Long-range correlations in adsorbed layers

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(Received 18 August 1981)

We report regions of long-ranged correlations parallel to a surface as revealed in the calculation of the correlation functions and density profile for a vapor adsorbed on a solid substrate. The method underlying the calculations uses the modified hypernetted-chain equation in conjunction with the first Yvon-Born-Green equation.

Vapors in contact with solid substrates constitute an interesting class of physical systems which can be relatively dilute far from the interface yet, depending on the nature of the interactions, relatively dense close to the interface. There has been considerable interest in the theoretical description of such manifestly inhomogeneous systems.[1-4] While most work has concentrated on the single-particle density profile, only recently have results become available for the correlation functions.[5] The purpose of this Report is to present the results of the application of the method of Ref. 5 to cases where *layering* occurs at the interface. Specifically, we find interesting physical behavior in the manner in which the range of correlations parallel to the surface grows in the transition region adjacent to the substrate.

The approach employed in Ref. 5 includes the effect of the substrate by imposing an external potential $V_{ext}(\vec{r})$ on a vapor of particles whose mutual interactions are described by pair potentials $\phi(\vec{r})$, taken to have the Lennard-Jones form. The number density profile $\rho(\vec{r})$ is computed from the first member of the exact Yvon-Born-Green hierarchy[6] which is derived from the requirement of mechanical equilibrium:

$$\vec{\nabla}\rho(\vec{r}) = -\beta\rho(\vec{r})\vec{\nabla}V_{ext}(\vec{r})$$
$$+\rho(\vec{r})\int c(\vec{r},\vec{r}')\vec{\nabla}\rho(\vec{r}')d\vec{r}' . \qquad (1)$$

Here $c(\vec{r},\vec{r}')$ is the Ornstein-Zernike direct correlation function for the inhomogeneous fluid. The Ornstein-Zernike equation provides an additional relationship between $c(\vec{r},\vec{r}')$ and the pair correlation function $g(\vec{r},\vec{r}') \equiv h(\vec{r},\vec{r}')+1$, namely

$$h(\vec{r},\vec{r}') = c(\vec{r},\vec{r}')$$
$$+\int h(\vec{r},\vec{r}'')\rho(\vec{r}'')c(\vec{r}'',\vec{r}')d\vec{r}'' .$$

$$(2)$$

To close these equations, we require a relationship between $h(\vec{r},\vec{r}')$ and $c(\vec{r},\vec{r}')$. This may be obtained in three steps. First, we note the exact result

$$1+h(\vec{r},\vec{r}') = \exp[\,-\beta\phi(\vec{r}-\vec{r}')+E(\vec{r},\vec{r}')$$
$$+h(\vec{r},\vec{r}')-c(\vec{r},\vec{r}')] , \qquad (3)$$

where $E(\vec{r},\vec{r}')$ is the bridge function or sum of elementary diagrams.[7] Second, it has been shown[8] that for *uniform* fluids $E(r)$ is highly universal and short ranged. In addition, it is well represented by the form appropriate for a hard-sphere system. Third, as shown in Ref. 5, it is physically justifiable for an inhomogeneous system to use a *local* approximation for $E(\vec{r},\vec{r}')$, i.e.,

$$E(\vec{r},\vec{r}')\simeq E(\,|\,\vec{r}-\vec{r}'\,|\,,\bar{\rho}=[\rho(\vec{r}')+\rho(\vec{r}')]/2) ,$$

$$(4)$$

where $E(r,\bar{\rho})$ is actually determined from the Percus-Yevick solution for a hard-sphere system of local density $\bar{\rho}$.[9] Equations (1) — (4) now provide a closed set of coupled integro-differential equations which may be used to describe inhomogeneous systems. In particular, for a planar interface, they may be solved directly by using an iterative numerical procedure.

The external one-body potential used in this study is identical, except for an adjustable scale parameter α, to the one used in Refs. 1 and 5, i.e.,

$$V_{\text{ext}}(z)=\alpha 4\pi\epsilon_W\rho_W\sigma_W^3\left[\frac{1}{45}\left[\frac{\sigma_W}{z}\right]^9-\frac{1}{6}\left[\frac{\sigma_W}{z}\right]^3\right],$$

(5)

where $\epsilon_W/k_B=153$ K, $\sigma_W=3.727$ Å, and $\rho_W\sigma_W^3$ $=0.988$. For $\alpha=1$ it corresponds to the argon-carbon dioxide system. All quantities are reported in units reduced by the Lennard-Jones parameters for argon ($\epsilon/k_B=119.8$ k and $\sigma=3.405$ Å). The results we discuss are appropriate to a bulk density of $\rho^*=0.03$, a reduced temperature T^* $=1.1$, and $\alpha=1.0$, 1.2, 1.25, and 1.35. The density profiles resulting from the converged iterative procedure are presented in Fig. 1. The layered structure displayed there agrees with previous work.[1,3]

Somewhat more interesting, however, is the behavior of the pair correlation function in the interfacial region. For points whose relative separation is *perpendicular* to the surface, the correlations are quite similar to those of dense homogeneous fluids. The results for $g(z=z',R_{||})$, the pair correlation function for two points *equidistant* from the surface as a function of their mutual separation parallel to the surface, are presented in Fig. 2 ($\alpha=1.35$). For points in the first adsorbed layer ($z\sim\sigma$), these correlations again have structure
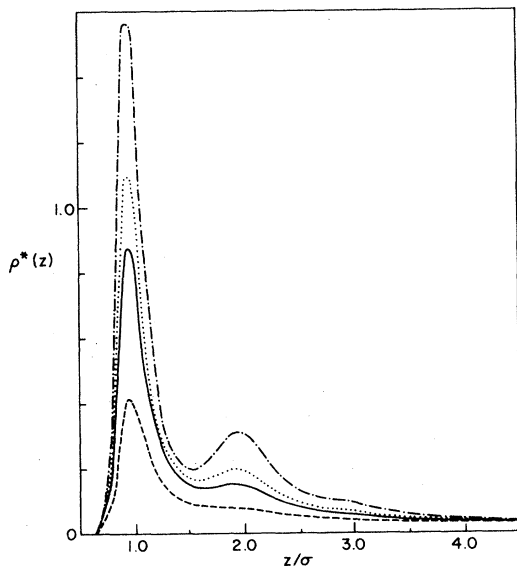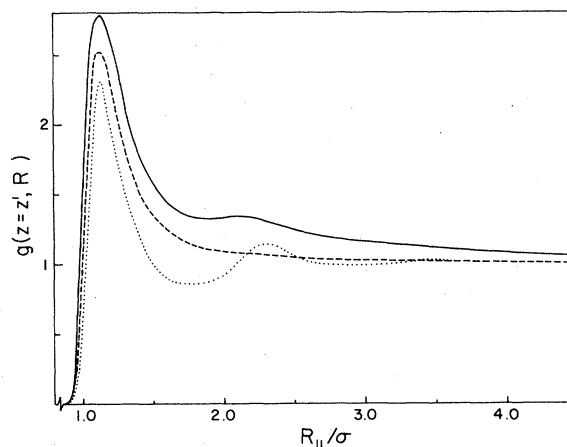

FIG. 2. Pair correlation function for two points a distance z from the surface as a function of separation parallel to the surface for $T^*=1.1$, bulk density ρ^* $=0.03$, and $\alpha=1.35$. The curves show $z=5.0\sigma$ (— — —), $z=3.05\sigma$ (———), and $z=1.1\sigma$ ($\cdots$).

similar to that of dense fluids. This is expected. Far from the surface they approach normal bulk values. The new feature, however, is the *slow decay* of the correlations in the transition region between the bulk and layered regions (see Fig. 1).

The spatial extent of this behavior is displayed most effectively by computing the planar integral parallel to the surface of the total correlation function, i.e.,

$$h(z,z',Q=O)=\int d\vec{R}_{||}h(z,z',\vec{R}_{||}),$$

where $\vec{R}_{||}$ is the projection onto the plane parallel to the surface of $(\vec{r}-\vec{r}')$. This is presented as a function of $z=z'$ in Fig. 3 for different values of α. For $\alpha=1.0$, 1.2 the parallel correlations are

FIG. 1. Density profile of a Lennard-Jones fluid in contact with a solid substrate at $T^*=1.1$ and bulk density $\rho^*=0.03$. The wall-particle interaction is given by Eq. (5) with $\alpha=1.0$ (— — —), $\alpha=1.2$ (———), $\alpha=1.25$ ($\cdots$), and $\alpha=1.35$ (— $\cdot$ — $\cdot$ — $\cdot$).
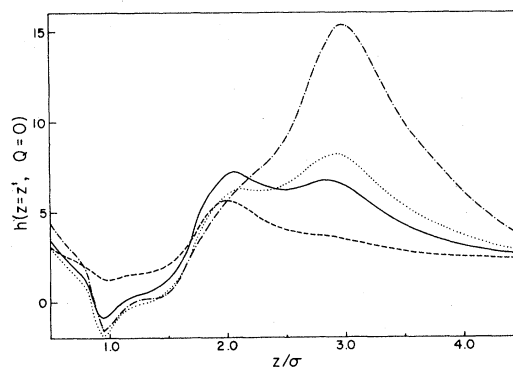

FIG. 3. Total correlation function integrated in a plane parallel to the surface for the conditions of Fig. 1.

centered near $z = 2\sigma$; for larger α, they are centered near $z = 3\sigma$, and so on. Comparison with the density profiles in Fig. 1 shows clearly that the correlations are largest exactly where the new layers are beginning to form.

Some insight into the variation of the density profile with a change in bulk density can be obtained by computing the response to a change in chemical potential, μ. It can be shown that[6]

$$\frac{\delta\rho(z)}{\delta\mu} = \beta\rho(z)\left[1 + \int h(z,z',Q=0)\rho(z')dz'\right].$$

$$(6)$$

The quantity in large parentheses is plotted in Fig. 4. It is apparent that the tendency toward layering increases with bulk density. We also note that the response near the first peak in the density decreases with stronger potentials. This signals the onset of density saturation in the first layer as must happen for a system with repulsive cores.

To verify that these general features are not artifacts of the closure approximation, we repeated the calculations for $\alpha = 1.25$ with Eq. (3) replaced by (a) the hypernetted-chain equation $[E(\vec{r},\vec{r}') = 0]$, and (b) by the Percus-Yevick equation. In both cases, the quantitative results are somewhat different, but the qualitative behavior is preserved.

We also examined effects due to changing the conditions in the bulk vapor. Calculations performed at a lower density ($\rho^* = 0.01$, $T^* = 1.1$), show less layering, as expected, but again the qualitative features described above are still present though certainly less pronounced. Increasing the temperature rapidly washes out these features. For example, in calculations for $\rho^* = 0.03$ and $\alpha = 1.25$, both the increased correlations parallel to the surface and the formation of secondary layers are substantially reduced for $T^* = 1.4$ and are almost entirely eliminated for $T^* = 1.7$.

The new aspect present in these results, the long-ranged correlations in the transition region, is physically plausible if one accepts the formation of layers as an essential feature of adsorption. The growth of a new layer requires that quantities such as $\delta\rho(z)/\delta\mu$ be large in that region. This in turn suggests that $h(z,z',Q=0)$ will be large for z and z' near the new layer as our results show.

The analogy with bulk fluids near a liquid-vapor critical point, where the correlations look qualitatively similar, implies the existence of large density fluctuations in the transition region. Such a possibility is supported by the following simple argu-

ment. A vapor is manifestly highly compressible and so can sustain large fluctuations in the local chemical potential. The results presented in Fig. 4 show that such changes will produce the largest relative density fluctuations in the transition region. Large density fluctuations in a weakly absorbed layer are also intuitively appealing since the effective mean potential responsible for the local accumulation of particles is weak and the density is thus easily perturbed.

Computer simulations of fluid-solid interfaces have not so far revealed the behavior of the pair correlation function that we describe. In the main, these studies have focused on dense Lennard-Jones fluids[10] and dilute hard-sphere gases[4] at solid substrates, and have found no significant variation with the distance from the surface of the pair correlations parallel to the surface. A dense fluid in contact with a solid differs qualitatively from the systems studied here in that there is no transition from a dilute to a dense region. Thus, the qualitative behavior need not be the same. The hard-sphere results are certainly consistent with our observation of the temperature dependence of the effect. At higher temperatures, the interparticle attractions become less important and the system approaches a hard-sphere system. Comparison of these physical situations implies that strong particle-particle interactions and dilute bulk conditions are both required. Thus, the long-ranged correlations appear to be associated with a *local*
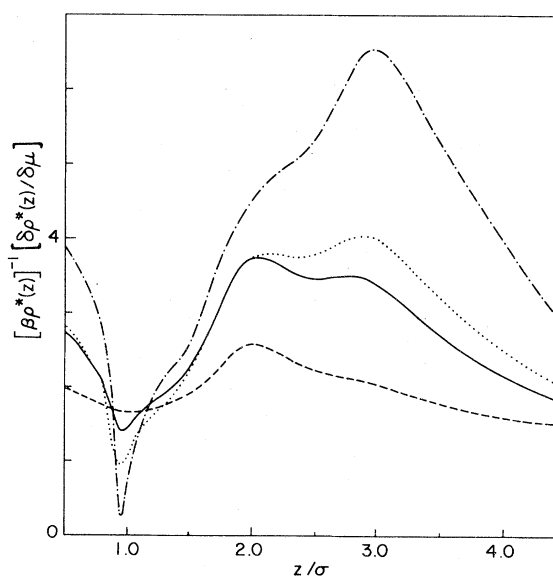

FIG. 4. Relative density response to a change in chemical potential for the conditions of Fig. 1.

condensation of a dilute gas into a dense layer as a consequence of the *interparticle* interactions. Computer simulations for parameters similar to those studied here would therefore be of great interest.

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