

Inconsistency of the density-functional theory of adsorption when using computer simulations

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The authors compare predictions of a recent density-functional theory for adsorption of argon onto a solid-carbon-dioxide substrate with Monte Carlo simulations of exactly the same system. The basic predictions of the density-functional theory are shown to be qualitatively at variance with the simulation results. In particular, the simulations show predominantly monolayer adsorption, with a second layer forming at higher bulk densities. There is no sign of the thick structureless films predicted by the recent density-functional theory.

I. INTRODUCTION

It is the main purpose of this paper to discuss the recently proposed "density-functional" theory of interfacial phenomena of Ebner, Saam, and Stroud (ESS)¹ and in particular to examine claims made recently² about its superiority over the Percus-Yevick theory (PY)³⁻⁵ in describing adsorption at surfaces. The two theories are examined by comparing both theories with simulation data. Unlike the PY theory, the density-functional theory is in qualitative disagreement with machine simulations in that it predicts the formation of thick unstructured films in the adsorption of argon on to carbon dioxide at elevated subcritical temperatures. The machine simulations reported here are carried out for the system examined by Saam and Ebner,² who used the density-functional theory. The potentials, temperatures, and pressures used are identical. There is no evidence for film formation in the simulations under the conditions reported by Saam and Ebner. The work of Saam and Ebner also shows a density profile of argon away from an adsorbing surface for which the height of the first peak appears independent of substrate [Xe (Ref. 6) or CO₂ (Ref. 2)], temperature and bulk adsorbate density. This independence is not observed in the simulations. The density profiles of Saam and Ebner away from the wall show peaks at approximately 1.0, 1.5, and 2.5 times the bulk adsorbate Lennard-Jones parameter σ , again at variance with the simulation results and the predictions of the PY theory.

The recent upsurge of interest in the statisti-

cal theory of interfacial phenomena has involved a generalization of the techniques which have been successful in elucidating the properties of homogeneous fluids. These generalizations have involved applications to the problem of the methods of computer simulation,⁷⁻⁹ numerical solution of the Born-Green equation,¹⁰ perturbation theory,¹¹ cluster expansions,^{12,13} and a technique based on closure of the limiting form of the Ornstein-Zernike equation for a mixture in the limit as one species becomes dilute and large.^{3-5,14-19} Further, a technique closely related to the functional differentiation derivation of the PY and hypernetted chain equations (HNC),^{1,2,6} has been put forward by Ebner, Saam, and Stroud. These equations are discussed in Sec. II. We see that an equation very similar to that of the density-functional theory may be obtained from the limiting mixture Ornstein-Zernike equation and the HNC closure. In Sec. III we review the main results of these theories as applied to simulation results on real gas adsorption. As has been remarked elsewhere, the PY theory of Perram and Smith^{18,19} appears to correlate quite well with all of the data of which we are aware.

In Sec. IV we report Monte Carlo simulations of the adsorption of Lennard-Jones (LJ) particles appropriate to argon on to a model CO₂ surface. The model surface used is exactly that used by Saam and Ebner² as are the LJ parameters used for argon. The simulations were carried out at the temperatures and densities reported by Saam and Ebner.² As remarked earlier, the simulations show no sign of the formation of thick films. In their reporting of thick-film formation, Saam and

Ebner² were severely critical of the PY theory. In contrast to their density-functional theory, PY theory predicts adsorption confined mainly to a monolayer at the bulk adsorbate densities studied by Saam and Ebner.² The height of the peak in the density profile corresponding to the monolayer found in PY theory is strongly dependent on system, temperature, and bulk adsorbate density. This feature of PY theory is in qualitative agreement with the machine simulations.

In Sec. V we discuss the possibility of the formation of thick films from the point of view of the Lifshitz theory of macroscopic dispersion forces. We also offer possible reasons for the failure of the density-functional theory as used by Saam and Ebner.²

II. FORMAL THEORIES OF INTERFACIAL PHENOMENA

We begin with a brief description of the method by which integral equations for the density profile of a fluid adsorbed at a surface may be obtained by taking limits on the mixed correlation functions of a two component fluid. The adsorbate of density ρ_2 is considered as component 2 of a mixture, component 1 being composed of hard spheres of diameter R_1 at density ρ_1 . The 1-2 potential may be written $v(r)$. It is claimed that the quantity

$$\rho_2(z) = \lim_{R_1 \rightarrow \infty} \lim_{\rho_1 \rightarrow 0} \rho_2 [1 + h_{12}(\frac{1}{2}R_1 + z)] \quad (2.1)$$

measures the density of adsorbate at a distance z from a planar wall. Under these limits, the 1-2 potential reduces to a wall particle potential.

$$V(z) = \lim_{R_1 \rightarrow \infty} v(\frac{1}{2}R_1 + z). \quad (2.2)$$

Under these limits the Ornstein-Zernike equation becomes

$$\rho_2(\vec{r}_z) = C_{22}(\vec{r}_z) + \rho_2 \int_{\vec{s}_z \geq 0} [\rho_2(|\vec{s}_z|) - \rho_2] \times C_{22}(|\vec{r} - \vec{s}|) d\vec{s}, \quad (2.3)$$

where the subscript z refers to that component of a vector normal to the adsorbing surface,

$$C_2(z) = \lim_{R_1 \rightarrow \infty} \lim_{\rho_1 \rightarrow 0} \rho_2 [C_{12}(\frac{1}{2}R_1 + z) + 1] \quad (2.4)$$

and $C_{22}(r)$ is the bulk direct correlation function for the adsorbate at density ρ_2 . If one accepts

that the limiting process is exact, then so is (2.3). Perram and White³ and others have tended to work with the Percus-Yevick closure applied to the Ornstein-Zernike equation. Under the limits used this gives

$$C_2(z) = \rho_2(z)(1 - e^{\beta V(z)}) + \rho_2. \quad (2.5)$$

Equation (2.3) then becomes, upon rearrangement

$$\rho_2(\vec{r}_z) = \rho_2 e^{-\beta V(\vec{r}_z)} \left(1 + \rho_2 \int_{\vec{s}_z \geq 0} C_{22}(|\vec{r} - \vec{s}|) \times [\rho_2(\vec{s}_z) - \rho_2] d\vec{s} \right). \quad (2.6)$$

Other workers^{15,16} have used the mean spherical approximation closure of the Ornstein-Zernike equation. We could also use the hypernetted chain closure. In the limit this closure is

$$C_2(z) = \rho_2(z) - \rho_2 \ln(\rho_2(z)/\rho_2) - \beta \rho_2 V(z) \quad (2.7)$$

and gives

$$\rho_2(\vec{r}_z) = \rho_2 e^{-\beta V(\vec{r}_z)} \exp \left(\int_{\vec{s}_z \geq 0} C_{22}(|\vec{r} - \vec{s}|) \times (\rho_2(\vec{s}_z) - \rho_2) d\vec{s} \right). \quad (2.8)$$

The exact part of the density-functional theory in applications to adsorption is the equation

$$\rho_2(\vec{r}) = \rho_2 e^{-\beta V(\vec{r})} \times \exp \left(\int_0^1 d\alpha \int d\vec{s} C(\vec{r}, \vec{s}; \alpha) [\rho_2(\vec{s}) - \rho_2] \right), \quad (2.9)$$

where $C(r, s; \alpha)$ is the inhomogeneous direct correlation function, the parameter α describing an integration path in the space of density functionals. This equation may be obtained by a variational principle applied to the grand canonical free energy followed by a direct integration with respect to density. Saam and Ebner supplement their variational principle with the closure

$$\int_0^1 d\alpha \int_0^\alpha d\alpha^1 C(\vec{r}, \vec{s}; \alpha^1) = \frac{1}{2} C_{22}(|\vec{r} - \vec{s}|; \bar{\rho}), \quad (2.10)$$

where

$$\bar{\rho} = \frac{1}{2} [\rho_2(\vec{r}) + \rho_2(\vec{s})] \quad (2.11)$$

is the density at which the bulk direct correlation function is evaluated. Integration by parts of Eq. (2.10) transforms Eq. (2.8) to

$$\rho_2(\vec{r}) = \rho_2 e^{-\beta V(\vec{r})} \exp \left[\int d\vec{t} \left(C_{22}(|\vec{r} - \vec{t}|; \bar{\rho}) + \int_0^1 d\alpha \alpha [C(\vec{r}, \vec{s}; \alpha) - C_{22}(|\vec{r} - \vec{s}|; \bar{\rho})] \right) \right] \quad (2.12)$$

This form of Saam and Ebner's result invites comparison with the hypernetted chain result (2.8).

Saam and Ebner,² quite rightly, point out that Eq. (2.9) connecting $\rho_2(r)$ with the inhomogeneous direct correlation function $C(r, s; \alpha)$ is exact.

Other exact results for inhomogeneous systems are the first-order Born-Green equation

$$\nabla \rho_2(\vec{r}) + \beta \rho_2(\vec{r}) \nabla V(\vec{r}) + \beta \rho_2(\vec{r}) \int \rho_2(\vec{s}) g(\vec{r}, \vec{s}) \nabla_{\vec{r}} \phi(|\vec{r} - \vec{s}|) d\vec{s} = 0 \quad (2.13)$$

and the inhomogeneous system Ornstein-Zernike equation

$$h(\vec{r}, \vec{s}) = C(\vec{r}, \vec{s}) + \int d\vec{t} C(\vec{r}, \vec{t}) \rho_2(\vec{t}) h(\vec{t}, \vec{s}), \quad (2.14)$$

and these equations may be thought of as containing exactly the same amount of information as Eq. (2.9). The point we make here is that exact hierarchical equations of the type (2.9), (2.13), or (2.14), which relate the function $\rho_2(r)$ which we wish to calculate to more complex unknown functions, are without value unless a second relation between these quantities may be found. For example, the HNC, PY, mean spherical, and superposition approximations are well-known closures of this type. The equation (2.10) of Saam and Ebner² is also precisely of this type. Much work in the theory of fluids has been devoted to the question of which closure is to be preferred under which circumstances. The usual test of the complete set of equations is by comparison with experiment, either physical or numerical. To our knowledge, in every such test, no appeal is made to the exactness of just one of the equations. We believe it to be misleading of Saam and Ebner² to contrast the "formally exact equation (4)" [Eq. (2.9) of this paper, without the closure (2.10)] with the "linearized Percus-Yevick equation" to which a closure has been applied.

III. ADSORPTION OF NOBLE GASES ON SOLIDS: RECENT RESULTS

In a series of papers^{8,9} Lane and Spurling have described the results of Monte Carlo simulations of the adsorption of rarefied gases on to solid substrates. The substrate is considered as an inert hard wall with an interaction potential with noble-gas atoms appropriate for the basal plane of graphite. These calculations were carried out under physical conditions different from those studied by Saam and Ebner, but provide an opportunity to check the appropriateness of the closures discussed in Sec. II. The adsorbate was a Lennard-Jones model of krypton with the 10-4-3 potential developed by Steele²⁰ for noble gases ad-

sorbed onto graphite. At temperatures in the range 77–90 K at bulk densities of the order $\rho\sigma^3 = 10^{-8}$, monolayer adsorption of Kr on graphite is observed. A transition in the monolayer from two-dimensional gaslike to two-dimensional liquidlike behavior was seen as the bulk density increased. The experimental work of Thomy and Duval²¹ and others shows precisely this behavior, and the simulation adsorption isotherms are in excellent agreement with the experimental ones. The Percus-Yevick theory, applied to the adsorption of adhesive hard spheres onto an adhesive hard wall shows behavior in good agreement with both experiment and simulation, predicting the temperature dependence of the bulk transition density quite well. Beyond this bulk density, the PY theory for adhesive spheres ceases to predict physically meaningful quantities for gas phase adsorption of interacting gases. It should be noted that the adsorption potentials considered here are much stronger than those appropriate for the adsorption of argon onto carbon dioxide.

At supercritical temperatures and pressures up to 150 atm, Gibbs surface excess adsorption isotherms show a maximum²² as a function of bulk density or pressure. This behavior is predicted quite well by the PY theory applied to adhesive hard spheres.¹⁹

An advantage of using the adhesive hard sphere system is that all the calculations may be carried out analytically. This enables any singularities in the adsorbing system to be identified precisely. Further, the difficulties inherent in the system when either the adsorbed monolayer or the bulk adsorbate are in a two-phase region are made quite clear. Use of the PY theory in this way does not (unlike the closure for the density-functional theory) require evaluation of correlation functions at states inside the coexistence region, where they do not exist.

IV. COMPUTER SIMULATIONS OF ADSORPTION OF ARGON ON CARBON DIOXIDE

Monte Carlo simulations, using the method described earlier^{8,9} of sampling the grand canonical ensemble are reported here for a system of Lennard-Jones particles with interaction potential

$$\phi(r) = 4\epsilon[(\sigma/r)^{12} - (\sigma/r)^6] \quad (4.1)$$

with parameters $\epsilon/k = 119.726$ K and $\sigma = 3.405$ Å, appropriate to argon as used by Saam and Ebner,² which interact with a wall via a potential of the form

$$V(z) = 4\pi\epsilon_\omega n_\omega \sigma_\omega^3 \left[\frac{1}{45} (\sigma_\omega/z)^9 - \frac{1}{3} (\sigma_\omega/z)^3 \right] \quad (4.2)$$

with parameters $\sigma_\omega = 3.727$ Å, $\epsilon_\omega/k = 153$ K, and

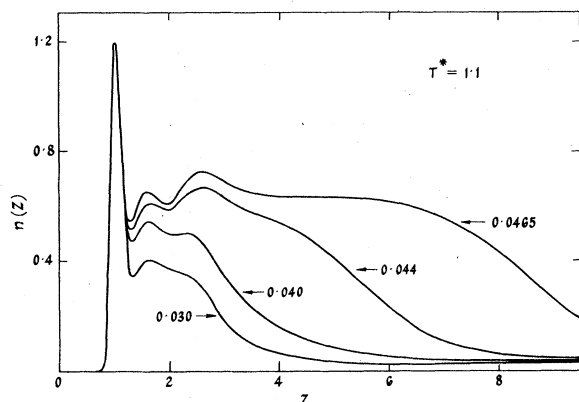


FIG. 1. Density profiles as obtained by the density-functional theory (Ref. 2) at $T^* = 1.1$. Reduced bulk phase densities are indicated on the figure.

$n_{\omega}\sigma_{\omega}^3 = 0.988$. This adsorption potential is precisely that used by Saam and Ebner and is appropriate to the adsorption of argon on carbon dioxide. Note that it is a different potential from that used in Refs. 8 and 9. In all the calculations reported here we used a box of size $4 \text{ nm} \times 4 \text{ nm} \times 10 \text{ nm}$. The usual periodic boundary conditions extended the box to infinity in the x and y directions, while in the $\pm z$ directions solid CO_2 extends to infinity. The grand ensemble Monte Carlo runs commenced with two particles and went for 800 000 configurations. Averages were taken over the final 500 000 configurations. The final averages were independent of the number of particles used in the initial configuration. This system has been studied by Saam and Ebner² at reduced temperatures $T^* = kT/\epsilon$ of 0.9, 1.1, and 1.4 and various low bulk adsorbate densities. At $T^* = 1.1$ and reduced densities $\rho\sigma^3 = 0.03, 0.04, 0.044,$ and 0.0465 , these authors observe the formation of thick films as $\rho\sigma^3$ is increased, as shown in Fig. 1. In Fig. 2, for contrast, we show the PY

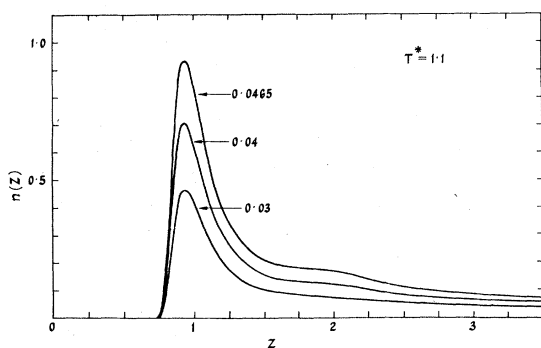


FIG. 2. Density profiles as obtained by the Percus-Yevick theory (Ref. 2) at $T^* = 1.1$. Reduced bulk phase densities are indicated on the figure.

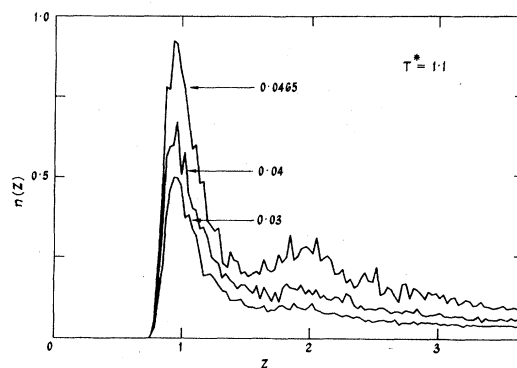


FIG. 3. Density profiles obtained by the Monte Carlo simulation at $T^* = 1.1$. Reduced bulk phase densities are indicated on the figure.

theory density profiles obtained by Saam and Ebner² at the above temperature. In Fig. 3 we display the density profiles calculated in the Monte Carlo simulations at $T^* = 1.1$ and $\langle\rho\sigma^3\rangle \approx 0.03, 0.040,$ and 0.0465 . In Fig. 4 we display the radial distribution function for the monolayer shown in Fig. 3 at $\langle\rho\sigma^3\rangle \approx 0.0465$, together with the radial distribution function $g^{(2)}(r)$ for the bulk gas at a density of $\rho\sigma^3 = 0.0465$ and $T^* = 1.1$ using the virial expansion appropriate to the LJ parameters for argon and up to the term proportional to the gas density. The definition of the radial distribution function $g^{(2)}(z_1, \beta, \vec{r})$ for surfaces is

$$\rho^{(2)}(\vec{r}_1, \vec{r}_2) = \rho^{(1)}(\vec{r}_1)\rho^{(1)}(\vec{r}_2)g^{(2)}(z_1, \beta, r) \quad (4.3)$$

where \vec{r}_1 and \vec{r}_2 are the vector coordinates of the

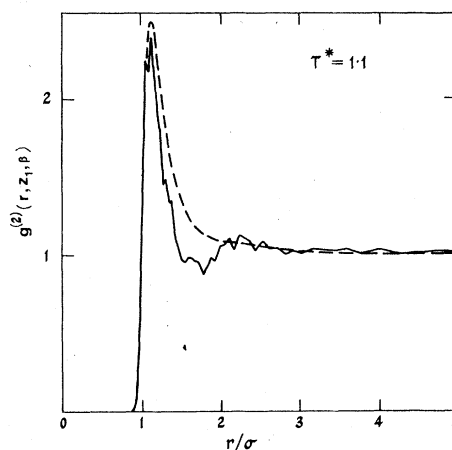


FIG. 4. Radial distribution functions at $T^* = 1.1$. Full line is the Monte Carlo result for the particles in the monolayer and the broken line is for particles in the bulk phase calculated from a virial expansion. The reduced bulk phase density is 0.0465 , $\langle z_1 \rangle = 0.39 \text{ nm}$ and $\langle \beta \rangle = \frac{1}{2}\pi \text{ rad}$.

particles, $r = |\vec{r}_2 - \vec{r}_1|$ the distance between the particles, z_1 is the z coordinate of one particle, β is the angle between the line joining the two particle centers and the normal to the interface, and $\rho^{(2)}(\vec{r}_1, \vec{r}_2)$ is the average number density function for pairs of particles. The similarity of the monolayer and bulk radial distribution functions suggests that the monolayer structure is similar to that of a dense gas. This is true of all densities and temperatures reported here and suggests that no transition occurs in the monolayer under these conditions. Ebner and Saam²³ also report calculations at $T^* = 0.9$ for $\rho\sigma^3 = 0.009, 0.0092, 0.0095, 0.0097, 0.0099,$ and 0.0101 . They show the growth of thick films as the density increases and locate a phase transition in the film thickness at $\rho\sigma^3 = 0.0097$. Their results are shown in Fig. 5. In Fig. 6 we show the density profile from a Monte Carlo simulation at $T^* = 0.9$ and $\langle\rho\sigma^3\rangle \approx 0.0101$, and in Fig. 7, the radial distribution function for particles confined to the monolayer shown in Fig. 6. Also in Fig. 7 is the radial distribution function for a bulk gas at $T^* = 0.9$ and $\rho\sigma^3 = 0.0101$ calculated as before.

It may be noted that the simulations show no sign of the formation of a film and, for that matter, show only very slight evidence of second layer adsorption at these gas densities. It may be seen from the $g^{(2)}(r, z_1, \beta)$ for particles in the monolayer that the monolayer is a two-dimensional fluid.

A second curious feature of the density profiles reported by Saam and Ebner is the independence of the height and shape of the first peak of the density profile on bulk density and temperature and adsorption potential.²⁰ Both the simulations and PY theory show a variation approximately described by¹²

$$\rho_2(\vec{r}) = \rho_2[1 + \alpha\rho_2]e^{-\beta V(\vec{r})}, \quad (4.4)$$

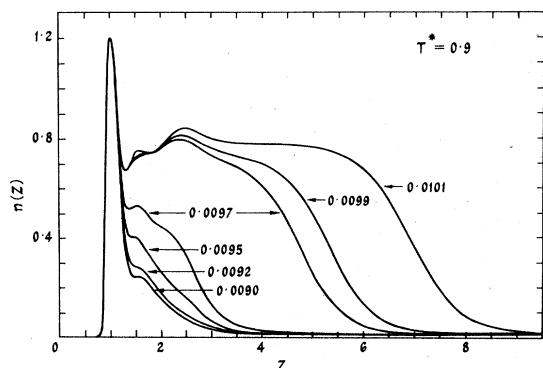


FIG. 5. Density profiles as obtained by the density-functional theory (Ref. 2) at $T^* = 0.9$. Reduced bulk phase densities are indicated on the figure.

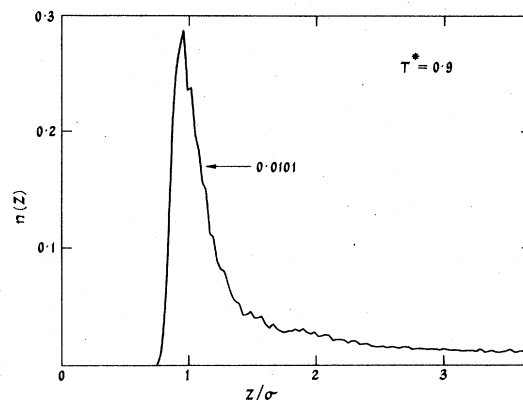


FIG. 6. Density profile obtained by the Monte Carlo simulation at $T^* = 0.9$ at a reduced bulk phase density of 0.0101.

where α is a constant, which would be expected if the virial expansion of $\rho_2(\vec{r})$ was dominated by the first two terms. Such behavior reduces to Henry's law at low densities in the situation under consideration, for which the adsorption potential is quite weak.

A third feature of the predictions of the Saam and Ebner density-functional theory which is at qualitative variance with both computer simulations and the Percus Yevick theory is the position of the second and third peaks of $\rho_2(\vec{r})$ for the adsorption of supercritical gas on the solid. In both simulations and the PY theory^{14,24} under all circumstances, these peaks are seen (if present) at approximately $\sigma, 2\sigma,$ and 3σ , where σ is a measure of the particle diameter. The density-func-

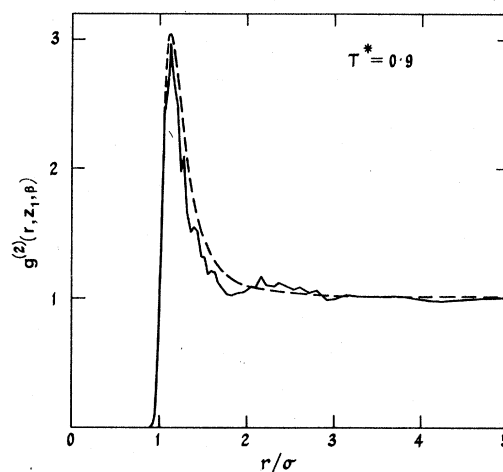


FIG. 7. Radial distribution functions at $T^* = 0.9$ and a bulk phase density of 0.0101. Full line is the Monte Carlo result for particles in the monolayer and the broken line is for particles in the bulk phase calculated from a virial expansion, $\langle z_1 \rangle = 0.38$ nm and $\langle \beta \rangle = \frac{1}{2}\pi$ rad.

tional theory sees the second and third peaks at approximately 1.5σ and 2.5σ . Further, for dense fluids in contact with a wall, both the simulations²⁵ and PY theory show very pronounced oscillations in the density profile, in contrast to the smooth structureless density profiles predicted by the density-functional method.

We note that the conditions reported by Saam and Ebner lie close to the Percus-Yevick coexistence curve for this system. The simulation coexistence curve has recently been published by Adams,²⁶ who finds that at $T^*=1.1$ it is very close to the Percus-Yevick curve. Work by two of us confirms Adams' calculation.²⁷ We have performed a simulation at $T^*=1.1$ and a gas density of $\langle\rho\sigma^3\rangle=0.049$, which is just below the simulation coexistence curve, and this produced a density profile which is superposable on the one for $\langle\rho\sigma^3\rangle=0.0465$ in Fig. 3. At chemical potentials corresponding to a gas density above $\langle\rho\sigma^3\rangle=0.049$, the grand ensemble simulation produces a liquid and under these circumstances no comparison with Saam and Ebner's work is possible. In our previous work,⁸ we have noted that for chemical potentials close to a surface transition the grand ensemble Monte Carlo calculation produces binodal distributions for the number of particles in the system. No such behavior was observed in the present calculations for either $\langle\rho\sigma^3\rangle=0.0456$ or $\langle\rho\sigma^3\rangle=0.049$.

V. DISCUSSION

The possibility of the formation of thick homogeneous liquid films on certain substrates can be seen from the following simple argument based on the Lifshitz theory of macroscopic dispersion forces, as noted by Saam and Ebner.² Provided the thickness l of a film is large enough for macroscopic thermodynamics to be valid, the free energy per unit area of a film of liquid at chemical potential μ_L in contact with a substrate on one side and the unsaturated vapor on the other side, present at chemical potential μ_G may be written as

$$F = A/l^2 + \mu_L \rho_L l, \quad (5.1)$$

where ρ_L is the number density of the liquid film and A is a complicated function of l and the dielectric spectroscopic properties of the substrate and the liquid. This free energy may be differentiated with respect to the number of particles per unit area of liquid layer to give an approximate chemical potential

$$\mu_L^1 = -2A/\rho_L l^3 + \mu_L = \mu_G. \quad (5.2)$$

If A is positive, which can indeed be the case, this

equation gives an approximate layer thickness l , where

$$l \sim (\bar{\rho}_G - \rho_G)^{-1/3} |2A\bar{\rho}_G/\rho_L kT|^{1/3} \quad (5.3)$$

and $\bar{\rho}_G$ is the density of the saturated vapor. We stress that this argument, while appealing, is based on macroscopic thermodynamics. In the situation where thick films may form from an unsaturated vapor, we would expect that the density profile in the film would be similar to the highly oscillatory profiles predicted by the PY theory¹⁴ for the adsorption of hard-sphere liquids on solid substrates and confirmed by computer simulations.²⁴ The density profiles in the films predicted by Saam and Ebner show only weak oscillations with peaks at positions different from those predicted by the PY theory and observed in simulations.

We must now consider the possible reasons why the density-functional theory of Saam and Ebner predicts film growth phenomena which are not seen in the simulation results. Apart from the exact equation (2.9), the density-functional theory as used by Saam and Ebner has two inexact inputs. These are the closure equation (2.10) and the parametrized trial density functions which were

$$\rho_2(z) = \left(\frac{\beta}{e^{r(z-s)} + 1} + \sum_{j=1}^5 \theta_j z^{j-1} e^{-\epsilon z^2} + \rho_2 \right) e^{-\alpha/Tz^9} \quad (5.4)$$

for $T^*=1.1$

and

$$\rho_2(z) = \left(\sum_{j=1}^5 \theta_j z^{j-1} e^{-\epsilon z^2} + \rho^2 \right) e^{-\alpha/Tz^9} \quad (5.5)$$

for $T^*=1.4$. In testing an approximate theory of this type against experiments, either numerical or physical, one is really testing the accuracy of the approximate closure employed. Under these circumstances, errors may be introduced in a variational calculation by the use of an unsuitable trial function. We find it surprising that the last exponentials in the trial density functions [Eqs. (5.4), (5.5)] do not contain the attractive part of the wall particle potential, so that they will not explicitly reduce to Henry's law at low bulk densities.

This being so, the failure of the Saam and Ebner theory to agree, even qualitatively with the results of computer simulations must mean that the closure [Eq. (2.10)] is very bad in this situation. The present agreement between the PY theory and experimental results, both numerical and physical, suggests that an alternate approach which is more complicated and cannot improve the agreement is unnecessary.

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