with the Yukawa form in (1 *b*), the form (5) is useful not only in MSA treatments of fluids with Yukawa interactions but also in GMSA treatments of this and other fluids.

2. RESULTS

We find that the Laplace transform of $g_{21}(x) = h_{21}(x) + 1$ is given by

$$G_{21}(s) = \int_0^{\infty} g_{21}(x) \exp(-sx) dx = \frac{a}{s} (1-\eta)^2 \exp(s) f(s) + C(1-\eta)^4 \exp(s) f(s) / (s + z_{21}), \quad (6)$$

where $\eta = \pi\rho\sigma^3/6$,

$$a = (\beta \partial p / \partial \rho)^{1/2}, \quad (7)$$

$$C = K_{21} \exp(z_{21}) f(z_{21}, \eta), \quad (8)$$

$$f(s) = \frac{s^3}{L(s) + S(s) \exp(s)} \quad (9)$$

$$L(s) = 12\eta(1-\eta)^2 s^3 \tau(s), \quad (10)$$

$$S(s) = (1-\eta)^2 s^3 [1 - 12\eta\sigma(s)]. \quad (11)$$

The parameters a , b , c , d and the polynomials $\tau(s)$ and $\sigma(s)$ are defined by Høye and Blum [7] and describe the bulk Yukawa fluid. For example, the Laplace transform of $g(r) = h(r) + 1$ is

$$\int_0^{\infty} \exp(-sr)g(r) dr = \frac{sL(s)}{12\eta[L(s) + S(s)\exp(s)]} \quad (12)$$

In the limit $K \rightarrow 0$, $L(s)$ and $S(s)$ are the usual polynomials arising in the solution of the Percus–Yevick equation for a hard sphere fluid [9, 10]. Hence, in the limit $K \rightarrow 0$, equation (6) reduces to the results of Waisman *et al.* [1].

The contact value of $g_{21}(x)$ is

$$g_{21}(0) = a + C(1 - \eta)^2 \quad (13)$$

and the contact value of the derivative of $g_{21}(x)$ is

$$\left. \frac{\partial g_{21}(x)}{\partial x} \right|_{x=0} = [a - g_{21}(0)]z_{21} - 12\eta g_{21}(0)[a/2 + b + c \exp(-z) - (c + d)] \quad (14)$$

It is interesting to compare (13) with the exact result of Henderson *et al.* [11].

$$g_{21}(0) = \frac{\beta p}{\rho} + \beta \int_0^{\infty} \frac{\partial W_{21}}{\partial x} g_{21}(x) dx, \quad (15)$$

where W_{21} is the interaction potential between the molecules and the wall. If the integral in (15) is known or can be approximated, then in a GMSA treatment, C can be adjusted to bring (13) into agreement with (15). On the other hand, in a MSA treatment, the degree of consistency between (13) and (15) gives an estimate of the accuracy of the calculation. Proceeding in the latter mode by assuming that $W_{21}(x)$ is indeed an exponential function we may evaluate (15) by using the solution given in (6). This yields

$$g_{21}(0) = \beta p/\rho + z_{21}\beta\epsilon_{21}G_{21}(z_{21}) = \beta p/\rho + a(1 - \eta)^2 C + \frac{1}{2}(1 - \eta)^4 C^2 \quad (16)$$

Equations (13) and (16) are generally in poor agreement. Equation (16) is exact when $C = 0$ (that is, $\beta\epsilon_{21} = 0$). In equation (13) $\beta p/\rho$ is incorrectly replaced by $a = [\beta \partial p/\partial \rho]^{1/2}$. This is a poor approximation, particularly near the coexistence curve where $p \simeq 0$ and $a \gg 0$. In addition, (16) has a higher-order term in $\beta\epsilon_{21}$ than does (13). Further (13) is based only on the contact value of $g_{21}(x)$ whereas (16) results from an integration of $g_{21}(x)$ over all values of x . As a result, it seems likely that $g_{21}(0)$ is given more accurately by (16) than by (13). Hence, we conclude that the MSA density profiles calculated by inversion of (6) may be significantly in error for $x \simeq 0$.

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

$$N_a = \int_0^{\infty} [\rho(x) - \rho] dx. \quad (17)$$

This integral can be calculated by expanding (6) in powers of s . Thus, using equations (20 a) and (20 b) of Høye and Blum [7],

$$N_a = \rho \left[-\frac{b}{a} + \frac{C}{z_{21}} \frac{(1 - \eta)^2}{a} \right]. \quad (18)$$

If $z_{21} \rightarrow \infty$,

$$C = K_{21}/(1 - \eta)^2, \quad (19)$$

and if $z_{21} \rightarrow 0$,

$$C = K_{21}/[a(1-\eta)^2], \quad (20)$$

so that particularly simple expressions are obtained.

3. REMARKS

Equations (13) and (18) have been used in a GMSA treatment of hard spheres near a hard wall by adjusting K and z to give a good GMSA description of the bulk hard spheres and adjusting K_{21} and z_{21} to fit equations (46) and (54) of Waisman *et al.* [1]. The results are only very slightly better than those obtained by Waisman *et al.* [1].

We have inverted equation (6) to obtain density profiles similar to those of Thompson *et al.* [3]. However, for the reasons given above we believe these curves are, at best, only qualitatively reliable. Near the coexistence curve, these curves may not be even qualitatively reliable. Some improvement is obtained if a , b , c , and d are determined by a GMSA description of the Yukawa fluid. However, without a good GMSA criteria for determination for K_{21} and z_{21} , the difficulties remain.

Thompson *et al.* interpret the maximum which often occurs in the density profile as evidence of monolayer formation. While the structure of the density profile may be indicative of monolayer formation, this treatment is not likely to be a good theory of physical adsorption since fluid in contact with the wall is considered to be in only one phase.

Finally, we have calculated N_a and obtained results similar to those reported in [2] except that a singularity, which may be interpreted as indicative of wetting, occurs when $a=0$.

Perram and Smith [12] have calculated N_a for a 'sticky' interaction potential using the Percus-Yevick approximation and have found an additional singularity (i.e., one not associated with $a^2 = \beta \partial p / \partial \rho = 0$). They interpret this new singularity as predicting the formation of a condensed film on the surface. Since the Perram-Smith singularity is present for all radii of the solute molecule and no analogue of it is present in this analysis, we believe that this singularity is an artifact of the 'sticky' interaction and is unrelated to any adsorption phenomena.

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REFERENCES

- [1] WAISMAN, E., HENDERSON, D., and LEBOWITZ, J. L., 1976, *Molec. Phys.*, **32**, 1373.
- [2] HENDERSON, D., WAISMAN, E., and LEBOWITZ, J. L., 1976, *Colloid and Interface Science*, edited by M. Kerker (Academic Press), Vol. 3, p. 37.
- [3] THOMPSON, N. E., ISBISTER, D. J., BEARMAN, R. J., and FREASIER, B. C., 1980, *Molec. Phys.*, **39**, 27.
- [4] WAISMAN, E., 1973, *Molec. Phys.*, **25**, 45.
- [5] HENDERSON, D., STELL, G., and WAISMAN, E., 1975, *J. chem. Phys.*, **52**, 4247.
- [6] HØYE, J. S., and STELL, G., 1976, *Molec. Phys.*, **32**, 195.
- [7] HØYE, J. S., and BLUM, L., 1977, *J. statist. Phys.*, **16**, 399.
- [8] HENDERSON, D., WAISMAN, E., LEBOWITZ, J. L., and BLUM, L., 1978, *Molec. Phys.*, **35**, 241.
- [9] WERTHEIM, M., 1963, *Phys. Rev. Lett.*, **10**, 321 ; 1964, *J. math. Phys.*, **5**, 643.
- [10] THIELE, E., 1963, *J. chem. Phys.*, **39**, 474.
- [11] HENDERSON, D., BLUM, L., and LEBOWITZ, J. L., 1979, *J. electroanal. Chem.* (in the press.)
- [12] PERRAM, J. W., and SMITH, E. R., 1976, *Phys. Lett. A*, **59**, 11.