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Nature, Strength, and Consequences of Indirect Adsorbate Interactions on Metals

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Atoms and molecules adsorbed on metals affect each other even over considerable distances. In a tour-de-force of density-functional methods, we establish the nature and strength of such indirect interactions, and explain for what adsorbate systems they can critically affect important materials properties. These perceptions are verified in kinetic Monte Carlo simulations of epitaxial growth, and help rationalize a cascade of recent experimental reports on anomalously low diffusion prefactors.

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Just like a spider senses prey that happen to get stuck on its web, so also do atoms feel the presence of each other through the lattice of substrate atoms on which they are adsorbed. Complementary to this elastic type of interaction, adsorbates on metals can also interact over large distances by polarizing the electron gas in which they are embedded [1–4]. Since little is known about the relative and absolute strength of indirect interactions, it is unclear how they modify adsorbate behavior, and consequently how important they are in general for understanding and modeling materials properties.

Microscopic studies that have addressed this problem are utterly scarce [5–7]. Quite recently, detailed experimental measurements have suggested that long-range interactions strongly influence adsorbate ordering and aggregation on metals, and shown that traditional analyses fail to account for this [5,8,9]. While such accounts are invaluable for quantifying adsorbate interactions, direct studies are needed to pin down their nature and, most importantly, address a fundamental question: when must we worry about indirect interactions?

In this Letter, we address these issues from first principles. A tour-de-force of density-functional calculations reveals that indirect adsorbate interactions on metals are predominantly electronic in origin, oscillatory in nature, and intrinsically long-ranged. By comparing the perturbations in the potential-energy landscape that arise from such interactions with the overall surface corrugation and adsorbate binding energies, we can understand for what materials systems indirect interactions are maximally important. These perceptions are corroborated by kinetic Monte Carlo simulations of epitaxial growth which, for example, show a large increase in island density when indirect adsorbate interactions are taken into account. An immediate consequence of this particular result is that it offers an explanation to a series of recent reports on anomalously low diffusion prefactors.

For reasons outlined below, we focus our study on two metal systems: Al/Al(111) and Cu/Cu(111). The calculations are based on density-functional theory (DFT) [10,11], using a pseudopotential method, as implemented in the VASP code [12]. For the exchange-correlation functional, the local-density approximation (LDA) [13] is used for Al, and the generalized gradient approximation (GGA) [14] for Cu. The one-electron wave functions are expanded in a plane-wave basis with an energy cutoff of 9.0 (17.2) Ry for Al (Cu), using ultrasoft Vanderbilt pseudopotentials [15]. To improve convergence with respect to Brillouin zone sampling, a fictituous electronic temperature is employed according to the Methfessel-Paxton scheme [12], using a small smearing width of 0.01 eV (to avoid extrapolation errors). The Kohn-Sham equations are solved self-consistently, and the atomic structure is optimized until forces on all unconstrained atoms are less than 0.03 eV/Å.

To reduce "ghost" interactions, the periodic super-cells used in the calculations span at least twice the maximum adsorbate-adsorbate distance examined in a specific direction. For Al, our (111) super-cell consists of $14 \times 4 \times 6$ (336) atoms; for Cu we employ a $12 \times 4 \times 4$ cell containing 192 atoms (memory requirements in the case of Cu are too large to permit a bigger super-cell). Above an additional adsorbate layer [16], there is $\simeq 9$ (13) Å of vacuum for Al (Cu). The Brillouin zone is sampled using a 6×2 (3×1) k-point mesh for Al (Cu). This dense sampling yields excellent overall convergence for these large cells — adatom diffusion barriers and dimer binding energies for Al on both unrelaxed and relaxed surfaces are within 2 meV of previous calculations using a $6 \times 5 \times 6$ atom super-cell and 6×6 k-point mesh [17]. First-principles calculations of long-range interactions neccessarily involve very large systems and are immensely computer intensive; the work presented here is based on largely parallelized calculations that would take half a human lifetime to produce on a standard workstation.

To separate electronic and elastic adsorbate interactions, all calculations are performed at two levels of relaxation. In the first case, the slab (no adsorbates) is first fully relaxed, and the atomic coordinates are then kept frozen during subsequent calculations. In the second case, all atoms are allowed to relax, save for the bottom two layers which in both cases are kept fixed at bulk

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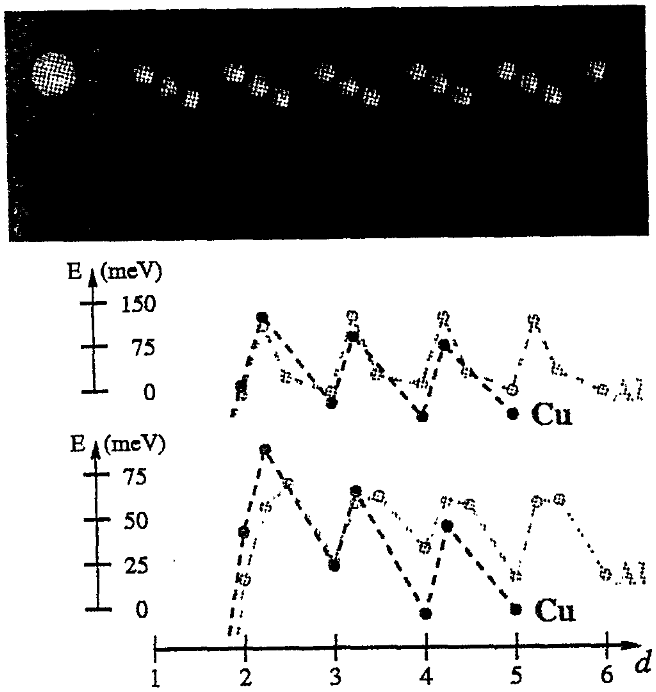

FIG. 1. Top view of adsorption geometries in the DFT calculations. One adatom is placed at its preferred binding site (hcp for Al and fcc for Cu; mid-size circles), and another atom is then placed at successive binding sites and saddle-points (tiny circles) along the ⟨110⟩ direction (half the length of the Al super-cell is shown). The binding energy is defined as $E = E_1^1 + E_1^2 - E_0 - E_2$, where the subscript denotes the number of adatoms in the cell and the superscript identifies the individual atomic positions, and is shown as a function of adsorbate separation d in terms of lattice sites. Both frozen (middle graph) and relaxed (bottom graph) cases are truncated at short separations to enhance resolution.

coordinates. In both instances, two atoms are adsorbed on top of the slab, and (always) allowed to completely relax. The actual adsorption geometries differ somewhat between Al and Cu, as in the former case adatoms prefer the hcp site at low coverage. Thus, for Al/Al(111), one atom is placed in an hcp site, and the other atom is placed at consecutive hcp, bridge, and fcc sites along the ⟨110⟩ direction. The maximum adatom-adatom separation is 17 Å (slightly less than half the length of the 4 nm long super-cell to avoid image interactions). In the Cu/Cu(111) calculations, one atom is placed in an fcc site, and the other in alternating bridge and fcc sites along the ⟨110⟩ direction with a maximum separation of 13 Å (super-cell length: 31 Å). Saddle points for atomic diffusion are located by mapping out the total energy on a dense grid near bridge sites; in this case one or two of the lateral adsorbate coordinates are locked at each point on the mesh. Part of the super-cell with its adsorption configurations is illustrated in Fig. 1.

To set the stage and establish part of the unperturbed potential-energy surface, we first consider self-diffusion of isolated adatoms. The corresponding activation energies E_d are given in Table I. Note that the elastic substrate response considerably smoothes out the surface corrugation, which greatly facilitates the diffusion process in lowering the activation energy by a factor of three for both Al/Al(111) and Cu/Cu(111). In addition, we find that the previously reported bridge-fcc degeneracy for Al [18,19] is a purely elastic effect; if the substrate is frozen, the degeneracy is lifted, and the fcc site is markedly favored over the near-bridge site.

To better assess the implications of our adatom-adatom interaction study, we start out by identifying three distinct interaction regimes according to adsorbate separation: (i) At minimal interatomic separations, direct electronic interactions dominate, and localized chemical dimer bonds are formed [17,19]. This interaction falls off exponentially, and is therefore very short-ranged [1]. At its extreme, it can effectively extend up to a couple of lattice sites, and form a "denuded" zone on weakly corrugated surfaces, where adatom pairs are unstable with respect to dimerization (c.f. the issue of capture radii in Ref. [7,19,20]). (ii) At larger separations, adsorbate interactions are predominantly indirect, and mediated in three ways: via electrostatic (dipole-dipole) and elastic fields, which both decay monotonically with separation d as $1/d^3$, and via oscillatory Friedel-type quantum corrections [1,2]. (iii) The most long-ranged form of indirect interaction is found for metals with a partially filled surface band (assuming a near-spherical Fermi surface), where the Friedel-type interaction energy decays asymptotically as $-\sin(2k_F d)/d^2$ [1,2,4], k_F being the Fermi wavevector. In the absence of a surface band, the same interaction falls off much faster, as $\cos(2k_F d)/d^5$ [1,2,4].

These observations motivate our choice of systems. Cu(111) is chosen because it does have a surface band, and a Fermi surface prone to give stronger interactions than, e.g., Ag and Au [4]. Al(111), on the other hand, is a near-free electron gas conductor with no surface band. The intention here is hence to try to span intermediate systems and indirect interaction energies.

The DFT computed adatom-adatom interaction energetics for Al/Al(111) and Cu/Cu(111) are illustrated in Fig. 1 and summarized in Table I. Since short-range interactions are well understood [17,19], we focus on regimes (ii-iii). With adatom separation d, we find variations in the total energy at both binding sites and saddle points.

TABLE I. DFT values for the atomic diffusion barrier in the case of an isolated adatom (E_d) and the range of variation in barriers produced by the presence of another adatom (E_d^*) on the frozen and relaxed substrates. All values are in meV.

	Frozen		Relaxed	
System	E_d	E_d^*	E_d	E_d^*
Al/Al(111)	115	110-126	42	24-53
Cu/Cu(111)	134	110-146	50	41-69

The fact that the range of variations in the interatomic potential due to indirect interactions are still there in their full extent even when elastic response is frozen (Fig. 1, Table I) indicates that *indirect interactions are mainly electronic in this regime.* It is interesting to note though that elastic substrate response is still very important, in that it lowers the atomic diffusion barriers by smoothening out the surface corrugation. This effect triples the $(E_d^* - E_d)/E_d$ ratios—E_d^* (E_d) being the atomic diffusion barriers with (without) adsorbate interactions—and thereby increases the relative magnitude of indirect electronic interactions.

Although the super-cells used are extraordinarily large for this systematic first-principles study, they still capture only part of the indirect interaction curve. We certainly note a long-ranged oscillation for Cu, but it is hard to discern how well its periodicity agrees with half the Fermi wavelength $\pi/k_F = 15$ Å measured by Crommie *et al.* [21]. A density-of-states examination does show a surface band, although it is clear that its position and characteristics are plagued by slab-thickness convergence problems as well as intrinsic shortcomings of DFT. A graphic indication of the importance of indirect interactions on Cu(111) is given by recent scanning-tunneling microscopy (STM) observations of long-range ordering of sulphur atoms with a periodicity of 15 Å [22]. There are similar variations in the case of Al, but it is hard to discern any periodicity.

The qualitative features of our results so far are thus encouraging. We now turn to discuss the magnitude of the indirect interactions, and their impact on surface morphology. At high enough temperatures, the surface structure is dictated by relative adsorbate binding energies [7,20,23]. We find a binding energy variation of about 17 meV for Al, and about 46 meV for Cu due to indirect adsorbate interactions. At low temperatures, kinetic limitations strongly affect the surface morphology [7,20,23]. The computed total-energy variations at binding sites and saddle points translate into *separation and direction dependent atomic diffusion barriers* (Fig. 1, Table I). For Al/Al(111), the activation energy assumes values of 24-53 meV, to be contrasted against the nominal 42 meV of isolated adatoms. For Cu/Cu(111), the activation energy is 41-69 meV, compared with 50 meV for isolated adatoms. For both systems, the "perturbations" are therefore almost as large as the atomic diffusion barrier itself!

The magnitude of indirect interactions is measured on the mRy scale, and hence relatively weak by conventional standards. This explains why it is possible in general to understand and model many materials properties while completely neglecting long-ranged interactions. The key to understanding *when* indirect interactions are important is to compare the energy perturbations with other characteristic energies. For many systems, mRy perturbations in the potential-energy landscape are small compared with adsorbate bond energies and surface diffusion barriers, and we therefore expect them to only weakly perturb adsorbate interactions. Conversely, it is also clear that indirect interactions should be important for adsorbate-metal systems with weak ad-ad bonds and/or a weakly corrugated surface. Examples hereof include, but are not limited to, homogeneous and heterogeneous M/M(111) and R/M(111) systems, where M can be Al, Cu, Ag, Au, and R any of the rare gases (He, Ne, Ar,...), and judging from recent reports [8,22], possibly chalcogens and halogens as well. In these cases, the perturbation of the energy landscape that results from indirect adsorbate interactions is comparable to the corrugation of the landscape itself, and (except for pure metal systems) of the same magnitude as chemical adsorbate bonds.

Indirect interactions are consequently expected to have a strong effect on the diffusion kinetics and aggregation for this type of adsorbate-metal systems. To test these ideas on laboratory time and length scales, we perform *ab initio* kinetic Monte Carlo simulations [24] (KMC) of the low-temperature growth of Al(111) and Cu(111). The only input to these calculations is a set of previously DFT-computed activation energies [20] and the current long-range perturbations to the energy landscape. Possible angular dependencies of interaction energies are unknown, and thus neglected, and the interaction between more than two adatoms is described by pair-wise summation. Theoretical studies by Einstein [1] suggest that the latter is a good approximation beyond the shortest adatom separations, as corroborated in a recent (STM) study [9]. A detailed account of these calculations will be presented elsewhere; below a brief summary follows.

As a representative indicator of surface morphology, we focus on the island density. With a deposition flux $F = 0.01$ ML/s, coverage $\Theta = 5\%$, and substrate temperature of 25 K, the computed indirect interactions roughly triple the island density in the case of Al (compared with neglecting all long-range interactions). Efforts to better account for the asymptotic decay in the KMC simulations further augment this effect. For Cu/Cu(111) (25 K, $F = 0.01$ ML/s, $\Theta = 5 - 10\%$), indirect interactions lead to a fivefold increase of the island density, see Fig. 2. The enhanced nucleation results from the fact that the diffusion barriers are notably larger for associating adatoms than dissociating them. Assuming pair-wise additive interactions, such *a repulsion inhibits attachment to existing islands and leads to an increased island density* compared with the same system devoid of long-range effects.

The fact that indirect long-ranged adsorbate interactions can drastically increase the island density is very interesting from another point of view. A common way of experimentally determining adsorbate diffusivities is to measure the island density and then via mean-field nucleation theory or kinetic simulations deduce the corresponding activation energy and diffusion prefactor. If long-range interactions are unaccounted for, the island

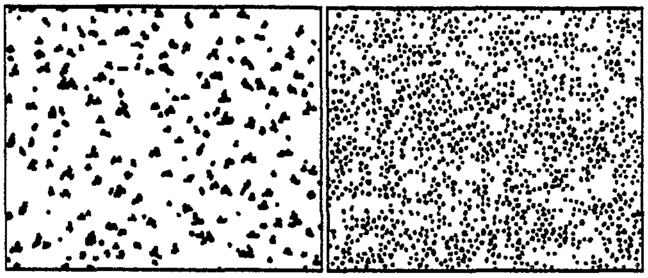

FIG. 2. KMC-computed surface morphology (500×425) Å of Cu/Cu(111) at $T = 25$ K, $F = 0.01$ ML/s, $\Theta = 5\%$ without (left) and with (right) taking into account the DFT-calculated long-range interactions [25].

density will be too low, and artifically low diffusion prefactors will be deduced this way. For example, if the island density decreases by a factor of ten because long-range interactions are neglected, the deduced prefactor will typically appear three orders of magnitude smaller than it really is. Over the last few years, a series of anomalously low (by up to ten orders of magnitude!) diffusion prefactors have been reported for weakly corrugated systems [26]. According to our analysis above, this particular class of systems is *exactly* where indirect interactions should be important. It is thus quite possible, even likely, that such anomalies are unphysical, and a mere consequence of neglecting to account for indirect interactions in the analysis of island density data.

In summary, through an extensive first-principles analysis, we have determined the nature and strength of indirect adsorbate interactions in some common systems, and shown these to strongly alter the binding and motion of otherwise isolated adsorbates. We explain where it is important to take such long-ranged interactions into account, and demonstrate via kinetic Monte Carlo simulations the strong effects they can have on surface morphology. These results also suggest that reports of anomalously low diffusion prefactors may be an artifact of neglecting indirect interactions in analyses of experimental island density data.

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