Evidence Concerning Drying Behavior of Ne near a Cs Surface

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Using density functional and Monte Carlo methods, we have studied the properties of Ne adsorbed on a Cs surface, focusing on the region at and near saturated vapor pressure (SVP). In the case of Ne/Rb, the experimental data of Hess, Sabatini, and Chan are consistent with the calculations based on an ab initio fluid-substrate potential, while in the Ne/Cs case there is indication that the potential is ~9% too deep. In that case, the calculations yield partial drying behavior consistent with the experimental finding of depressed fluid density near the surface, above SVP. However, we find no evidence of a drying transition, a result consistent with the mean-field calculation of Ebner and Saam.

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The subject of wetting has stimulated both basic and applied research for nearly two centuries. The Young equation implies the possibility of several alternative varieties of wetting behavior as a function of the adsorption system and the temperature \( T \). For example, at saturated vapor pressure (SVP), a liquid drop may bead up on a surface exhibiting a finite contact angle \( \Theta \). This “nonwetting” behavior occurs when the following relation between three surface tensions is satisfied:

\[
|\Delta \sigma| = |\sigma_{sv} - \sigma_{lv}| < \sigma_{lv}
\]

\[0 < \Theta < \pi, \text{ nonwetting} \quad \] \( (1) \)

Here \( v, l, \) and \( s \) refer to vapor, liquid, and solid, respectively. An alternative possibility is “wetting” (sometimes called “complete wetting”)

\[
\Delta \sigma \geq \sigma_{lv} \quad (\Theta = 0, \text{ wetting})
\]

in which case a very thick liquid film (in equilibrium) is spread uniformly across the surface. The transition between these regimes occurs at the wetting temperature \( T_W \). Such a transition, anticipated by general arguments by Cahn [1] and Ebner and Saam [2], has been seen in a number of instances where the gas-surface attraction is weak. The theory envisions a third possible scenario, “drying,” in the case of a very weakly attractive interaction:

\[
\Delta \sigma < -\sigma_{lv} \quad (\Theta = \pi, \text{ drying})
\]

Such behavior is manifested, in principle, as the presence above SVP of a thick region of vapor intervening between the surface and the asymptotic bulk liquid. A recent experiment by Hess, Sabatini, and Chan (HSC) [3] found some evidence for such drying behavior for Ne adsorbed on the Cs surface. This drying system is a promising candidate for drying since the theoretical well depth \( |\varepsilon| \approx 25 \) K of the gas-surface interaction is significantly less than the well depth \( |\varepsilon| = 33.9 \) K of the Ne-Ne pair potential. In this paper, we report calculations relevant to the drying behavior observed in the HSC experiment. We have employed two methods, a density functional (DF) approach and grand canonical Monte Carlo (GCMC) simulations; we have improved somewhat upon techniques used in our previous studies of wetting transitions [5,6]. The DF method involves an empirical free-energy functional written in terms of the density \( \rho(\vec{r}) \) of the fluid as

\[
F[\rho] = F_{HS}[\rho] + \frac{1}{2} \iint \rho(\vec{r})\rho(\vec{r}')u_a(|\vec{r} - \vec{r}'|) \, d\vec{r} \, d\vec{r}' + \int \rho(\vec{r})V_s(\vec{r}) \, d\vec{r} + \gamma F_{id} \quad (4)
\]

Here \( F_{HS} \) is the free-energy functional for an inhomogeneous hard-sphere (HS) reference system, the second term is the usual mean-field approximation for the attractive part of the fluid-fluid intermolecular potential \( u_a \), while \( V_s(\vec{r}) \) is the external, static adsorption potential due to the surface. \( F_{id} \) is the ideal (classical) gas contribution. For \( F_{HS} \) we use the nonlocal functional of Ref. [7].

The functional (4) involves three parameters: (i) a correction to the HS diameter, (ii) a parameter enhancing the effective potential well depth of the fluid-fluid interaction, and (iii) the coefficient \( \gamma \) in the last term of (4). A previous version of the functional (4), involving only the two parameters (i) and (ii), has been applied with success to the study of the wetting properties of Ar and Ne on different surfaces [5,8]. In particular, a remarkably good agreement has been found [5] between DF calculations for the Ne/Rb system and the experimental results [3], both showing a first-order wetting transition between 43 and 44 K. The small revision used here is to let the coefficient \( \gamma \) in Eq. (4) be a free parameter; the best-fit values are very close, for each value of \( T \), to the value \( \gamma = 1 \) assumed previously.

These three adjustable parameters are fit to reproduce properties of bulk Ne. In particular, we require that the experimental pressure and densities for the homogeneous system be reproduced at liquid-vapor coexistence (see Fig. 1, upper panel), and moreover that the stability
condition $\mu_v = \mu_l$, involving the chemical potentials of the two phases, is also satisfied. We then use the functional to study the Ne liquid-vapor free interface and confirm that it yields good agreement with the Ne surface tension $\sigma_{lv}$ (see Fig. 1, lower panel).

When studying fluid-surface interactions, it is important to employ an accurate adsorption potential. Ab initio potentials for many adsorption systems were derived recently by Chizmeshya, Cole, and Zaremba (CCZ) [4]. Overall, these have proven to be reliable for predicting contact angle and wetting temperatures of He and Ne on several surfaces [5,9,10]. Using the Ne/Cs potential, our previous GCMC study [6] found negligible adsorption of Ne over the entire range ($T < 43$ K) of that study, for which the correlation length $\xi$ of critical fluctuations is smaller than the smallest dimension (29 Å) of the periodically replicated simulation cell; this result is consistent with the HSC data for this system. To more closely approach the critical point ($T_c = 44.4$ K), we increased the cell dimensions to 100 Å $\times$ 100 Å $\times$ 200 Å. Our previous DF study [5] found a wetting transition for Ne/Rb at $T_W \sim 43$ K, consistent with the HSC data. With the revised DF method described above we confirm the Ne/Rb result and find a wetting transition for Ne/Cs at a similar temperature ($T_W \sim 43$–44 K). This is seen in Fig. 2 as a crossing of the two curves $\Delta \sigma(T)$ [curve (a)] and $\sigma_{lv}(T)$ [for the details of the method used to compute the surface tensions $\sigma_{ij}$ ($i,j = s,l,v$), see Ref. [9]]. Such a prediction disagrees with the HSC findings for Ne/Cs, of nonwetting at all $T$. We conjecture that this discrepancy occurs because the CCZ potential is somewhat too attractive. We therefore modify the original Ne/Cs potential in such a way that the modified potential has a slightly smaller well depth than the original one. When using the modified-CCZ potential, the wetting transition disappears, as can be seen from the curve (b) in Fig. 2 which no longer crosses $\sigma_{lv}(T)$, i.e., a rather small ($\sim 9\%$) correction to the theoretical well depth brings the wetting behavior into consistency with experiment. Such an “error” in the CCZ potential is compatible with the uncertainties present in its derivation (such as the jellium model of the surface and an empirical damping procedure applied to the dispersion part of the attraction).

Values of the contact angle $\cos(\Theta) = \Delta \sigma/\sigma_{lv}$ can be immediately extracted from Fig. 2. For the modified-CCZ potential we find, for instance, $\Theta = 94^\circ$ at $T = 38$ K, $\Theta = 84^\circ$ at $T = 40$ K, and $\Theta = 64^\circ$ at $T = 42$ K. Measurements of these angles should provide a direct test of our calculations.

Figure 2 presents results for $\Delta \sigma(T)$ also for still smaller hypothetical well depths. To simulate such ultraweak (UW) adsorbing surfaces, we use for simplicity a tunable 3-9 model potential

$$V_s(z) = \frac{4c_3^3}{27D^2z^9} - \frac{C_3}{z^2},$$

FIG. 1. Upper panel: pressure-density phase diagram of bulk Ne at SVP, at various temperatures. The squares are experimental points at coexistence, which are reproduced by construction with our functional. Lower panel: liquid-vapor Ne surface tension $\sigma_{lv}$. The squares are our calculated values, and the dashed line is a fit to the experimental data which goes to zero as $(1 - T/T_c)^{\beta}$, with the exponent $\beta = 1.27$ given by renormalization group theory.

FIG. 2. Calculated surface tensions for Ne on different substrates. The two solid lines show the liquid-vapor surface tension, $\sigma_{lv}$. Dashed lines labeled (a) and (b): $\Delta \sigma$ for the Ne/Cs system calculated with the CCZ potential [curve (a)] and the modified-CCZ potential [curve (b)], respectively. The other lines show $\Delta \sigma$ for Ne on ultraweak 9-3 surfaces, with decreasing values of the potential well depth $D$: $D = 24$ K (dotted line); $D = 5$ K (long-dashed line); $D = 2$ K (short-dash-dotted line); $D = 0.6$ K (long-dash-dotted line).
where $C_3$ is kept fixed to the Ne/Cs value [4] $[C_3 = (1.145 \text{ eV})a_0^3]$, while the well depth $D$ is arbitrarily varied. Figure 2 displays results for the dependence of $\Delta \sigma(T)$ on the well depth $D$ for such UW surfaces. Note that none of these curves crosses the curve $-\sigma_{lv}$. This means that no drying transition occurs below $T_c$ even for the weakest interaction considered, a conclusion that is consistent with the general (mean-field) result [11] of Ebner and Saam. That argument implies that a drying transition can occur only at $T_c$ as a consequence of the long-range van der Waals attraction. In order to check our DF results, we also performed extensive GCMC simulations and confirmed the absence of a drying transition below $T_c$.

Figure 3 exhibits the evolution of the Ne density profile (normalized to the asymptotic bulk liquid density $\rho_\infty$) slightly above SVP as $T_c$ is approached. We consider here, as a representative case, the adsorption of Ne on a UW surface characterized by a 3-9 potential with $D = 0.6$ K. Note that the region of density depletion extends ever farther, as the correlation length diverges. This behavior is similar to that predicted by Ebner and Saam [11], described by them as “the gas film is trapped by the long range potential and cannot dry until $T_c$ is reached.” Our methods do not allow, however, any quantitative description of the temperature behavior of the drying coverage very close to $T_c$, e.g., to estimate a critical exponent for the diverging vapor layer, being based on a mean-field density functional, on the one hand, or a Monte Carlo method with large but finite unit cells, on the other.

Having ruled out the occurrence of a drying transition below $T_c$, what is thus responsible for the apparent drying behavior for Ne/Cs reported by HSC? Figure 4 presents a set of density profiles, for the two systems investigated in HSC, Ne/Au and Ne/Cs, for different values of the chemical potential $\mu$ both below and above the value $\mu_0$ at liquid-vapor coexistence. Values of $\mu < \mu_0$ result in profiles that have the vapor density as the asymptotic density $\rho(\infty)$, whereas when $\mu > \mu_0$ the liquid density is reached far from the surface. We note that these DF results are consistent with the GCMC data simulated with the same conditions. From the profiles shown in Fig. 4, one can compute the surface excess coverage per unit area

$$\Delta N/A \equiv \int_{z_0}^\infty dz [\rho(z) - \rho(\infty)]$$

(here $A$ is the surface area, and $z_0$ is taken at the zero-energy turning point of the adsorption potential [12]). Results for $\Delta n \equiv \Delta N/A$ are shown in Fig. 5, both below and above SVP. Note that the excess coverage is positive below $\mu_0$ even if the attraction is very weak, as in the case of Ne/Cs. Above $\mu_0$, the excess coverage for Ne/Cs is negative, i.e., there is a deficiency in mass because the attraction is so weak. A positive $\Delta n$ is found
The expected shift in frequency in a quartz microbalance for a sufficiently low value of the ratio between the fluid-substrate and fluid-fluid interaction strengths, although with some controversy concerning the order of this transition (see Refs. [15,16], and references cited therein). However, the long-range fluid-surface potential used in these simulations is usually cut off, for computational reasons, at a short distance \( r_c \sim (2-3) \sigma_{LJ} \), thus resulting in an effective \textit{finite}-range fluid-surface interaction. As clearly shown by our results, inclusion of the full long-range part of the fluid-surface interaction (i.e., with no cutoff) results in the disappearance of the drying transition below \( T_c \).

In summary, DF and GCMC calculations find a wetting transition for Ne/Cs if the \textit{ab initio} potential is used to describe the fluid-substrate interaction, in disagreement with experiments. A plausible, small change in the attractive potential well depth changes the prediction to nonwetting for all \( T \). The resulting behavior of the mass excess per unit area \( \Delta n \) is qualitatively consistent with the experimental data. Below SVP, \( \Delta n \) is small and positive. Above SVP, an apparent discrepancy in the magnitude of \( \Delta n \) is attributed to the fact that significant slip occurs due to the weak interaction and resulting low density as suggested by the MD results of [14]. Finally, our results are consistent with a general prediction [11] that a drying transition is shifted to \( T_c \) by the long-range gas-surface attraction. Our results should be tested by contact angle and ellipsometric measurements of film thickness for Ne/Cs.

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[12] There is an ambiguity in the position chosen as the lower limit of the excess density integral. By choosing, e.g., \( z_0 \) at the potential minimum, the excess coverages in Fig. 5 would shift upward by \( \sim 0.025 \AA^2 \) at most on both sides of SVP. This would make no difference in any qualitative conclusion here.
[13] The values entering the prefactor \((4f^2/nR)\) are taken from Ref. [3].