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Elastic adsorbate interactions at the mesoscale

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Abstract

We show that elastic interactions between adatoms and small islands on a surface exhibit a novel intermediate-ranged oscillatory behaviour. Taking small Fe islands on Cu(111) as an example, we perform atomic-scale simulations and reveal that elastic interactions strongly depend on the size of the islands. Stress variation on the atomic scale is found to be the driving force for the size effect in elastic interactions.

The understanding of interactions between adatoms and clusters on surfaces is a topic of fundamental interest for the fast-growing area of nanoscience. With shrinking size of nanostructures, which may approach atomic distances, the control of interactions between individual atoms becomes crucial. At small adatom separations direct electronic interactions dominate, but for intermediate and large adatom–adatom distances, substrate-mediated electronic and elastic interactions prevail [1]. Recent experiments [2, 3] and *ab initio* calculations [4] have resolved the long-range oscillatory electronic interaction between adatoms caused by the quantum interference of surface-state electrons. It has been found that adatoms may attract or repel each other, depending on the separation. Electronic interactions between adatoms and small clusters at intermediate distances have also been found to strongly affect growth processes [4–6].

The classical works of Lau and Kohn [7], and Marchenko and Parshin [8], predicted that the elastic interaction between identical adatoms on isotropic surfaces should be repulsive, with energy varying with distance as d^{-3}. Anisotropy of the substrate can lead to attraction between like adatoms [9, 10]. Recent advances in nanoscale fabrication, self-assembly and self-organization [11] of nanostructures have created renewed interest in the substrate-mediated elastic interactions between nanostructures. For example, the importance of elastic interactions for the nucleation of islands in submonolayer epitaxy has been demonstrated by means of a Monte Carlo simulation [12]. Rickman and Srolovitz [13] have found that the interaction energy between circular islands on an isotropic surface is repulsive. Recent work of Peyla *et al* [14] has shown that elastic interactions between defects in thin layers may be either attractive

or repulsive. Kukta *et al* [15] have reported that the sign of step–step elastic interactions can change with separation distance.

The main goal of this letter is to show that the elastic interactions between small supported islands at intermediate separations exhibit a novel unexpected size effect. Performing atomic-scale simulations with *ab initio*-based many-body potentials, we reveal that the driving force for the strong variation in the elastic interactions is the size-dependent stress relaxation in the substrate near the islands. Our results indicate that at intermediate distances the elastic interactions between small clusters can affect the growth process. Due to the great importance of the Fe/Cu system for material science, we concentrate in this paper on Fe clusters on Cu(111), while the main results and conclusions are of general importance.

Atomic relaxations of adatoms, clusters and the substrate were performed using a quenched molecular dynamics (MD) technique [16]. The simulation cell representing Cu(111) consists of 11 layers with 1250 atoms in each layer. Two bottom layers are kept fixed and periodic boundary conditions are applied in the two directions of the surface plane. The equilibrium configuration of the surface with adatoms (or clusters) is determined by minimizing the total energy with respect to the position of all of the atoms. During our simulations, the maximum relaxation time we used was 40 ps. The minimization procedure was stopped when the residual force on all atoms was less than 10^{-5} eV/a_0, where a_0 is the equilibrium Cu lattice constant. The relative error in the determination of the total energy is about of 10^{-7}. We performed several calculations of the elastic interactions between adatoms (and clusters) increasing both the lateral and vertical dimensions of the slab. Our results proved to be practically insensitive to these changes.

The electronic interaction between atoms is described by the many-body *ab initio* fitted potentials formulated in the framework of the second moment approximation of the tight-binding (TB) model [17–20].

The parameters of the potentials are determined by fitting to *ab initio* Korringa–Kohn–Rostoker (KKR) Green's function results [21] for surface properties. Binding energies of supported clusters of different sizes and geometries, Hellmann–Feynman (HF) forces acting on adatoms near the surface, as well as bulk properties of Fe and Cu, are accurately fitted to correctly describe interactions between atoms. The full potential approximation is used in calculations of HF forces. Parameters of the potentials for Fe/Cu(001) are given in our previous works [18]. To link the interaction between atoms near the surface to that in the bulk the set of data used for fitting includes such bulk properties as bulk modulus, lattice constant, cohesive energy and elastic constants.

Very recently we performed fully *ab initio* calculations of atomic relaxations in small magnetic clusters on a copper substrate [22]. Our results have shown that the interatomic potentials constructed as described above provide a very good approximation for atomic displacements found in *ab initio* calculations. Therefore, we believe that reliable results for atomic relaxations can be obtained using our potentials.

In the present simulations, electronic interactions described by the TB potential extend only to third-nearest-neighbour shells (the cut-off radius). Therefore, displacements of surface atoms from equilibrium positions caused by adatoms are determined by these short-range electronic interactions. As an accumulative effect of the short-range interaction, atomic relaxations in the substrate yield long-range interactions between adatoms. Note that the key point in calculations of elastic interactions between adatoms or clusters is to put them beyond the cut-off radius of the potentials used in simulations, where no direct electronic interactions can occur.

The elastic interactions between adatoms, clusters or steps on metal surfaces are usually small in magnitude (meV or smaller). Therefore, the computational approach used for

calculations of elastic interactions should be well justified. Several works on elastic interactions have demonstrated that many-body interatomic potentials give reliable results. For example, Shilkrot and Srolovitz [23] have performed atomistic simulations of the interaction energy between Ni adatoms on Ni(100) using the embedded-atom method (EAM) potentials. Results were analysed in terms of a dipole model for an adatom and were found to be in good agreement with the elastic theory. Kukta *et al* [15] have developed a new model for the elastic interaction of surface steps based on the elastic approach of Marchenko and Parshin, and Eshelby's method for calculations the interaction energy between sources of stress. They have reported an excellent agreement between the results of their model and atomistic calculations with many-body potentials. Kouris *et al* [24] have shown that the lattice discrete model based on the concept of eigenstrains and the EAM calculations give very similar results for the interaction of adatoms with steps. Very recently Prevot and Croset [25] have presented an anisotropic linear elasticity approach for computing elastic displacements and interactions due to steps for Cu, Pt(001) and (111) vicinals. The results obtained have shown a remarkable agreement with molecular dynamics simulations performed with the interatomic potentials calculated in the TB approach. Croset *et al* [26], performing a grazing incident x-ray diffraction study of the self-organized N/Cu(001) system, have demonstrated that molecular dynamics simulations with the TB potentials can explain the elastic relaxations very well. In similar simulations of Prevot *et al* [27], a good agreement with the experiments for atomic relaxations on Cu(211), Cu(322) and Pt(977) has been reported.

The above examples present clear evidence that using many-body potentials for computing elastic interactions is well justified. To our knowledge calculations of elastic interactions between transition metal adatoms and small clusters on metal surfaces are still beyond the capabilities of modern *ab initio* methods.

The elastic interaction between the two adatoms (clusters) is calculated by means of the expression $E = E_t - E_s - 2(E_1 - E_s)$, where E_t is the total energy of the slab with two adatoms (clusters), E_s is the energy of the clean slab, and E_1 is the energy of the slab with one adatom (cluster).

In order to get insight into the origin of elastic interactions we calculate atomic resolved stress in the substrate between two adatoms or clusters [28]: $\sigma_{\alpha\beta}(i) = -\frac{1}{\Omega_0}[\frac{p_i^\alpha p_i^\beta}{m_i} + \frac{1}{4}\sum_j (r_{ij}^\beta f_{ij}^\alpha + r_{ij}^\alpha f_{ij}^\beta)]$, where $(\alpha\beta) \equiv (x, y, z)$, m_i and p_i are the mass and momentum of atom i, r_{ij} is the distance between atoms i and j, f_{ij} is the force acting between atom i and atom j, and Ω_0 defines the average atomic volume. The magnitude we are interested in is the atomically resolved hydrostatic stress, i.e., $P_\sigma = \mathrm{Tr}(\sigma_{\alpha\beta})$. Forces are calculated using the TB potentials.

Our calculations for the interaction energy between Fe adatoms on Cu(111) as a function of the adatom separation are presented in figure 1. A strongly non-monotonic behaviour of the interaction energy is seen. We find that identical adatoms may either attract or repel each other depending on the direction. The maximum attraction corresponds to ⟨120⟩ and ⟨010⟩, and maximum repulsion to the ⟨100⟩ directions (the other atom is fixed at the origin).

We have also found that the repulsive interaction for ⟨100⟩ directions can be well fitted by the power law $U(d) = U_0/d^3$ predicted by continuum elasticity [8]. Results of fitting are presented in figure 1 (dotted lines). We find $U_0^{\mathrm{Fe/Cu(111)}} = 0.38$ eV Å^3. One should note that at low temperature the parameter U_0/T was found to mark the changes of island density [12], and on increasing the elastic interaction strength U_0/T, island formation is hampered and deferred to higher coverages.

Atomistic simulation of adatom–adatom interactions by means of the EAM performed by Shilkrot and Srolovitz [29] and Peralta *et al* [30] have shown that the interaction energies have a

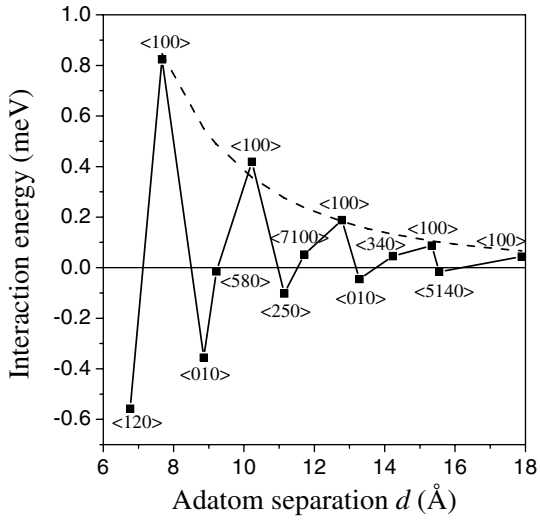

Figure 1. Energy of elastic interaction between two Fe adatoms on a Cu(111) surface as a function of adatom–adatom separation d. For each separation the corresponding crystallographic direction is shown. A fit based on the power law $U(d) = U_0/d^3$ is presented.

strong angular dependence and can change sign with angle. These results are in the agreement with the prediction of Lau [10], who reported on attractive interaction of identical adatoms in cases involving bulk anisotropy. The above findings suggested that adatom attraction is possible even for bulk isotropic materials, as long as the surface is anisotropic.

Since the interaction of adatoms has a long-range nature, it is important to verify the convergence of the simulation results with respect to the cut-off radius of the model interatomic potential. We have performed calculations with different cut-off radii ranging from 3 to 12 Å. Convergence of the interaction energy was found for cut-off radius 6 Å and larger, with an accuracy better than 0.5%.

We have found that the elastic interaction between small supported clusters strongly depends on the number of atoms in the island. As an example, we present in figure 2 our results for Fe islands on Cu(111) for intermediate separation (about 9 Å). One might wonder, why do the two dimers strongly repel each other, while two adatoms exhibit attractive interaction? For clusters bigger than the ones shown in the picture the interaction energy is repulsive and increases monotonically with the number of atoms until reaching the step size, in agreement with the classical continuum elasticity.

To understand these results, we recall our recent work on the mesoscopic scenario of strain relief in heteroepitaxy and homoepitaxy [19, 31]. We have shown that if the deposited system is of mesoscopic size, its intrinsic bond lengths are different from the bond length in the bulk material. Therefore, the strain induced at the interface can locally be much larger than that expected from the lattice mismatch of bulk materials. Our studies have revealed the strong impact of the size-dependent mismatch on the strain field. In particular, one might expect significant adsorbate-induced structural modification on the surface, which should depend on the size of the islands. This finding suggests that the size effect in the interaction energy between small clusters is caused by size-dependent stress relaxations. To verify this we have calculated the atomically resolved hydrostatic stress in the Cu substrate near small Fe clusters. The average stress per atom integrated over the surface area surrounding the clusters is shown in

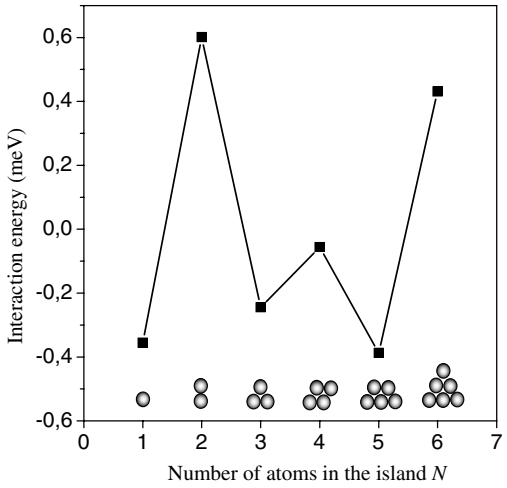

Figure 2. Energies of elastic interaction between small Fe islands on Cu(111). The island separation is 8.85 Å and the mutual island orientation corresponds to ⟨010⟩ directions.

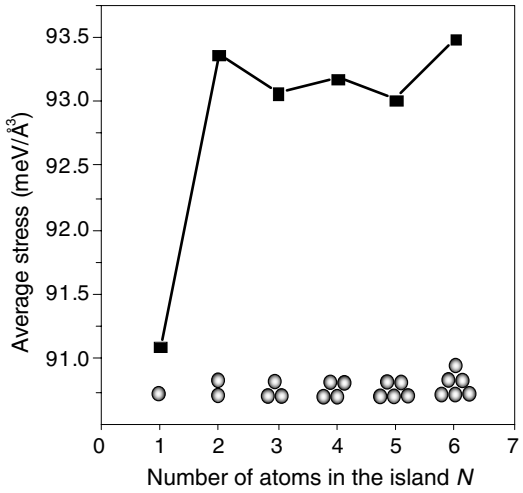

Figure 3. Average stress in the Cu(111) substrate for different small Fe islands.

figure 3.[3] Stress oscillations are found to perfectly match the oscillation in elastic interactions. To complement our interpretation of this effect we have performed a number of calculations of elastic interactions between small islands for different separations between them. As an example, we present in figure 4 the energy of elastic interaction between Fe dimers together with changes in the average stress. One can see that the stress variation very nicely corresponds to oscillations in the energy of interaction.

The above results demonstrate that elastic interactions between small islands can be much more complex than expected. The continuum approach completely fails to describe the stress relief scenario and elastic interactions between small clusters at intermediate distances.

[3] Different sizes of the area for the integration have been tested. We have found that the main contribution to the average stress comes only from the surface area near adatoms or islands.

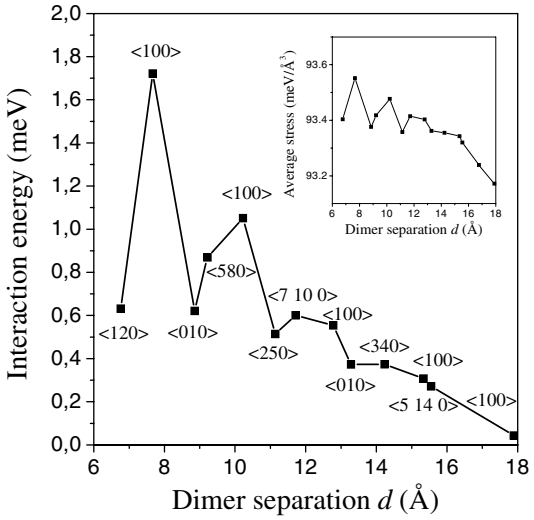

Figure 4. Energy of elastic interaction between Fe dimers supported on Cu(111) as a function of the distance between them. The inset shows the average stress.

Something that should be investigated in view of our findings is the possible impact of the elastic interactions at intermediate distances on surface morphology in the early stages of heteroepitaxy. In particular, one might expect that the repulsive interaction between small islands can hinder their coalescence at low temperature and can lead to the typical length separation between them.

We have recently performed fully *ab initio* calculations of the electronic interactions between magnetic Co adatoms on Cu(111) caused by the quantum interference of the surface-state electrons [4, 32, 33]. We have found that the interaction energy is oscillatory, with a period of $\lambda_F/2 = 15$ Å (λ_F is a surface state Fermi wavelength of Cu(111)). Calculations of the electronic interaction energies between the two adatoms for separations up to 50–60 Å have revealed that they decay as $1/d^2$. Comparison of the electronic and elastic interactions for Cu(111) shows that for the adatom–adatom separations larger than 14–15 Å the electronic interaction between Fe adatoms is more than ten times larger than the elastic one. Therefore, we believe that for large distances elastic interactions can be ignored on Cu(111). However, for intermediate distances (8–13 Å) the electronic interaction is about 1 meV (repulsive or attractive; see [4]) and, in fact, is of the same order of magnitude as the repulsive elastic interaction (0.2–0.8 meV; see figure 1). Therefore, we expect that elastic interactions at the intermediate distances may play an important role in atomistic processes.

In conclusion, we have revealed a strong size effect in elastic interactions between small transition-metal islands on Cu(111) at the intermediate distances. Size-dependent stress relaxations on the atomic scale are shown to cause this behaviour. Our work clearly shows that atomistic details need to be considered in appropriate modelling of elastic interactions between small islands. We expect that the novel intermediate-ranged oscillatory behaviour of elastic interactions reported in this letter is a general phenomenon, likely to be found in numerous other heterosystems.

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