Evidence concerning Drying behavior of Ne near the Cs surface

Francesco Ancilotto\textsuperscript{1}, Stefano Curtarolo\textsuperscript{2}, Flavio Toigo\textsuperscript{1}, and Milton W. Cole\textsuperscript{3}

\textsuperscript{1}Istituto Nazionale per la Fisica della Materia and Dip.to di Fisica G. Galilei
Universit\`a di Padova, via Marzolo 8, 35131 Padova, Italy
\textsuperscript{2}Department of Materials Science and Engineering, MIT, Cambridge, MA 02139, USA
\textsuperscript{3}Department of Physics, Penn State University, University Park, PA 16802, USA

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Using density functional (DF) 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 $\sim 9\%$ 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 a 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 "non-wetting" behavior occurs when the following relation between three surface tensions is satisfied:

$$|\Delta \sigma| \equiv |\sigma_{sv} - \sigma_{sl}| < \sigma_{lv} \quad (0 < \Theta < \pi, \text{nonwetting})$$

(1)

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

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

(2)

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 \textsuperscript{[1]} and Ebner and Saam \textsuperscript{[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. The criterion is:

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

(3)

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 of Hess, Sabatini and Chan \textsuperscript{[3]} (HSC) found some evidence for such drying behavior for Ne adsorbed on the Cs surface. This system is a promising candidate for drying since the theoretical well depth $D \sim 25 K$ of the gas-surface interaction is significantly less than the well depth ($\epsilon = 33.9 K$) 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 \textsuperscript{[4],[5]}. The DF method involves an empirical free-energy functional written in terms of the density $\rho(\vec{r})$ of the fluid as:

$$F[\rho] = F_{HS}[\rho] + \frac{1}{2} \int \int \rho(\vec{r})\rho(\vec{r}')u_a(|\vec{r} - \vec{r}'|)d\vec{r}d\vec{r}'$$

$$+ \int \rho(\vec{r})V_s(\vec{r})d\vec{r} + \gamma F_{id}$$

(4)

Here $F_{HS}$ is the free-energy functional for an inhomogeneous hard-sphere 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 non-local functional of Ref. \textsuperscript{[7]}. The functional \textsuperscript{[4]} involves three parameters: (i) a correction to the 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 \textsuperscript{[4]}. A previous version of the functional \textsuperscript{[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 \textsuperscript{[8],[9]}. In particular a remarkably good agreement has been found \textsuperscript{[9]} between DF calculations for the Ne/Rb system and the experimental results \textsuperscript{[9]}, 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.\textsuperscript{[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 are 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.

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). Overall, these have proven to be reliable for predicting contact angle and wetting temperatures of He and Ne on several surfaces. Using the Ne/Cs potential, our previous GCMC study found negligible adsorption of Ne over the entire range ($T < 43$ K) of that study, that 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 have increased the cell dimensions to $100\text{Å} \times 100\text{Å} \times 200\text{Å}$. Our previous DF study 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 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 $\sigma_{\text{lv}}(T)$ (for the details of the method used to compute the surface tensions $\sigma_{ij}$ ($i,j = s,l,v$), see Ref. 4). 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, as can be seen in Fig. 3. When using the modified CCZ potential, the wetting transition disappears, as can be seen from the curve (b) in Fig. 3 which no longer crosses $\sigma_{\text{lv}}(T)$, 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 $\cos(\Theta) \equiv \Delta \sigma/\sigma_{\text{lv}}$ can be immediately extracted from Fig. 3. 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.

Fig. 3 presents results for $\Delta \sigma(T)$ even for quite small hypothetical well depths. To simulate such ultraweak (UW) adsorbing surfaces, we use for simplicity a tunable 3-9 model potential.

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 of our functional. Lower panel: Liquid-vapor Ne surface tension $\sigma_{\text{lv}}$. The squares are experimental points, the triangles are our calculated values, and the dashed line is a fit to the experimental data which goes to zero as $1/T$ 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, $\sigma_{\text{lv}}$. 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 $D$, as described in the text.
\[ V_s(z) = \frac{4C^3}{27D^2z^3} - \frac{C_3}{z^3} \]

where \( C_3 \) is kept fixed to the Ne/Cs value, while the well depth \( D \) is arbitrarily varied. Fig. 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 \( (D \sim 0.5K) \), a conclusion that is consistent with a 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 performed extensive GCMC simulations and confirmed the absence of a drying transition. What is thus responsible for the apparent drying behavior for Ne/Cs reported by HSC? Fig. 3 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 \( \rho(\infty) \) far from the surface whereas when \( \mu > \mu_0 \) the liquid density is reached far from the surface. We note that these DF results are quite consistent with the GCMC data simulated with the same conditions. From the profiles shown in Fig. 3 one can compute the surface excess coverage per unit area

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

(here \( A \) is the surface area and the lower limit \( z_0 \) is taken at the zero energy turning point of the adsorption potential).

Results for \( \Delta n = \Delta N/A \) are shown in Fig. 4, 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 instead for Ne/Au, due to the compression of the liquid layers close to the surface induced by the strong adsorption interaction. The small excess below SVP is in accord with HSC data. The deficit coverage for Ne/Cs above \( \mu_0 \) is \( \Delta n \sim 2.2 \times 10^{-8} g/cm^2 \), corresponding to \( \sim 0.9 \) ML.

The expected shift in frequency in a quartz microbalance experiment \[12\] is \( \Delta f = (4f^2/nR)\Delta n \sim 4Hz \), i.e. at least one order of magnitude smaller than the deficit reported by HSC above SVP. We believe that this apparent "discrepancy" is misleading. The experiment measures missing mass by its effect on the resonant frequency shift of the shear wave of the microbalance. However, a contributing factor is that a fluid which interacts weakly with a surface exhibits significant slip, as reported by Thompson and Robins \[13\]. Hence the reported mass deficiency implicitly includes the reduction in mass dragged by the oscillator (as well as the reduced density of the neighboring fluid).

![FIG. 3. Ne/Cs interaction potentials. The solid line shows the original CCZ potential, the dashed line shows the modified CCZ potential described in the text.](image)

![FIG. 4. Equilibrium calculated density profiles for Ne/Au and Ne/Cs at \( T = 43K \), respectively, for different values of the chemical potential both below and above coexistence. \( z \) is the coordinate normal to the surface, measured from the surface plane position.](image)
$T_c$ is invariably observed in these simulations 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 Ref. [14,15] and references cited therein). However, despite the long-range character of the fluid-wall potential used in these simulations, the interaction is usually cut-off, for computational reasons, at a short distance ($r_c \sim (2-3) \sigma_{LJ}$), thus resulting in an effective finite range fluid-wall interaction. Inclusion of the full range of such interaction would result, as clearly shown by our results, in the absence of such drying transition for any $T < T_c$.

In summary, DF and GCMC calculations find a wetting transition for Ne/Cs if the 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 is suggested by molecular dynamics results of [13].

Finally, our results are consistent with a general prediction of Ebner and Saam that a drying transition is shifted to $T_c$ by the long-range gas-surface attraction. Our results (to be reported in detail elsewhere) should be tested by contact angle and ellipsometric measurements of film thickness for Ne/Cs.

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