Potential energy surface for rare gases adsorbed on Cu(111): parameterization of the

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Abstract

We propose a model potential function to describe the interaction between rare-gas atoms and a metal surface with parameters derived on the basis of *ab initio* calculations. We discuss the merits of the proposed functional form for applications in molecular dynamics studies of nanotribology.

(Some figures in this article are in colour only in the electronic version)

1. Introduction

The microscopic origin of friction for thin films adsorbed on surfaces has recently attracted considerable interest. Progress in understanding the fundamental processes that contribute to friction at an atomic scale is essential to all areas of friction, since macroscopically observed friction is known to depend on the local chemical and atomic details of the surfaces in contact, and also on whether monolayers (MLs) or submonolayers of adsorbates are present on these surfaces [1]. Quartz crystal microbalance (QCM) measurements, first realized by Krim *et al* [2], provided novel understanding in this context. The basic component of a QCM is a single crystal of quartz that oscillates at an extremely sharp resonance frequency. Atomically thin films of material, usually of rare-gas atoms, are then adsorbed onto the electrodes that cover the quartz crystal. By measuring the broadening of the resonance peak the friction force per atom can be extrapolated. The sensitivity of the technique and the simplicity of the systems to which it has been applied have stimulated a number of theoretical studies and corresponding molecular dynamics simulations [3–7]. In the numerical calculations the interactions between rare-gas atoms were modelled by pairwise Lennard–Jones (LJ) potentials, while the interaction of the rare-gas atoms with the metallic surface was represented by a periodic potential $V(x, y, z)$, with the substrate being approximated as rigid since the compressibilities of the noble metals are much lower than those of the rare gas and, therefore, the deformation of the metal surface can be neglected. In most cases the analytical form chosen for the periodic potential V follows the model derived by Steele [8] by assuming that the interaction of a rare-gas

atom and the metal surface can be represented by a sum of LJ pairwise interactions. Since the LJ potential favours close-packed structures, the minima of $V(x, y, z)$ were assumed to correspond to the threefold hollow sites of the surface in all the previous simulations. However, several experimental studies revealed that for most systems of rare gas on metal surfaces the adatom adsorption occurs at the top sites [9–12]. This observation was also confirmed by first-principles calculations for Xe adsorption on several metal surfaces [13–16] and for He adsorption on Cu(111) [17]. Due to the wrong assignment in the location of the potential minima, none of the analytical forms adopted in the previous molecular dynamics simulations of sliding MLs is able to reproduce correctly the dependence of the potential corrugation on the adatom–surface distance (z), which is unusual in rare-gas–metal adsorbate systems. Finally, due to the scarcity of specific direct measurements, the amplitude of the potential corrugation was often chosen with a high degree of arbitrariness. The limitations and uncertainties in the description of the interface potential led to contradictory results on the tribological properties of sliding MLs, and a quantitative theory of QCM experiments is still lacking.

The aim of this paper is to propose a model potential, derived on the basis of *ab initio* calculations, which can overcome the limitations described above. The analytical form we propose in this paper is (i) consistent with the experimental observations of low-coordination adsorption, (ii) reproduces the changes in the relative stability of the adsorption sites induced by the variation of the adatom–surface distance, and (iii) reduces the uncertainties on the potential corrugation due to the lack of direct measurements because it relies on first-principles energetics. In this regard we point out that the lack of van der Waals interactions in the density-functional theory with local density approximation (DFT-LDA) description causes the first-principles energies calculated within this approach not to be accurate at long range. To minimize the corresponding inaccuracies, the parameterization of the model potential was constructed by restricting the fitting procedure to the *ab initio* data in near-surface region, where the DFT-LDA energies become more reliable. In this way the strength of the long-range dispersion cannot be directly fitted but is indirectly determined by the position and the depth of the adsorption minima, which are fairly well reproduced by DFT-LDA. Nevertheless, further improvements would indeed be necessary to provide a more correct theoretical description of physisorption. At present there is not a commonly accepted, well-establish method to treat dispersive forces within first-principles calculations. Investigating the relative merit and reliability of the different currently available approaches is beyond of the scope of this paper, in which we wish to focus on the introduction of a novel analytical expression for the interface potential, which, by including a more accurate description of corrugation, can provide an improved description of the tribological properties of sliding rare-gas MLs.

The paper is organized as follows. In section 1 we present the results of first-principles plane-wave/pseudopotential/DFT-LDA calculations for Ar, Kr, Xe adsorption on the close-packed surface of Cu. We find that the on top site is the energetically most favourable site for the adsorption of all the investigated rare-gas atoms. In section 2 we describe the procedure for the construction of the potential energy surface (PES). For the sake of exemplification we present the result for Xe on the Cu(111) adsorbate system, but the analytical expression we propose can be used to model the interaction of all the different rare-gas–metal systems. A comparison with the model potentials previously adopted in molecular dynamics simulations of sliding MLs is also discussed.

2. *Ab initio* calculations of Ar, Kr, Xe adsorption on the Cu(111) surface

We performed calculations for Ar, Kr, Xe adsorption in the $(\sqrt{3} \times \sqrt{3})$R30° structure ($\sqrt{3}$ from now on) (figure 1). A commensurate phase is experimentally observed for Xe adsorption
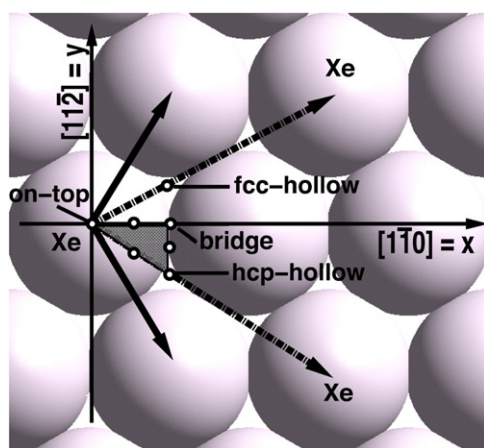
Figure 1. Top view of the Cu(111) surface: the primitive vectors of the (1 × 1) cell are indicated
by full arrows, and the C_{3v} high-symmetry sites are explicitly labelled. The shaded triangular area
defines the irreducible zone if a C_{6v} surface symmetry is imposed (i.e., assuming the hcp-hollow and
the fcc-hollow sites to be equivalent). The points along the edges of the irreducible zone indicate
the adatom lateral positions sampled in order to construct the PES. The locations of the Xe atoms in
the commensurate $(\sqrt{3} \times \sqrt{3})R30°$ structure are indicated by the 'Xe' labels; the primitive vectors
of this structure are also displayed (dashed arrows).

at temperatures higher than 50 K, in particular at $T = 77$ K, consistently with the fact that a
very small lattice mismatch is present between the Xe lattice parameter at this temperature and
the $\sqrt{3}a_{Cu}$ distance [19]. We adopted the $\sqrt{3}$ geometry also for Ar and Kr because it has been
shown that the main features of the rare-gas–metal interaction potential are not affected by the
lateral interaction between the adatoms [13]. In our calculations [20] the surface was modelled
by repeated supercells with $\sqrt{3}$ in-plane size, containing a slab of seven Cu layers and a vacuum
region 18 Å thick. The surface Brillouin zone was sampled with a (6 × 6) Monkhorst–Pack
grid [21]. Ultrasoft and norm-conserving pseudopotentials were used to describe the metal and
the gas ions respectively. The electronic wavefunctions were expanded in a plane-wave basis
with a 25 Ryd kinetic energy cutoff. LDA was used for the exchange–correlation functional.
This approximation was proven to work better than the generalized gradient approximation
(GGA) in describing the rare-gas adsorption on metallic surfaces. It was in fact shown by a
previous comparative study on the $\sqrt{3}$ Xe on the Pt(111) system [15], that the GGA predicts an
extremely weak binding in qualitative, as well as quantitative, disagreement with experiments.
On the other hand, the LDA interaction potential in the near-surface region agrees reasonably
well with the empirical Barker–Rettner potential, taken as a reference since it agrees with a
great number of experimental data [15].

The geometrical parameters and the energetics that characterize the adsorption of Ar, Kr
and Xe on the Cu(111) surface were calculated by means of a structural relaxation procedure.
Two rare-gas atoms were placed on both side of the slab at 4 Å distance from the surface. All the
system degrees of freedom except for the (x, y) adatom coordinates were allowed to relax until
the forces become smaller than 0.05 eV/Å, and the energy varied by less than 1 meV. In figure 2
the relative adsorption energy and equilibrium vertical distance for a Xe atom adsorbed on the
Cu(111) surface are displayed with respect to the on-top site. We can see that the adatom is
more tightly bound at the low coordination on top site: this adsorption configuration is, in fact,
characterized by the lowest adsorption energy ($V(z_0) = -261$ meV per atom in the $\sqrt{3}$ ML)
and by the shortest adsorption distance ($z_0 = 3.27$ Å). These results are similar to those
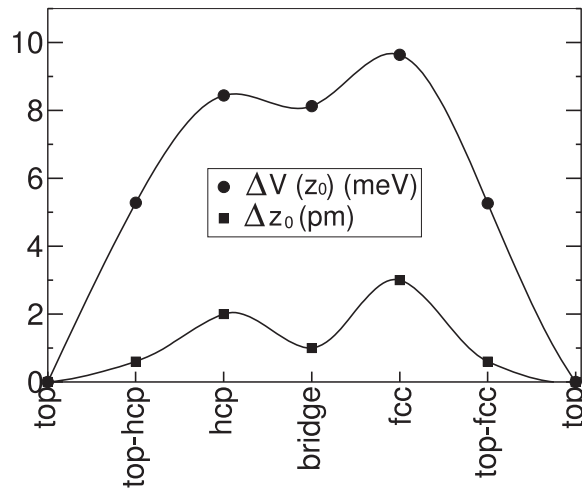
Figure 2. The modulation of the adsorption energy ($V(z_0)$) and of the equilibrium distance (z_0) of Xe atoms adsorbed on the Cu(111) surface is displayed along the [11$\bar{2}$] direction (see figure 1). The on-top site is taken as reference. The continuous line is a guide for the eyes.

Table 1. Adsorption properties of rare-gas atoms on the Cu(111) surface in the $\sqrt{3}$ structure. The adsorption energy ($\Delta V(z_0)$) and the equilibrium distance (Δz_0) from the topmost substrate layer are reported for the hcp-hollow site relative to the on-top site. The outward displacement d of the metal atom under the adsorbed atom is also displayed.

Atom	$\Delta V(z_0)$ (meV)	Δz_0 (Å)	d (Å)
Ar	3.89	0.03	0.014
Kr	6.33	0.04	0.01
Xe	8.44	0.03	0.03

obtained by Da Silva *et al* ($V(z_0) = -277$ meV and $z_0 = 3.26$ Å) adopting the all-electron full-potential linearized augmented-plane-wave method with the LDA for the exchange correlation energy [13], and to those obtained within a first-principles approach which includes the van der Waals interaction calculated within the DFT ($V(z_0) = -250$ meV and $z_0 = 3.20$ Å) [14]. The on-top site preference is reproduced, as observed by low-energy electron diffraction (LEED) experiments for Xe on Cu(111) [10], with the typical LDA underestimation of the bond lengths (the measured equilibrium distance is $z_0 = 3.60$ Å).

As a novel result, our calculations reveal that the on-top site preference also holds true for Ar and Kr adsorption on Cu(111), thus suggesting that adsorption on the low-coordinated sites is the rule for all the noble gases on copper (first-principles calculations for He can be found in [17]). As can be seen in table 1, the heavier is the adatom, the higher is the difference between the adsorption properties at the top and at the hollow sites (in table 1 the hcp-hollow site is considered). This result is most likely related to the fact that the dipole moment induced on the adatom by the presence of the metallic surface increases with the atomic number. The relative amplitude of the energy corrugation suggests that phononic dissipation during ML sliding on the metallic surface of the QCM should be higher for Xe MLs than for Ar and Kr ones. Our estimate of the potential corrugation for the Xe/Cu system (ranging from 8.44 meV for the hcp-hollow to 9.64 meV for the fcc-hollow site), is in agreement with that obtained

by Da Silva *et al* [13] and is a few meV larger than that calculated by Lazic *et al* [14] (3.8 meV) by including the van der Waals interactions in the DFT calculations. The frequency of the longitudinal mode calculated in the latter approach is in agreement with the experiments of inelastic scattering of He atoms [18]. We are, instead, not aware of any experimental or theoretical data on the potential corrugation for Ar and Kr on Cu(111).

The adatom equilibrium adsorption distance z_0 varies along the surface (see figure 2 and table 1): we can infer that the atoms of a sliding ML move up and down in order to adjust their equilibrium distance according to the underlying lattice. This up and down motion can excite phonons in multilayer films. Thus, in order also to take into consideration this channel of dissipation, it is important to model the atom–surface interaction with a three-dimensional potential that is able to capture the modulation of the adatom equilibrium distance. A specular vertical displacement occurs in the topmost substrate layer: the metal atom on the top of which the rare-gas atom is adsorbed relaxes slightly outwards from the surface. The amplitude of the surface rumpling is small (see last column of table 1), especially for the lighter rare gases, and the rigidity of the substrate prevents this local deformation from extending further.

3. Construction of the potential energy surface

In order to derive an analytical expression for the potential energy surface (PES) $V(x, y, z)$ experienced by a rare-gas atom adsorbed on the metal, the characteristic features of the physisorption process must be taken into account. It is known that the interaction between the rare-gas atoms and the metal surfaces is attractive at long range (van der Waals attraction), and highly repulsive at short range (Pauli repulsion). The combination of both the repulsive and the attractive part gives rise to a shallow physisorption well in the substrate potential whose depth ranges from few meV for He up to about 300 meV for Xe on Pt. The relative strength of the attractive and repulsive interactions varies according to the adatom lateral positions, giving rise to a lateral dependence of the well minimum $z_0(x, y)$, and of the well depth $V(x, y, z_0)$. The peak-to-peak amplitude ΔV is referred to as the potential corrugation, adopting the same term that the literature on helium atom scattering (HAS) experiments [22] indicates for the lateral modulation of He adsorption distance Δz_0, more precisely of its turning point. HAS experiments revealed that the classical turning point of He scattering off close-packed surfaces is closer to the metal when the adatom is at the top site than when it is at the higher coordinated sites [23, 24]. The origin of this effect, known as *anticorrugation*, has been long debated. Recently Da Silva *et al* [13] suggested that the on-top site preference is caused by the site dependence of the surface electronic character: donor-like at the on-top region and acceptor-like at the hollow region. Thus when the adatom approaches the surface, the Pauli repulsion is reduced at the on-top region by a transfer of electrons towards the hollow region. We point out that, at distances closer than the equilibrium one, the depopulation of the metal outermost orbitals is not enough to decrease the Pauli repulsion; thus at distances closer to the surface than the equilibrium one, the interstitial hollow site becomes more favourable than the on-top one. This implies that the PES changes shape with z, passing from anticorrugated (minima at top sites) around z_0 to corrugated (minima at hollow sites) close to the surface. This effect has been noted for He on Cu(111) [17] and for Xe on Pd(111) [13]. The corrugation ΔV of the rare-gas–metal potential must then be regarded as a changing-sign function of z.

In order to construct the PES experienced by a Xe atom on the Cu(111) surface, we calculated the Xe adsorption energy for several adatom positions. To reduce the computational effort we performed self-consistent calculations at fixed atomic positions (the Cu substrate was kept frozen in its ideal geometry). This approximation is justified by the shallow relaxation of the surface occurring upon adatom adsorption, as shown in the previous section. In our procedure for the PES construction the hcp-hollow and the fcc-hollow sites are considered
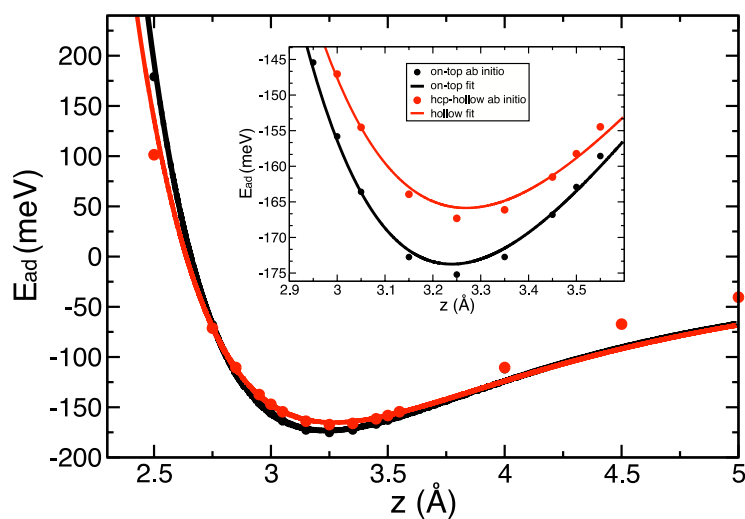
Figure 3. Adsorption energy (see footnote 1) for one Xe adatom deposited on the Cu(111) surface as a function its distance (z) from the outermost Cu layer. The *ab initio* results (dots) and the parametric functions described in the text (full lines) are reported both for Xe adsorption at the on-top and at the hcp-hollow site.

equivalent for adsorption because of the small differences in the adsorption properties (less than 1 meV in the adsorption energy and 0.01 Å in the equilibrium distance). A sufficiently accurate sampling of $V(x, y, z)$ was obtained by choosing the adatom lateral positions (x, y) on a grid of points with 0.4 Å average separation along the two perpendicular wedges of the irreducible surface unit cell (shaded area in figure 1). At each grid point the adsorption energy for an isolated Xe atom was calculated for different vertical distances z.[1] The results were fitted with the function $f(z) = A_0 \exp(-z/A_1) - A_2/z^3$, that is a sum of two contributions. The attractive part is proportional to z^{-3}, as it can be derived either from a classical calculation of dipole–image dipole interaction [25], or from a quantum mechanical approach [26]. The repulsive contribution is described by an exponential decay that mimics the decay of the surface charge density into the vacuum. The fitting was restricted to the *ab initio* data falling around the minimum. In this way we obtained a model potential which on one hand reproduces the *ab initio* energies at the short range highly weighted by the fitting procedure and well described by the DFT-LDA, and on the other hand possesses the correct z^{-3} asymptotic character of the van der Waals interaction which is absent in the DFT-LDA energies at long range which, for this reason, were neglected in the fitting procedure. Although the strength of the long-range dispersion cannot be directly fitted, it is indirectly determined by the position and the depth of the adsorption minima, which are well reproduced by DFT-LDA. As can be seen from figure 3,

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[1] The adsorption energy of a single adatom on the surface was derived from slab calculations by subtracting from the total energy of the adsorbate system the energy of the clean metal surface, the energy of the isolated atom, and the adatom–adatom interaction energy. The latter was evaluated by comparing the energy per atom for an adsorbed layer at 1/3 surface coverage ($\sqrt{3}$ periodicity) with that at 1/12 coverage ($2\sqrt{3}$ periodicity). Even if this procedure contains some residual source of error such as the fact that at $2\sqrt{3}a_{Cu}$ distance (8.7 Å in our calculations) a weak adatom–adatom interaction can still be present, we consider it more reliable than the value obtained by subtracting from the total energy of the slab, the energy of an isolated $\sqrt{3}$ ML plus the energy of the clean metal surface. In this case, in fact, the repulsion between equally oriented dipoles, induced on the rare-gas atoms by the presence of a metallic surface, is completely neglected.
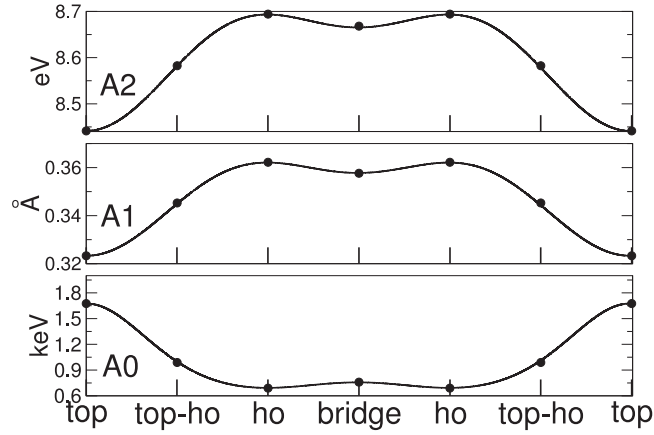
Figure 4. The circular spots indicate the values of the parameters (A_0, A_1, A_2) obtained by fitting the shape of the physisorption well for different adatom lateral positions along the $[11\bar{2}]$ direction. The continuous lines represent the profile of the two-dimensional functions $A_i(x, y)$ defined by equations (1) and (2) along the same direction.

the fitting is very satisfactory in the near-surface region, while it departs from the DFT-LDA points at long range, due to the presence of the z^{-3} term which improves the description of the long-range interaction with respect to the DFT-LDA.

As a result of this fitting procedure we obtained site-dependent terms of parameters $(A_0, A_1, A_2)_{\text{site}}$, each of them accounting for the equilibrium energy and distance that characterize the adatom adsorption at a given lateral position (x, y). The parameter values along the $[11\bar{2}]$ direction are reported in figure 4 as circular spots. We can see that the lateral variation of each parameter $A_i(x, y)$ presents the periodicity of the underlying lattice. This observation suggests to employ the Bloch theorem to derive analytical expressions to describe the parameter variation along the surface. We considered the first terms of the Fourier expansion over the reciprocal **g** vectors:

$$A_i(x, y) = A_i^{\text{top}} + \Delta_i u(x, y) \qquad i = 1, 2 \qquad (1)$$

where $u(x, y) = [3 - \sum_{\mathbf{g}} \cos(\mathbf{g} \cdot \mathbf{r})]$, where the sum runs over the first three equivalent **g** vectors of the triangular lattice. The amplitude of $u(x, y)$ was normalized to 1. $\Delta_i = A_i^{\text{ho}} - A_i^{\text{top}}$ measures the amplitude for the ith parameter swing between the top-site and hollow-site values. For the parameter A_0 it was necessary to adopt a slightly different analytical expression in order to accurately fit the data. The expression we derived is

$$A_0(x, y) = A_0^{\text{top}} \exp\left(\frac{\alpha(A_1^{\text{top}} - A_1(x, y))}{A_1^{\text{top}} A_1(x, y)}\right) \qquad \alpha = \ln\left(\frac{A_0^{\text{ho}}}{A_0^{\text{top}}}\right) \frac{A_1^{\text{top}} A_1^{\text{ho}}}{A_1^{\text{top}} - A_1^{\text{ho}}}. \qquad (2)$$

As can be seen in figure 4, the parameter fitting obtained by using the functions of equations (1) and (2) is extremely accurate and, therefore, there is no need to add higher harmonics in the Fourier expansion.

We arrived in this way at the definition of a three-dimensional function

$$V(x, y, z) = A_0(x, y) \exp(-z/A_1(x, y)) - A_2(x, y)/z^3 \qquad (3)$$

which parameterizes the PES experienced by rare-gas atoms deposited on a metal surface. This function presents minima at the on-top sites, saddles at the bridge sites and maxima at the hollow sites of a triangular lattice. A bidimensional representation of the PES can be seen
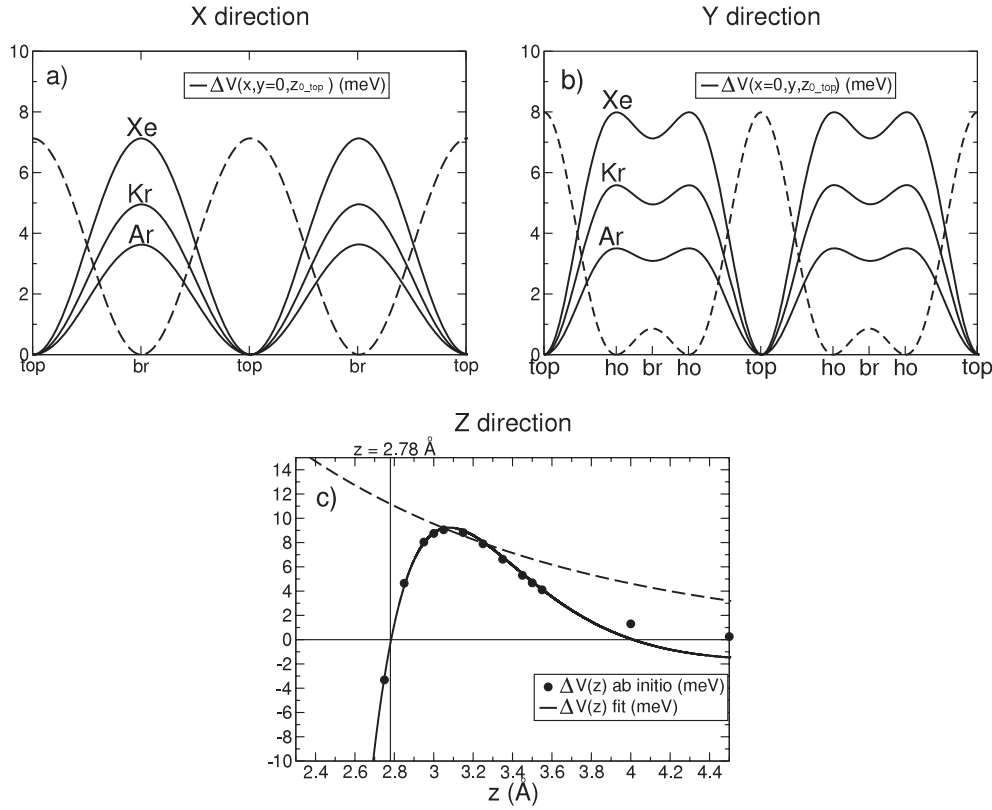
Figure 5. The lateral modulation of the Ar–, Kr–, Xe–Cu(111) interaction potential ΔV is plotted for $z = z_{\mathrm{eq}}^{\mathrm{top}}$ along the $[1\bar{1}0]$ (a) and the $[11\bar{2}]$ (b) directions of a triangular lattice (see figure 1). In panel (c) the difference between the Xe adsorption energy at the hollow and at the on-top sites is represented as a function of the adatom–surface distance; both *ab initio* and fitted values are shown. The dashed lines refer to analytical expressions previously adopted (see text).

in panels (a) and (b) of figure 5. The (c) panel represents instead the z-dependence of the potential corrugation, i.e., the difference between the on-top and the hollow curves of figure 3. We can see that $\Delta V(z)$ gradually decreases as the adatom approaches the surface, becoming equal to zero at about 0.5 Å below the equilibrium distance, and reverts its sign closely to the surface. This is determined by the anticorrugated nature of the rare-gas–metal interaction potential which transforms to corrugated in the near-surface region. The lateral modulation of the equilibrium adsorption distance $z_0(x, y)$ is also reproduced with a maximum amplitude of 0.03 Å in agreement with the *ab initio* results and with the experimental data [10].

We conclude this session by pointing out some differences between the model described above for the rare-gas–metal potential and those adopted in previous molecular dynamics simulations of QCM experiments, discussing their relevance in the calculation of tribological properties. The analytical expression adopted to describe the substrate potential in previous QCM simulations [3–7] is the following:

$$V(x, y, z) = V_0(z) + V_1(z)u(x, y) \tag{4}$$

where $V_0(z)$ represents the physisorption well, $V_1(z)$ the corrugation of the potential, and $u(x, y)$ is the periodic function with the symmetry of the lattice. Analytical expressions for the Fourier coefficients $V_0(z)$ and $V_1(z)$ were derived by Steele [8] by assuming that the gas–metal

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interaction potential can be expressed as a sum of LJ interactions. Because the LJ potential favours close-packed structures, the previous simulations always considered a corrugated PES. The dashed lines in figures 5(a), (b) show the profile of a corrugated PES (the amplitude of the corrugation was assumed equal to that of Xe on Cu(111) in our model). The symmetry of the triangular lattice causes the PES saddle points to correspond to the bridge sites both in the anticorrugated and in the corrugated regime, with a significant difference in energy which is close to that of the PES maxima in the first case, and to that of the PES minima in the second case (see figure 5(b)). This difference can deeply affect the calculation of friction properties. We verified that even if a lateral force is applied in a specific direction, particle movements inside the ML follow the minimum energy path, as happens in ordinary surface diffusion. Thus what governs the static and kinetic friction is the height of the PES saddle points, and not the height of the PES maxima relative to the PES minima, as is often considered. Since bridge sites in the corrugated PES lie very close in energy to the PES minima (hollow sites), the friction calculated using a model potential with the wrong sign of corrugation can be highly underestimated. Furthermore, $V_1(z)$ was often described by monotonic functions that represent a potential corrugation that increases from the vacuum to the surface. The behaviour of one of the forms often adopted ($V_1(z) = -\alpha(z - z_0)$) is represented in figure 5(c) by a dashed line. According to the monotonic function, the PES corrugation should increase when the ML is pressed against the surface, while according to our calculations an opposite behaviour is predicted for rare-gas MLs on metal surfaces. This fact has important consequences on the tribological properties of these systems because it represents a violation of the Amonton's law of a linear increase of friction with load, and suggests the presence of a state of superlubricity at some value of the pressure where the corrugation becomes equal to zero.

4. Conclusions

We studied the adsorption of Ar, Kr, Xe on the Cu(111) surface by means of plane-wave/pseudopotential/DFT calculations. In addition to previously reported results, our calculations reveal that the on-top site preference is the rule for all rare-gas adsorption on copper. By fitting the *ab initio* energies in the near-surface region, we derived a novel model potential function for the interaction between a rare-gas atom and a metallic surface that is able to reproduce the anticorrugation and its change of sign to corrugation at short adatom–surface distances. We discussed the validity of our model potential for molecular dynamics simulations of the tribological properties of sliding MLs, with reference to the previously adopted model potentials.

Acknowledgments

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