

## Adsorption of Ar on planar surfaces studied with a density functional theory

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The adsorption of Ar on planar structureless substrates of alkali metals, alkaline-earth metal Mg, CO<sub>2</sub>, and Au was analyzed by applying a density functional formalism which includes a recently proposed effective attractive pair potential conditioned to Ar. It is shown that this approach reproduces the experimental surface tension of the liquid-vapor interface over the entire bulk coexistence curve for temperatures  $T$  spanning from the triple point  $T_t$  up to the critical point  $T_c$ . The wetting properties were studied over the entire range temperatures  $T_t \leftrightarrow T_c$ . It was found that Ar wets all the investigated surfaces. The adsorption isotherms for alkali metals exhibit first-order phase transitions. Prewetting lines were resolved even for the less attractive surfaces. In the cases of Mg, CO<sub>2</sub>, and Au a continuous growth for  $T \geq T_t$  was obtained. A comparison with experimental data and other microscopic calculations is reported.

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In a previous paper [1] (henceforth referred to as I), we analyzed the wetting properties of the physisorption of Ne on planar alkali surfaces. In that work, the phase behavior when a liquid phase ( $l$ ) is adsorbed on a solid substrate ( $s$ ) in the presence of a vapor atmosphere ( $v$ ) was studied. It is known that for moderate substrates [i.e., when the well depth of the substrate-fluid ( $s$ - $f$ ) interaction,  $\mathcal{W}_{sf}$ , is not much bigger than the strength of the fluid-fluid ( $f$ - $f$ ) attraction,  $\epsilon_{ff}$ ] there is a first-order wetting transition at the point [ $T_w, \mu_w = \mu_0(T_w)$ ] between  $T_t$  and  $T_c$ .  $T_w$  is characterized by the appearance of coexisting thin and very thick adsorbed fluid films, while for  $T < T_w$  the coverage of adsorbed films is finite (incomplete wetting). Under these conditions for  $T \geq T_w$  there is an associated prewetting line which extends away from ( $T_w, \mu_w$ ) into the region of pressures below the corresponding bulk saturation value  $P_0(T)$  and terminates at the surface critical point ( $T_{cpw}, \mu_{cpw}$ ). A prewetting transition is marked by a jump in coverage, often expressed in nominal layers  $\ell$  as  $\Gamma_\ell = (1/\rho_l^{2/3}) \int_0^\infty dz [\rho(z) - \rho_B]$ , where  $\rho(z)$  is the density at distance  $z$  perpendicular to the substrate,  $\rho_B = \rho(z = \infty)$  the asymptotic bulk density, and  $\rho_l$  the liquid density at saturation for a given temperature. The discontinuity in  $\Gamma_\ell$  vanishes at  $T_{cpw}$  (see, e.g., Fig. 4 in I), where the coexisting thin and thick films become identical. For  $T > T_{cpw}$  the adsorbed stable film grows continuously for increasing coverage. In the case of strong substrates the wetting may be observed at  $T_t$ .

First-order surface phase transitions have been extensively investigated experimentally for quantum and classical simple gases on alkali-metal substrates. The data for <sup>4</sup>He are summarized in Ref. [2], for H<sub>2</sub> are reported in [3,4], and for Ne in [5]. Prewetting transitions have been also measured in

the cases of binary mixture methanol-cyclohexane [6], and of Hg adsorbed on the walls of Mo and Nb cells [7]. On the other hand, triple-point wetting has been measured for inert classical gases, N<sub>2</sub>, O<sub>2</sub>, and CH<sub>4</sub>, adsorbed on the strongly attractive surface of Au [8] and for the systems Ar/CO<sub>2</sub> [9] and Xe/NaF [10].

The aim of the present Brief Report is to account for our investigation about the adsorption of Ar on planar surfaces of alkali metals, Mg, CO<sub>2</sub>, and Au. Table I indicates that in the case of this series of substrates the ratio  $\mathcal{W}_{sAr}/\epsilon_{ArAr}$  increases from about 1 to 8. A variety of theoretical approaches have been applied to study the wetting properties of such systems. There are estimations based on a so-called simple model (SM) [11,12] as well as microscopic calculations performed by using density functional (DF) theories [9,13] and grand canonical Monte Carlo (GCMC) simulations [14]; all the obtained information are also provided in Table I. The overall agreement between the results yielded by these different calculations is not satisfactory. According to the SM [12] Ar would wet all the alkali surfaces. The DF calculations of Ref. [13] suggest wetting in the cases of Li and Na, however, nothing was said on what is going on for heavier substrates; while GCMC simulations [14] indicate wetting for Li and nonwetting for Na and Rb. Concerning the Ar/CO<sub>2</sub> system the authors of Ref. [9] claim that the continuous growth of the film exhibited by their own experimental data for  $T > T_t$  can be well described in the framework of their DF calculations. However, the adsorption isotherm reported in Fig. 4 of Ref. [9] for  $T = 85$  K (close to  $T_t = 83.78$  K) presents drawbacks, in particular, an unexpected noticeable crossing at  $\Gamma_\ell \approx 3$  with the isotherm corresponding to  $T = 105$  K.

In a DF theory the Helmholtz free energy  $F_{DF}$  of a fluid embedded in a potential  $U_{sf}(\mathbf{r})$  is expressed as a functional of the local density  $\rho(\mathbf{r})$  (see, e.g., Ref. [15]):

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TABLE I. Wetting properties of Ar adsorbed on alkali metals, Mg, CO<sub>2</sub>, and Au substrates. The ratio  $\mathcal{W}_{\text{sAr}}/\varepsilon_{\text{ArAr}}$ , the wetting  $T_w$ , and the prewetting critical temperatures  $T_{cpw}$  are listed. NW stands for nonwetting, C indicates continuous growth at  $T \geq T_t$ , and PW denotes present work.

Wall	$\mathcal{W}_{\text{sAr}}/\varepsilon_{\text{ArAr}}$	Expt. [8,9]	$T_w$ (K)			$a_{pw}/k_B$ (K <sup>-1/2</sup> )		$T_{cpw}$ (K) <sup>a</sup>		
			SM [12]	GCMC [14]	DF [9,13]	DF (PW)	DF (PW)	GCMC [14]	DF [13]	DF (PW)
Cs	1.1		125							
Rb	1.1		125	NW		138.7	-0.14			142
K	1.2		124			137.7	-0.14			141
Na	1.6		117	NW	136	124.8	-0.14		140	131
Li	2.1		107	130 ± 4	123	110.0	-0.16		130	119
Mg	3.5		85	90		C		95		C
CO <sub>2</sub>	3.8	C			C	C				C
Au	8.2	C				C				C

<sup>a</sup>These values are upper limits for the critical prewetting temperatures.

$$\begin{aligned}
 F_{DF}[\rho(\mathbf{r})] = & \nu_{id} k_B T \int d\mathbf{r} \rho(\mathbf{r}) \{ \ln[\Lambda^3 \rho(\mathbf{r})] - 1 \} \\
 & + \int d\mathbf{r} \rho(\mathbf{r}) f_{\text{HS}}[\bar{\rho}(\mathbf{r}); d_{\text{HS}}] \\
 & + \frac{1}{2} \int \int d\mathbf{r} d\mathbf{r}' \rho(\mathbf{r}) \rho(\mathbf{r}') \Phi_{\text{attr}}(|\mathbf{r} - \mathbf{r}'|) \\
 & + \int d\mathbf{r} \rho(\mathbf{r}) U_{sf}(\mathbf{r}). \quad (1)
 \end{aligned}$$

The first term is the ideal gas free energy, where  $k_B$  is the Boltzmann constant,  $\Lambda$  is the thermal de Broglie wavelength, and  $\nu_{id}$  is a free parameter introduced in Eq. (2) of [16] (near  $T_t$  it is equal to unity as in the standard theory, but close to  $T_c$  amounts 0.9 accounting for residual interactions at this critical point). The second term accounts for the repulsive  $f$ - $f$  interaction approximated by a hard-sphere (HS) functional; we utilized the  $f_{\text{HS}}[\bar{\rho}(\mathbf{r}); d_{\text{HS}}]$  developed by Kierlik and Rosinberg (KR) [17], where  $\bar{\rho}(\mathbf{r})$  is a properly averaged density and  $d_{\text{HS}}$  is the HS diameter. The third term embodies the attractive  $f$ - $f$  interactions treated in a mean-field approximation (MFA). Finally, the last integral in Eq. (1) represents the effect of the external potential  $U_{sf}(\mathbf{r})$  exerted on the fluid. For  $\Phi_{\text{attr}}(r)$  we utilized an expression proposed in I on the basis of the separation of the Lennard-Jones (LJ) potential introduced by Weeks, Chandler, and Andersen (WCA) [18],

$$\Phi_{\text{attr}}^{\text{WCA}}(r) = \begin{cases} -\tilde{\varepsilon}_{ff}, & r \leq r_m \\ 4\tilde{\varepsilon}_{ff} \left[ \left( \frac{\tilde{\sigma}_{ff}}{r} \right)^{12} - \left( \frac{\tilde{\sigma}_{ff}}{r} \right)^6 \right], & r > r_m, \end{cases} \quad (2)$$

where  $r_m = 2^{1/6} \tilde{\sigma}_{ff}$  is the position of the LJ minimum. No cutoff for the pair potential was introduced. The well depth  $\tilde{\varepsilon}_{ff}$  and the interaction size  $\tilde{\sigma}_{ff}$  are considered as free parameters because the use of bare values  $\varepsilon_{\text{ArAr}}/k_B = 119.76$  K and  $\sigma_{\text{ArAr}} = 3.405$  Å overestimates the experimental result  $T_c = 150.86$  K.

The complete DF approach described above has three adjustable parameters (namely,  $\nu_{id}$ ,  $\tilde{\varepsilon}_{ff}$ , and  $\tilde{\sigma}_{ff}$ ), which were determined by imposing that at  $l$ - $v$  coexistence the pressure as well as the chemical potential of the bulk  $l$  and  $v$  phases should be equal [i.e.,  $P(\rho_l) = P(\rho_v)$  and  $\mu(\rho_l) = \mu(\rho_v)$ ]. The procedure is described in I. In summary, we set  $d_{\text{HS}} = \tilde{\sigma}_{ff}$  and imposed at each temperature  $T$  that the coexistence data of  $\rho_l$ ,  $\rho_v$ , and  $P(\rho_l) = P(\rho_v) = P_0$  for Ar quoted in Table X of Ref. [19] be reproduced. The fit is displayed in Fig. 1(a).

After establishing the MFA, we examined the prediction for the surface tension of the liquid-vapor interface,  $\gamma_{lv}$ , by solving DF equations for free slabs of Ar in a box of size  $L = 60\sigma_{ff}$  and, subsequently, computing the thermodynamic relation  $\gamma_{lv} = (\Omega/A + P_0 L)/2$ . Here  $\Omega = F - \mu N$  is the grand potential of the system and  $A$  is the area of the interface. Figure 1(b) shows the experimental data of  $\gamma_{lv}$  [20], the prediction of the fluctuation theory of critical phenomena evalu-

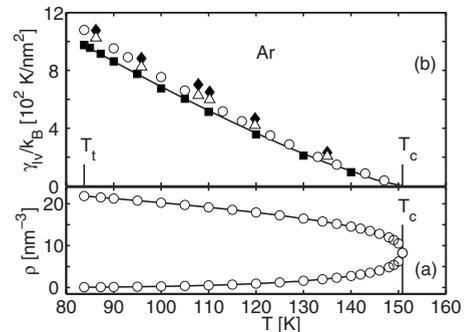


FIG. 1. (a) Phase diagram of bulk Ar. Circles denote selected points of the experimental coexistence curve taken from Table X of Ref. [19]. The solid line is the three-parameter fit. (b) Surface tension of Ar as a function of temperature. Squares are experimental data taken from Table II of Ref. [20] and the solid curve corresponds to the fluctuation theory of critical phenomena. Circles are present DF results; triangles and diamonds are MD values from Ref. [21] calculated with the cutoffs  $r_c = 4.4\sigma_{ff}$  and  $r_c = 5.5\sigma_{ff}$ , respectively.

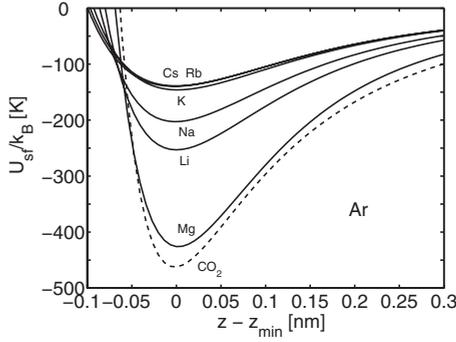


FIG. 2. Comparison of adsorption potentials for Ar; the curves are centered at  $z=z_{\min}$  corresponding to its minimum. Solid curves are CCZ potentials for alkali substrates [12], while the dashed curve is the Ar-CO<sub>2</sub> interaction [22].

ated as in I [ $\gamma_{lv} = \gamma_{lv}^0(1 - T/T_c)^{1.26}$  with  $\gamma_{lv}^0 = 17.4 \text{ K}/\text{\AA}^2$ ], the present DF results, and values from canonical molecular-dynamics (MD) simulations (from Table IV of [21]) for two choices of the cutoff radius,  $r_c$ , of the LJ potential. Our DF results agree satisfactorily well with experimental data over the entire range of temperatures  $T_l \leq T \leq T_c$  and with displayed MD values.

For the analysis of physisorption on alkaline substrates we adopted in all the cases the *ab initio* potentials of Chishemsha, Cole, and Zaremba (CCZ) [12] with the parameters listed in Table I therein. These potentials are displayed in Fig. 2. Let us mention that the SM suggests wetting of all these alkaline surfaces [12]. However, since such a model is only a crude approximation to the free energy balance [1], its predictions should be tested with microscopic calculations. Since the  $U_{sf}(z)$  for the Ar/Cs and Ar/Rb systems are almost equal, we shall not present results for the former one. The adsorption on CO<sub>2</sub> was studied by using the same *s-f* interaction adopted by Mistura *et al.* [9], which was taken from Marshall *et al.* [22] and included in Fig. 2. On the other hand, it was assumed that Ar atoms interact with a wall of Au via a 9-3 potential  $U_{sf}(z) = (4C_3^3/27W_{sf}^2)/z^9 - C_3/z^3$  with the parameters  $W_{AuAr} = 987 \text{ K}$  and  $C_3 = 2.05 \times 10^4 \text{ K \AA}^3$  taken from Tables I and II of [11].

The adsorption isotherms for Ar/Rb displayed in Fig. 3 indicate a wetting transition slightly below  $T = 139 \text{ K}$  and an

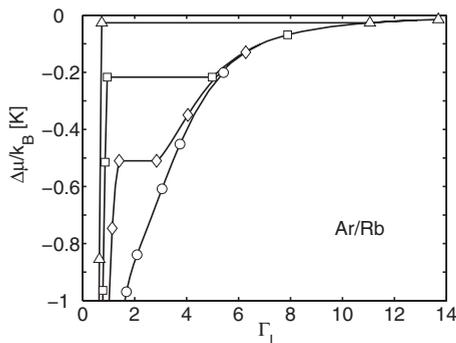


FIG. 3. Adsorption isotherms for the Ar/Rb system.  $\Delta\mu$  is measured from the saturation value at liquid-vapor coexistence for Ar.  $T = 142 \text{ K}$  (circles),  $141 \text{ K}$  (diamonds),  $140 \text{ K}$  (squares), and  $139 \text{ K}$  (triangles).

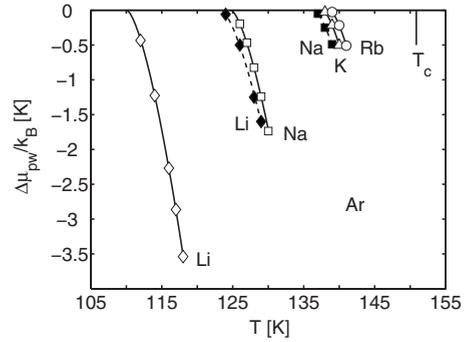


FIG. 4. Prewetting lines for Ar adsorbed on Rb, K, Na, and Li. The open symbols stand for present DF results and full symbols are data from Ref. [13]. The lines are fits to Eq. (3) which reach the  $\Delta\mu_{pw}/k_B = 0$  line at the corresponding  $T_w$  listed in Table I.

upper limit for critical prewetting point at about  $T_{cpw} \approx 142 \text{ K}$ . The dependence of  $\Delta\mu_{pw}(T)$  on temperature is

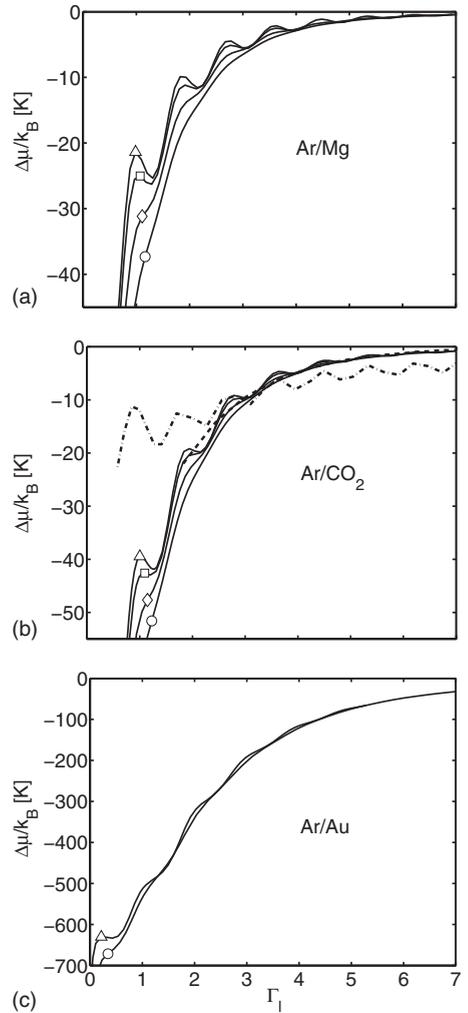


FIG. 5. [(a) and (b)] Adsorption isotherms for Ar/Mg and Ar/CO<sub>2</sub>.  $T = 105 \text{ K}$  (circles),  $95 \text{ K}$  (diamonds),  $87.78 \text{ K}$  (squares), and  $83.78 \text{ K}$  (triangles). (c) Same for Ar/Au, but only the results for  $T = 105$  and  $83.78 \text{ K}$  are displayed. In addition, in (b) the isotherms for  $T = 105 \text{ K}$  (dashed line) and  $85 \text{ K}$  (dash-dotted line) from Ref. [13] are displayed.

shown in Fig. 4. A form for determining  $T_w$  was derived from thermodynamic arguments [3]

$$\Delta\mu_{pw}(T) = \mu_{pw}(T) - \mu_0(T) = a_{pw}(T - T_w)^{3/2}. \quad (3)$$

Here  $a_{pw}$  is a model parameter. A fit of data to this expression yielded the values of  $T_w$  and  $a_{pw}$  quoted in Table I. There is no other DF calculation for this system reported in the literature, while contrary to our finding the GCMC simulations carried out by Curtarolo *et al.* [14] with a cutoff radius  $r_c = 5\sigma_{ff}$  indicate nonwetting.

The prewetting lines for Ar/K, Ar/Na, and Ar/Li are also displayed in Fig. 4 together with data from [13]. The fits to Eq. (3) yielded the values of  $T_w$  and  $a_{pw}$  listed in Table I. These results indicate that Ar would wet all these three surfaces. The DF study of Ref. [13] has also suggested wetting of Na and Li. The quantitative differences between our results and that of [13] are discussed below. On the other hand, there is a qualitative difference with GCMC simulations [14], which indicate wetting of Li but nonwetting of Na.

Some representative adsorption isotherms calculated for Ar/Mg, Ar/CO<sub>2</sub>, and Ar/Au are displayed in Fig. 5. No prewetting transitions are exhibited by these data because the substrates are significantly more attractive than the alkali metals. In all these cases a continuous (layer-by-layer) film growth above  $T_t$  may be observed in agreement with experimental data for CO<sub>2</sub> [9] and Au [8]. The similarity of the results for Mg and CO<sub>2</sub> is due to the fact that the difference between the corresponding adsorption potentials is small (see Fig. 2). The GCMC of [14] predicts for Ar/Mg wetting at  $T_w = 90$  K. In Fig. 5(b) for Ar/CO<sub>2</sub> we included the isotherms for  $T = 105$  and 85 K reported in Fig. 4 of Ref. [9]. The isotherm at  $T = 105$  K from [9] lies in the bundle of

present results, while that for  $T = 85$  K shows an unexpected crossing. On the contrary, our isotherms at  $T_t$  and  $T_{nb} = 87.78$  K (normal boiling temperature) show a regular behavior.

For Au, the strongest substrate, besides the condensation of successive Ar layers one may observe the formation of a submonolayer structure indicated by the triangle in Fig. 5(c). This behavior is similar to that displayed in Fig. 1.1 of Ref. [23] for Kr adsorbed on graphite.

The quantitative differences between our results and that from DF of Refs. [9,13] displayed in Figs. 4 and 5(b) and Table I can be attributed to the use of different MFA's as found in I for Ne. The effective attractive  $f$ - $f$  interaction adopted in [9,13] leads to a too early freezing above  $T_t$  and, accordingly, produces a shift of properties toward  $T_c$ . It is much harder to explain the qualitative difference between DF and GCMC calculations for Rb and Na because usually the GCMC results are taken as reference values. In this context, it becomes important to notice the failure of these GCMC simulations in reproducing the measured wetting of Rb by Ne [5]; see Table I in [14] and discussion in I.

In summary, we report DF calculations of  $\gamma_w$  for Ar by using the MFA introduced in I, which yield satisfactory values over the entire temperature range from  $T_t$  to  $T_c$ . Subsequently, we account for a detailed study of Ar adsorbed on planar surfaces with a variety of strengths. We are planning to search in the near future for the asymmetric solutions for density profiles in slits discussed in Ref. [24], but in realistic scenarios.

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