

## Adsorbate densities and surface potentials of physisorbed systems: A density-functional approach

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A density-functional approach for the calculation of the density of particles adsorbed on the surface of a solid is explored including the adparticle two-body interaction. The coverages and effective surface potentials so obtained compare very well with those of previous Hartree-Fock calculations for the system Ar/Ag.

### I. INTRODUCTION

A gas is said to physisorb onto the surface of a solid if the net interaction between a gas particle and the solid is accounted for by an effective surface potential,  $V_s(\mathbf{r})$ , the long-range part of which is essentially the interaction energy between the mutually induced fluctuating dipole moments in the adparticle and in the solid. The strong short-range repulsion is largely due to increasing charge fluctuations as the adsorbing particle gets confined close to the surface. At very low coverages  $\Theta$ , one may neglect interactions between the adparticles. However, as their average separation in the adsorbate approaches that of a liquid, this interaction plays a crucial role in determining the properties of the adsorbate. Two-dimensional lattice-gas models have been conceived in which this interaction is incorporated via hopping matrix elements between sites. To treat the dynamics of adsorption and desorption appropriately a fully three-dimensional theory was developed within the temperature-dependent Hartree-Fock approximation.<sup>1</sup> It yields such single-particle information as coverage-dependent bound-state energies and wave functions from which the adparticle density can be constructed as well as an effective, coverage-dependent surface potential

$$V_s(\mathbf{r}, \Theta) = V_s(\mathbf{r}) + V_{MF}(\mathbf{r}, \Theta). \quad (1)$$

Here  $V_s(\mathbf{r})$  is the bare surface potential between a single particle and the substrate and  $V_{MF}(\mathbf{r}, \Theta)$  is the mean-field potential experienced by one gas particle in the presence of all others. The theory was successfully applied to a study of the thermodynamics and the desorption kinetics of mobile helium adsorbates up to about two monolayers.

For adsorbates heavier than helium much of the information obtained in the Hartree-Fock approximation is redundant. It is the purpose of this paper to show that considerable simplification can be achieved, with little sacrifice of accuracy, by employing a density-functional approach<sup>2</sup> to the calculation of the adparticle density  $n(\mathbf{r})$  and the effective surface potential  $V_s(\mathbf{r}, \Theta)$ . Specifically, we use the statistical Thomas-Fermi model and its extension to include some nonlocal density corrections,<sup>3,4</sup> the formalism of which is outlined in the next section. To allow a comparison with the Hartree-Fock results we shall

assume an effective two-body potential identical to that derived by SSTK;<sup>1</sup> also, our formalism will be applicable to a mobile adsorbate only, at this stage. Results are presented for the relatively heavy adsorbate system, Ar on Ag. This will facilitate the calculation of  $n(\mathbf{r})$  in density-functional theory, as the semiclassical limit and subsequent simplifications enter into the calculation. The method is not confined to this limit, however. This is in contrast to recent work also employing the density-functional method,<sup>5,6</sup> there the adsorbate interaction is treated by way of a classical fluid analysis. Moreover, the fluid is assumed two dimensional (submonolayer coverage). It is already known that the three-dimensional character of the potential, (1), has important consequences for physisorption kinetics.<sup>7</sup>

### II. FORMALISM

We first outline the application of the density-functional formalism to an inhomogeneous system of neutral interacting fermions at finite temperature and introduce a number of justifiable simplifications, given the hindsight of the quantum-mechanical calculations of SSTK.

Consider the grand-canonical potential, which is a functional of the particle density  $n(\mathbf{r})$ ,<sup>2-4</sup>

$$\begin{aligned} \Omega[n] = & \int V_s(\mathbf{r}) n(\mathbf{r}) d\mathbf{r} \\ & + \frac{1}{2} \int \int d\mathbf{r} d\mathbf{r}' V_2(|\mathbf{r}-\mathbf{r}'|) n(\mathbf{r}) n(\mathbf{r}') \\ & + F_k[n] + F_{xc}[n] - \mu \int d\mathbf{r} n(\mathbf{r}). \end{aligned} \quad (2)$$

The contributions here are from, respectively, the (substrate) surface potential, the two-body Hartree interaction, the (kinetic) free-energy functional of noninteracting particles  $F_k[n]$ , the exchange and correlation functional  $F_{xc}[n]$ , and the chemical potential per particle,  $\mu$ . All contributions are implicitly temperature dependent. The density of the system at equilibrium is that which minimizes  $\Omega[n]$ , namely the solution of  $\delta\Omega[n]/\delta n(\mathbf{r})=0$ . The form of  $V_s(\mathbf{r})$  is prescribed. Also, far from the substrate, the fermionic gas phase is assumed large and dilute, and will determine  $\mu$ . However, some approximations to  $F_k$  and  $F_{xc}$  are required. One can include the nonlocal effects of density inhomogeneities in the kinetic

energy functional rather simply by an expansion in powers of the density gradient

$$F_k[n] = \int d\mathbf{r} [f_0(n(\mathbf{r})) + f_2(n(\mathbf{r})) |\nabla n|^2 + \dots]. \quad (3)$$

The coefficients  $f_0$  and  $f_2$ , functions of the local density, are known,<sup>3</sup> and while the coefficients of  $O((\nabla n)^4)$  terms at finite temperature are now available,<sup>4</sup> it will be sufficient, and practical, for our purposes to truncate the expansion at second order.

For our approximation of the two-body interaction terms in (2) we necessarily follow SSTK in order to allow a comparison between their method and ours. In particular, they considered the mean-field part of (2) (Hartree plus exchange) and introduced an effective potential  $V_{\text{eff}}(\mathbf{r})$  to replace  $V_2(\mathbf{r})$ .<sup>1</sup> Their reasons for this were two-fold: firstly, the short-range singularity of  $V_2(\mathbf{r})$  (as in, for example, a Lennard-Jones potential) leads to an infinite energy contribution, implying that the core of the potential must be softened; secondly, typical particle densities directly over the substrate can approach liquid densities, implying that two-body correlations must be accounted for. By extending the Hartree-Fock theory to Brueckner-Hartree-Fock (BHF) theory, involving the construction of a nonlocal  $K$  matrix,  $\langle \mathbf{r} | K | \mathbf{r}' \rangle$ , which partially includes correlations, both requirements are met. Further, by approximating the matrix by a local effective interaction,  $\langle \mathbf{r} | K | \mathbf{r}' \rangle = V_{\text{eff}}(\mathbf{r})\delta(\mathbf{r}-\mathbf{r}')$ , a manageable analytic form results. (The reader is referred to Ref. 1 for details.)

Thus, with the assumption that the exchange functional in (2) can be represented by the Fock contribution of mean-field theory, and the subsequent replacement of  $V_2(\mathbf{r})$  by  $V_{\text{eff}}(\mathbf{r})$ , the hard-core correlation contribution to  $F_{xc}$  is partly accounted for, in a first approximation, and we let  $F_{xc} \rightarrow F_x$ . One then hopes that the corresponding Euler equation gives an accurate representation of the particle density as calculated from the standard Hartree-Fock equations, with an interaction potential  $V_{\text{eff}}(\mathbf{r})$  [see Eq. (15) of SSTK].

Concerning the particle statistics: the above formalism should also be applicable to a boson system, provided the exchange term can be neglected. For heavy adsorbates and typical temperature and densities, the statistics are essentially Maxwell-Boltzmann and we may set  $F_x = 0$  with safety. This conjecture is borne out both by the results below and the calculations of SSTK for Ar/Ag. Calculated quantities are independent, to within a few percent, of the choice of statistics for Ar. (We shall continue our development assuming a fermion system, however.) Thus all quantum effects are removed from our calculation.

Gathering these approximations to (2), one derives the following Euler equation, which serves as the basis for our calculations:

$$\begin{aligned} V_s(\mathbf{r}) - \mu + \int d\mathbf{r}' n(\mathbf{r}') V_{\text{eff}}(\mathbf{r} - \mathbf{r}') \\ + \frac{\partial f_0}{\partial n(\mathbf{r})} - |\nabla n|^2 \frac{\partial f_2}{\partial n(\mathbf{r})} - 2f_2 \nabla^2 n = 0. \end{aligned} \quad (4)$$

The nonlocal corrections enter via the kinetic energy functional only. Finally, and in keeping with the work of

SSTK, we shall restrict our attention to mobile (fluid) adsorbates, in which case  $V_s(\mathbf{r}) \rightarrow V_s(z)$ , where  $z$  is the height above the substrate surface, and the problem becomes one-dimensional: the effective Hartree term in (4) is replaced by

$$\sigma^2 \int dz' n(z') \tilde{V}(z - z'),$$

where

$$\tilde{V}(z) = \sigma^{-2} \int dx dy V_{\text{eff}}(x, y, z), \quad (5)$$

and  $\sigma$  is the range of the interaction. SSTK have given a suitable parametrization of the screening of the short-range correlations which ensure  $V_{\text{eff}}(\mathbf{r}=0)$  and hence  $\tilde{V}(z=0)$  is finite, based upon the Lennard-Jones potential for  $V_2(r)$ ,

$$\begin{aligned} \tilde{V}(z) = 2\pi\epsilon & \left[ 1 + A \left( \frac{\sigma}{z} \right)^{10} \exp \left[ - \left( \frac{z}{z_1} \right)^\alpha \right] \right]^{-1} \\ & \times \left[ \frac{2}{5} \left( \frac{\sigma}{z} \right)^{10} - \left( \frac{\sigma}{z} \right)^4 \right]. \end{aligned} \quad (6)$$

The parameters  $z_1$  and  $\alpha$  in the screening factor are chosen such that the attractive well of the remaining unscreened potential is unaffected;  $A$ , which determines  $\tilde{V}(0)$ , becomes the adjustable parameter and may be fixed by fitting thermodynamic quantities to experimental data.<sup>8</sup> For our prototypical heavy adsorbate, Ar, we take  $\epsilon/k_B = 119.8$  K,  $\sigma = 3.42$  Å,  $z_1 = 2.85$  Å,  $\alpha = 15$ , and  $A = 0.133$ .

For the surface potential,  $V_s(z)$ , corresponding to the inert-gas–metal interaction, a Morse potential is adequate:

$$V_s(z) = U_0(e^{-2\gamma(z-z_0)} - 2e^{-\gamma(z-z_0)}). \quad (7)$$

We take  $U_0/k_B = 430$  K and  $z_0 = \gamma^{-1} = 0.594$  Å. A plot of these two potentials is shown in Fig. 1. The range of the Ar-Ar interaction is much larger than that of Ar-Ag; furthermore, the former is strongly repulsive and essentially constant over variations  $\sim \gamma^{-1}$  about the minimum of  $V_s(z)$ . One expects a significant shallowing of the bare surface potential and the formation of a repulsive barrier as the density of adatoms over the Ag surface increases.

### III. LOCAL-DENSITY APPROXIMATION

We first examine the solution of (4) in the simplest case of retaining the purely local-density terms. This local-density approximation (LDA), which is equivalent to the statistical Thomas-Fermi model, permits an investigation of the major effects of the two-body interaction in producing an effective surface potential. The latter then serves as a useful starting point for the solution when the gradient corrections are included [extended Thomas-Fermi model (ETF)].

The one-dimensional form of (4) in the LDA is

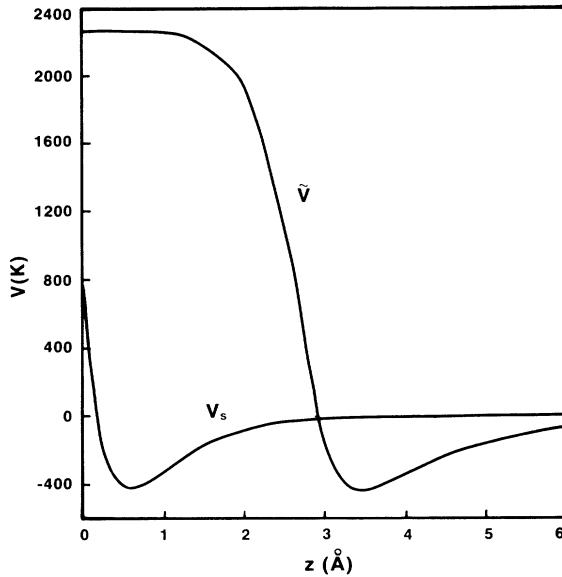


FIG. 1. Effective Ar-Ar potential  $\tilde{V}(z)$ , calculated from (6) with  $\epsilon/k_B = 119.9$  K,  $\sigma = 3.42$  Å,  $z_1 = 2.85$  Å,  $\alpha = 15$ , and  $A = 0.133$  [such that  $\tilde{V}(0) = -5\tilde{V}_{\min}$ ]; Ar-Ag surface potential (7) with  $U_0/k_B = 430$  K,  $z_0 = \gamma^{-1} = 0.594$  Å.

$$V_s(z) - \mu + \sigma^2 \int_0^\infty dz' n(z') \tilde{V}(z-z') + \frac{\partial f_0}{\partial n(z)} = 0. \quad (8)$$

$f_0$  and  $n$  are given by the expressions for a free uniform gas evaluated at the local density,

$$f_0 = (4/\sqrt{\pi}) \lambda^{-3} \beta^{-1} [-\frac{2}{3} I_{3/2}(\eta) + \eta I_{1/2}(\eta)], \quad (9a)$$

$$n = (4/\sqrt{\pi}) \lambda^{-3} I_{1/2}(\eta), \quad (9b)$$

where  $\eta = \eta(z)$ ,  $I_n(\eta)$  is the standard Fermi integral, and  $\lambda = (2\pi\hbar^2\beta/m)^{1/2}$  is the thermal de Broglie wavelength. One derives

$$\eta(z) = \beta \left[ \frac{\partial f_0}{\partial n} \right]. \quad (10)$$

This result, together with (9b), transforms (8) into an integral equation to be solved for a self-consistent  $n(z)$ . In principle, the solution could be found for any temperature, as  $I_{1/2}(\eta)$  has been given approximate analytic forms for the whole range of  $\eta$ .<sup>9</sup> However, we are interested in the semiclassical limit ( $\eta \rightarrow -\infty$ ) for which

$$I_{1/2}(\eta) = \frac{\sqrt{\pi}}{2} e^\eta \left[ 1 - \frac{e^\eta}{2^{3/2}} + \frac{e^{2\eta}}{3^{3/2}} - \dots \right]. \quad (11)$$

Indeed, for liquid Ar densities and temperatures  $\sim 20$  K, (9b) predicts  $\eta \lesssim -6$ , and we need only retain the leading term in (11). Our self-consistent results confirm this. In this case a convenient parametrization of the density is

$$n(z) = n_0 e^{f(z)} = 2\lambda^{-3} e^{\beta\mu} e^{f(z)}. \quad (12)$$

Equation (9b), (11), and (12) imply  $\eta(z) = \beta\mu + f(z)$ , and (8) becomes a nonlinear equation for  $f(z)$ :

$$f(z) = -\beta V_s(z) - \sigma^2 n_0 \int_0^\infty dz' e^{f(z')} \beta \tilde{V}(z-z'). \quad (13)$$

Far from the substrate surface,  $V_s \rightarrow 0$ , the gas is very dilute, approximating an ideal gas (the two-body term is negligible)  $f(z) \rightarrow 0$ , and  $n(z) \rightarrow n_0 = \beta P$ , where  $P$  is the pressure at the container wall.  $\mu$  is determined via (12). We define the coverage  $\Theta$  over the substrate as the ratio  $N/N_s$  where  $N$  is the excess areal density of particles,

$$N = n_0 \int_0^\infty (e^{f(z)} - 1) dz, \quad (14)$$

and  $N_s$  is the areal density of available sites. Clearly, the region of the minimum of the effective surface potential,  $V_s(z, \Theta) = -\beta^{-1} f(z)$ , is of primary importance in determining  $\Theta$ .

The numerical solution of (13) is straightforward. For low densities,  $n_0$ ,  $f(z) = -\beta V_s(z)$  suffices to initialize the integrand of (13). One then exploits the relative constancy of  $\beta \tilde{V}(z-z')$  for  $z \sim z' \sim z_0$  and the sharpness of the integrand to accurately estimate  $f(z)$  at higher densities. Equation (13) is transformed into a system of nonlinear equations upon choosing some adaptive mesh  $\{z_i\}$ , and the above estimate used as a starter. We employed the routine C05PCF to solve this system.<sup>10</sup>

The results of such calculations are shown in Fig. 2 where  $V_s(z, \Theta)$  is plotted for  $P = 10^{-2}$  Torr, and three temperatures. The effects of the increasing admixture of the two-body interaction as the temperature decreases, as implied by (13), are obvious: the primary minimum shallows, while a secondary minimum develops near  $\sigma$ , corresponding to that of the Lennard-Jones potential. The depth and shape of these primary wells is in very good agreement with results obtained by SSTK. We list the corresponding coverages in Table I (we set  $N_s = 0.074$  Å<sup>-2</sup>). The coverages obtained when the Ar-Ar interaction is ignored [ $f(z) \rightarrow -\beta V_s(z)$ ] are much larger, and clearly unphysical at these densities. [For example, at  $T = 25$  K,  $\Theta(V_2 = 0) = 0.81$ , with a rapid increase as  $T$  is lowered.]

#### IV. EXTENDED THOMAS-FERMI MODEL

We now modify (13) by the inclusion of the density-gradient terms present in (4). The function  $f_2(n)$  has been determined from the polarizability function of a noninteracting fermion gas at long wavelengths.<sup>3</sup> The result is<sup>11</sup>

$$f_2(n) = -\frac{1}{96\sqrt{\pi}} \frac{\lambda^5}{\beta} \frac{d}{d\eta} \left[ \frac{1}{I_{-1/2}(\eta)} \right].$$

TABLE I. Comparison of coverages obtained via two schemes within density-functional theory (local-density and extended Thomas-Fermi approximations), and the Brueckner-Hartree-Fock method of Ref. 1; free gas density  $n_0 = \beta P$ ,  $P = 10^{-2}$  Torr.

$T$ (K)	$\Theta_{\text{LDA}}$	$\Theta_{\text{ETF}}$	$\Theta_{\text{BHF}}$	$n_0$ ( $10^{16}$ cm <sup>-3</sup> )
25	0.064	0.062	0.057	0.386
20	0.128	0.124	0.119	0.483
15	0.201	0.195	0.190	0.644

Upon specializing (4) to the one-dimensional case, taking the semiclassical limit for  $f_2$  and  $(\partial f_2 / \partial n)$  and retaining leading terms, and using the parametric form (12), we eventually arrive at the following nonlinear integro-differential equation:

$$2f''(z) + [f'(z)]^2 - C \left[ f(z) + \beta V_s(z) + \sigma^2 n_0 \int_0^\infty dz' e^{f(z')} \beta \tilde{V}(z-z') \right] = 0, \quad (15)$$

with  $f' \equiv df/dz$ ,  $C \equiv 48\pi/\lambda^2$ . The effective surface potential is now defined by

$$V_s(z, \Theta) = V_s(z) + \sigma^2 n_0 \int_0^\infty dz' e^{g(z')} \beta \tilde{V}(z-z'), \quad (16)$$

where  $g$  is the self-consistent solution of (15).

It is instructive to examine the form the solution must take in the case of very low coverages for which we may set  $\tilde{V}(z)=0$ . Equation (15) then implies that, in the vicinity of its maximum,  $f(z)$  is reduced in magnitude and shifted from the maximum of the LDA solution,  $f(z) = -\beta V_s(z)$ . The exact amount depends upon the scale factor  $C \sim \lambda^{-2} \sim mT$  and will be least for heavy adsorbates at high temperatures. For Ar at 20 K, this reduction is found to be 22% of the LDA value, which is not an insignificant reduction in spite of the nearly classical nature of the system. Incidentally, the particle density obtained by solving Schrödinger's equation directly for the bound-state eigenfunctions in the Morse potential is in close agreement with that obtained from this corrected  $f(z)$ ; the coverage in the former case is reduced by 26% from the LDA result. Such good agreement justifies, in part, both the inclusion of the gradient corrections to  $F_k[n]$  and their truncation at second order [cf. (3)]. In the case where the two-body term is not negligible, we do not expect so large a reduction in  $n(z)$ , given the manner in which a change in  $f(z-z_0)$  drives a change in the effective potential in (15).

The solution of (15) is more difficult than may be apparent, even in the case where  $\tilde{V}(z)=0$ . Equation (15) is strictly an initial-value problem with  $f$  and  $f'$  specified at the right-hand boundary, well away from the substrate, where  $V_s(z)$  is slowly varying. However, initial-value codes based on a variety of standard methods fail to give a solution. This leaves two-point boundary-value codes. Although the position of the left-hand boundary is arbitrary, to the extent that we require  $V_s(z)$  to be large and repulsive here,  $z=0$  is a suitable choice. However,  $f(0)$  and  $f'(0)$  are not known *a priori*. Our procedure in the case of  $\tilde{V}(z)=0$  has been to assume the limiting form  $f(z) \sim -e^{-\gamma z}$  for  $z < 0$  and use (15) and (7) to estimate  $f'(z < 0)$ ; this and  $f'(z > z_0)$  become the boundary values. Once the solution, and  $f(0)$  in particular, ceases to alter as the left-hand boundary is moved to more negative  $z$  values, we deem this solution to be the required one. We have used the code COLSYS (Ref. 12) for our calculations and find it to be extremely robust under these conditions. At fixed temperature we may safely apply the same boundary conditions to the case of  $\tilde{V}(z) \neq 0$ . The routine is necessarily initialized with the LDA solution now, otherwise the integral in (15) changes so dramatically as to prohibit convergence with iteration upon the previous

solution. We have averaged the solutions at every second iterate using

$$f_m(z) = \rho f_m(z) + (1-\rho) f_{m-1}(z), \quad m \text{ even}.$$

With a suitably chosen  $\rho$ , convergence to the self-consistent  $f$  is achieved.

The coverages obtained by this method are listed in Table I. As expected, there is a reduction in  $n(z)$ , and hence  $\Theta$ , on the LDA results, but significantly less than in the case of very low coverages. We have not plotted the effective potential, (16), for comparison at each temperature—the differences between the LDA and ETF solutions are barely resolved on a reasonable scale. We note, however, that as a result of  $f(z)$ , and thus  $n(z)$ , decreasing upon inclusion of the gradient terms, the primary well of  $V_s(z, \Theta)$  actually deepens over the LDA results; moreover,  $n(z)$  peaks at  $z = z_0 + \delta$ , with  $\delta \approx 0.012 \text{ \AA}$  here. Thus the standard semiclassical result  $n(z) = n_0 \exp[-\beta V_s(z, \Theta)]$  is not strictly valid.

What is gratifying concerning Table I is the remarkable agreement between the coverages obtained via the solution of the Hartree-Fock equations and the density-functional approach—the differences amount to a few percent. Indeed, one might anticipate that  $\Theta_{\text{ETF}} > \Theta_{\text{BHF}}$  as a result of removing the exchange contribution from the free-energy functional in (2)—this has the effect of lessening the two-body repulsion (for bosons). The agreement between the two schemes is not as satisfactory away from the primary minima, as indicated in Fig. 2, where  $V_s(z, \Theta)$ ,  $T = 20 \text{ K}$ , is also plotted from SSTK's data. The magnitudes of the barrier and the secondary

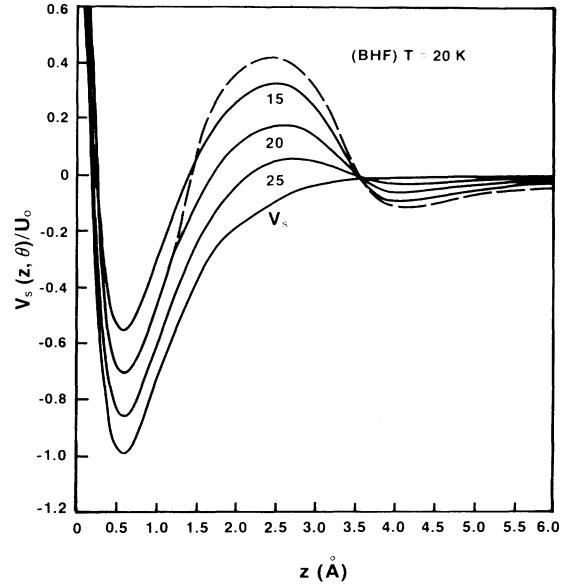


FIG. 2. Effective surface potentials,  $V_s(z, \Theta)$ , in LDA from which  $\Theta_{\text{LDA}}$  in Table I follows; the effect of gradient corrections is barely apparent on this scale. For  $T = 20 \text{ K}$ , we plot the result of the BHF method of Ref. 1 (---). The bare surface potential  $V_s(z)$  is included for comparison. The energies are normalized with  $U_0$ .

minimum are halved in the ETF case; of course, the coverage is completely insensitive to such variations. However, it should be noted that SSTK's effective surface potential is an average over the state-dependent potentials,  $V_s^{(i)}(z, \Theta)$ , which are to be employed in the Hartree-Fock equations: their first bound-state potential,  $V_s^{(1)}(z, \Theta)$ , agrees with our ETF result for  $T=20$  K over the whole domain. In addition, it is well known that the Thomas-Fermi method can yield inaccurate results at very low densities—in this case around the maxima of Fig. 2.

In conclusion, we observe that, as far as the calculation of coverages is concerned, we may replace the detailed computational method of SSTK with the density-functional scheme outlined above and still obtain results of high (comparative) accuracy, *even* in the local-density

approximation. The accuracy is somewhat reduced for the effective surface potential overall, but this is not necessarily an important factor. The problem of calculating the temperature-dependent coverage in the case of localized physisorption, for example, which was beyond the ability of SSTK, is certainly feasible within our present scheme. We intend to address this problem in a future publication.

#### ACKNOWLEDGMENTS

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