Effects of Long-Range Interactions in Metal Epitaxial Growth

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The van der Waals constant C_3 describing the long-range attractive interaction between a Cu atom and a Cu(100) surface is calculated, along with the dominant correction z_0 for the shift in the reference plane, using expressions derived by Persson and Zaremba which take into account the optical response of Cu. The result $C_3 \simeq 2.1$ eV-$\mathring{A}^3$ is significantly smaller than predicted by a simple Lennard-Jones (LJ) Cu potential used in recent simulations, but large enough to explain experimental observations of a significant increase in mound angle in Cu/Cu(100) growth for large angles of incidence. In contrast, trajectory calculations indicate that the LJ Cu potential appears to overestimate the effects of long-range attraction. Our results also indicate that for small angles of incidence ($\theta < 50^o$), the dominant effects of attraction on the surface morphology in Cu/Cu(100) growth are related to the short-range rather than to the long-range interaction. Similar results are presented for Ag/Ag(100).

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I. INTRODUCTION

Recent experiments by van Dijken et al [1] - [3] on Cu/Cu(100) and Co/Cu(100) epitaxial growth indicate that at a high angle of incidence with respect to the substrate normal, the long-range van der Waals attraction of the surface to incoming atoms can lead to steering and shadowing effects which dramatically alter the surface morphology. These effects can lead to a strong enhancement of the mound instability as well as facetting and ripple structures. For example, recent experiments on Co/Cu(001) growth [3] have shown that grazing incidence deposition can lead to a surface anisotropy which leads to strong uniaxial magnetic anisotropy. Such a magnetic anisotropy has also been observed in a variety of other systems [4] - [7] and may play an important role in magnetic superlattices as well as in epitaxial magnetic films used in low-field sensor devices. Thus, understanding the effects of steering and shadowing in oblique incidence deposition is important since it may lead to the possibility of controlling both structural and magnetic pattern formation in epitaxial growth.

Of particular interest are recent SPA-LEED diffraction experiments on Cu/Cu(001) growth near room temperature [1], [2]. In these experiments a gradual transition with increasing deposition angle from symmetric mound structures for deposition angles up to 55°, to mounds with increasing but asymmetrical slopes for deposition angles up to 70°, to long ($500\mathring{A}$ or more) ordered parallel ripples oriented perpendicular to the beam at higher angles of incidence ($\theta \simeq 80^o$) was observed. At large angles of incidence ($\theta \simeq 80^o$), anisotropic islands were also observed in the submonolayer regime[1], [2].

In order to quantify the effects of steering due to long-range attraction in these experiments, van Dijken et al [1], [2] carried out molecular dynamics simulations of single-atom trajectories near a monatomic step-edge using a Lennard-Jones (LJ) pair-potential for copper developed by Sanders and DePristo [8] of the form,

$$\phi(r) = 4\epsilon[(\frac{\sigma}{r})^{12} - (\frac{\sigma}{r})^6] \quad (1)$$

where $\epsilon = 0.4093$ eV and $\sigma = 2.338$ Å. Such a potential matches the lattice constant and cohesive energy of copper and has also recently been used [9] in combined molecular dynamics and kinetic Monte Carlo simulations in order to try to explain the submonolayer island anisotropy [1], [2] observed in the case of grazing incidence growth of Cu/Cu(100).

For normal incidence deposition and short-range interactions, the use of the two-body potential (1) may be justified by the fact that Sanders and DePristo [8] found that atom trajectory calculations for normal incidence deposition on a flat Cu(100) surface were satisfactorily close to calculations with their most accurate many-body density-functional-theory (DFT) based potential energy surface. However, neither the LJ potential nor the more accurate DFT potential are expected to accurately predict the strength of the long-range van der Waals interaction. Therefore, in order to accurately model deposition at grazing incidence, it is important to carry out a direct calculation of this interaction.

Here we present the results of calculations of the long-range van der Waals attraction for Cu/Cu(100) and Ag/Ag(100) based on expressions derived by Zaremba and Kohn (ZK) [10] and Persson and Zaremba (PZ) [11]. Our results for Cu/Cu(100) indicate that the van der Waals attraction is significantly weaker than predicted by the LJ Cu potential (1). However, they also indicate that it is sufficiently strong to lead to significant steering effects at large angles of incidence with respect to the substrate normal. In particular, we have derived
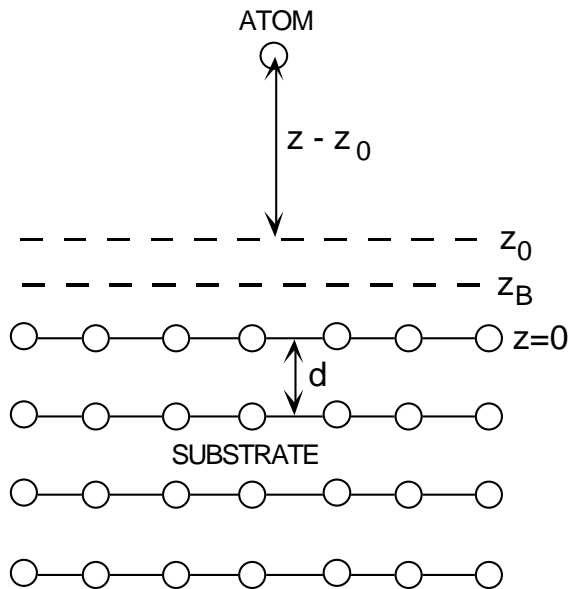
FIG. 1: Schematic showing interaction between atom and substrate. z_0 is height of reference plane above last plane of atoms while z_B corresponds to edge of positive background.

an expression for the deviation of an incoming atom approaching a flat substrate as a function of the strength of the van der Waals interaction, its height above the surface, its initial kinetic energy and its angle of incidence. Using this expression along with our calculated value for the van der Waals constant C_3 for Cu/Cu(100) we find, in good agreement with experiment [1], that for normal incidence and for angles up to approximately 55°, the long-range attraction has very little effect on the trajectory of an incoming particle. However, for larger angles of incidence, the effects of steering due to the long-range interaction become significant. These results, along with similar results obtained for Ag/Ag(100), also indicate that for small angles of incidence with respect to the substrate normal, the dominant effects of attraction on epitaxial growth are due to short-range rather than long-range attraction.

II. CALCULATION OF VAN DER WAALS INTERACTION

To leading order, the long-range van der Waals interaction between a neutral atom and a solid surface may be written [10], [12],

$$V(z) = -\frac{C_3}{(z - z_0)^3} \quad (2)$$

where z is the height of the atom above the surface and z_0 is a shift in the reference plane above the substrate. Following Zaremba and Kohn [10] an expression for the van der Waals constant C_3 may be written,

$$C_3 = \frac{1}{4\pi} \int_0^\infty du\ \alpha(iu)\ \frac{\epsilon(iu) - 1}{\epsilon(iu) + 1} \quad (3)$$

where $\epsilon(iu)$ is the frequency-dependent dielectric constant of the solid and $\alpha(iu)$ is the frequency-dependent atomic polarizability of the neutral atom. The latter may be expressed in terms of a sum over the oscillator strengths f_{0n} and excitation energies ω_{0n} of the neutral atom as follows [13],

$$\alpha(iu) = \sum_n \frac{f_{0n}}{u^2 + \omega_{0n}^2} \quad (4)$$

By considering the dominant $1/z^4$ correction, an expression for the reference plane position z_0 (see Fig. 1) may also be obtained [10],

$$z_0 = \frac{1}{4\pi C_3} \int_0^\infty du\ \alpha(iu)\ \frac{\epsilon(iu) - 1}{\epsilon(iu) + 1}\ d_{IP}(iu) \quad (5)$$

where $d_{IP}(iu)$ is the position of the frequency-dependent induced image plane.

Using a jellium model, Zaremba and Kohn obtained an explicit expression for the constant C_3 of the form,

$$C_3 = \frac{1}{8} \sum_n \frac{f_{0n}\ \omega_{sp}}{\omega_{0n}(\omega_{0n} + \omega_{sp})} \quad (6)$$

where $\omega_{sp} = \omega_p/\sqrt{2}$ is the surface plasmon frequency. Assuming that the position of the induced image plane corresponds to the centroid of induced charge, an expression for the ratio of the distance $z_0 - z_B$ of the reference plane from the edge of the uniform positive background to the distance $z_c - z_B$ of the center of mass of the induced surface charge density to the edge of the uniform positive background was also obtained,

$$\frac{z_0 - z_B}{z_c - z_B} = \frac{1}{16 C_3} \sum_n \frac{f_{0n}\ \omega_{sp}}{\omega_{0n}(\omega_{0n} + \omega_{sp})} \frac{\omega_{0n} + 2\omega_{sp}}{\omega_{0n} + \omega_{sp}}. \quad (7)$$

A recent comparison of the Zaremba-Kohn results [10] with modified density functional theory (DFT) calculations [14] for an atom interacting with jellium which were extended to take into account the van der Waals interaction has shown relatively good agreement for several different neutral atoms. Therefore, we expect Eqs. (6) and (7) to provide reasonably accurate estimates of the van der Waals attraction in metal-on-metal epitaxial growth.

However, more recently it has been shown [15] that a more general expression for the position of the frequency-dependent induced image plane may be written,

$$d_{IP}(iu) = \frac{d_{||}(iu) + \epsilon(iu)d_\perp(iu)}{1 + \epsilon(iu)} \quad (8)$$

where $d_\perp(iu)$ is the centroid of the induced surface charge due to a uniform external electric field normal to the

TABLE I: Parameters characterizing the optical response in Cu and Ag (from [11]).

	r_s	$\frac{m_{opt}}{m}$	ω_0	Ω
Cu	2.67	1.5	0.3458	0.7481
Ag	3.02	0.96	0.5443	1.001

surface and $d_{||}(iu)$ reflects the spatial distribution of currents induced parallel to the surface by a tangential electric field. Using this expression along with a more accurate model for the dielectric constant $\epsilon(iu)$ for the noble metals based on the measured optical response, Persson and Zaremba [11] obtained improved expressions for $d_{IP}(iu)$ and $\epsilon(iu)$. In particular, they assumed that the dielectric constant may be written $\epsilon(iu) = 1 + \epsilon_f(iu) + \epsilon_b(iu)$ where the intraband (free-electron) contribution has the form,

$$\epsilon_f(iu) = \frac{\omega_{pf}^2}{u^2} = \frac{m}{m_{opt}} \frac{\omega_p^2}{u^2} \qquad (9)$$

while the interband (bound-electron) contribution $\epsilon_b(iu)$ has the form,

$$\epsilon_b(iu) = \frac{\Omega^2}{u^2 + \omega_0^2} \qquad (10)$$

In addition, Persson and Zaremba assumed that one may write,

$$d_\perp(iu) = \frac{\epsilon_f(iu)d_\perp^f(iu) + \epsilon_b(iu)d_\perp^b(iu)}{\epsilon_f(iu) + \epsilon_b(iu)} \qquad (11)$$

where $d_\perp^f(iu)$ corresponds to the centroid of the free-electron component while $d_\perp^b(iu)$ corresponds to the centroid of the bound-electron component. To a good approximation one may take $d_\perp^b(iu) \simeq d_{||}(iu) \simeq z_B$ (where z_B is the position of the edge of the positive background) and $d_\perp^f(iu) \simeq z_c'$ where $z_c' - z_B$ corresponds to the position of the center of mass of the induced surface charge density relative to the positive-charge background calculated using the corrected density $r_{sf} = (3/\omega_{pf}^2)^{1/3}$ rather than the free-electron value. The position of the edge of the positive background z_B is typically assumed to be equal to one-half of the interplane spacing which implies for the (100) surface of an fcc crystal $z_B = a/4$ where a is the lattice constant. Thus, using the tabulated parameters for Cu and Ag shown in Table I [11], along with the known excitation energies and oscillator strengths, we expect that reasonably accurate estimates for the van der Waals constant C_3 and reference plane position z_0 may be obtained.

Table II shows the excitation energies and oscillator strengths for the first excited state transition $4s \rightarrow 4p_{1/2}$ and second excited state transition $4s \rightarrow 4p_{3/2}$ for atomic Cu in atomic units obtained from semi-empirical calculations [16] along with the corresponding surface plasmon

frequency for bulk Cu based on the free-electron density. We note that the oscillator strengths for transitions to higher excited states are significantly smaller and so may be neglected. Also shown is our result for the van der Waals constant C_3 calculated using the PZ expressions (3), (9), and (10). For comparison, the approximate result C_3^{ZK} calculated using the Zaremba-Kohn expression (6) is also shown. As can be seen there is relatively good agreement between the two results, although the ZK result is approximately 10% lower than the more accurate PZ result. Converting the latter from atomic units, we obtain for Cu,

$$C_3 = 2.1 \ eV - \mathring{A}^3 \qquad (12)$$

In order to compare this result with the long-range attractive $(-C_6/r^6)$ LJ Cu pair potential [8] in Eq. 1 we may integrate the latter over a semi-infinite slab. Doing this for an fcc metal, we find $C_3 = (\frac{2\pi}{3a^3})C_6$ where a is the lattice constant of the metal. For the LJ Cu interaction ($C_6^{LJ} = 4\epsilon\sigma^6 \simeq 267$ eV-A^6) this implies $C_3^{LJ} = 11.9$ ev-A^3. Thus our calculated value for the van der Waals interaction C_3 is almost 6 times smaller than the equivalent LJ Cu interaction [8] used in the molecular dynamics simulations of Refs. [1] and [9]. Alternatively, we may note that the corresponding effective van der Waals pair interaction $C_6 \simeq 47.2$ eV-A^6 is significantly smaller than the LJ Cu pair interaction $C_6^{LJ} \simeq 267$ eV-A^6. Thus, our results indicate that while the long-range attraction may be significant at large angles of incidence, it is significantly weaker than the LJ Cu potential given by (1).

We now consider the position of the reference plane z_0. Interpolating the results of Lang and Kohn [17] for $z_c - z_B$ as a function of r_s, we obtain $z_c - z_B \simeq 1.5$ a_0 for Cu. Using the ZK expression (7) along with the assumption that $z_B = a/4 \simeq 0.9\mathring{A}$ for the (100) surface of copper, we obtain $z_0^{ZK} \simeq 3.0$ $a_0 \simeq 1.6\mathring{A}$ for Cu/Cu(100) as shown in Table II. Similarly, calculating the corrected density $r_{sf} \simeq 3.05$ a_0 for Cu and again interpolating the results of Lang and Kohn [17], we obtain $z_c' - z_B \simeq 1.44$ a_0. Using Eq. 5 we obtain $z_0 \simeq 2.6$ $a_0 \simeq 1.4\mathring{A}$ as shown in Table II. Combining this result with our estimate $C_3 \simeq 2.1$ eV-$\mathring{A}^3$ leads to an estimate for the van der Waals energy correction at the typical short-range potential cutoff distance $z = 2 - 3$ σ from the Cu(100) surface given by $\Delta E_c \simeq 0.012 - 0.059$ eV. This is significantly smaller than the correction $\Delta E_c \simeq 0.03 - 0.12$ eV based on the Lennard-Jones pair-interaction used in Ref. [1] and is a relatively small fraction of the typical average incident kinetic energy $K_i = 2kT_m \simeq 0.23$ eV (where $T_m = 1356$ K is the melting temperature of copper) of an incoming Cu atom in epitaxial growth. Thus our results suggest that at normal incidence the van der Waals attraction provides a relatively small contribution to the uphill steering of atoms deposited at a step-edge.

Motivated in part by recent experiments on epitaxial growth of Ag [18], [19] we have also carried out a similar calculation of the van der Waals attraction of a Ag atom approaching a Ag(100) surface (see Table II). In

TABLE II: Excitation energies and oscillator strengths along with van der Waals constant C_3 and reference plane position z_0 in atomic units.

	ω_{01}	f_{01}	ω_{02}	f_{02}	ω_{sp}	C_3^{ZK}	C_3	z_0^{ZK}	z_0
Cu	0.139	0.263	0.140	0.530	0.281	0.47	0.52	3.0	2.6
Ag	0.135	0.22	0.139	0.46	0.233	0.39	0.46	3.1	2.9

this case the first and second excited state transitions correspond to the $5s \to 5p_{1/2}$ and $5s \to 5p_{3/2}$ transitions while experimental values for the transition energies and oscillator strengths (Refs. [20] - [22]) were used. As can be seen in Table II, the van der Waals constant C_3 for Ag/Ag(100) is comparable to but somewhat smaller than that for Cu/Cu(100). Interpolating as before the results of Lang and Kohn [17] to obtain z_c and z_c', we obtain for Ag/Ag(100), $z_0^{ZK} \simeq 3.1 \, a_0$ as well as the PZ result $z_0 \simeq 2.9 \, a_0 \simeq 1.5 \mathring{A}$. Thus our results indicate that a significant van der Waals attraction exists for both Ag/Ag(100) and Cu/Cu(100). While such an attraction may not not have a significant effect at normal incidence, it is likely to have a significant effect at off-normal incidence as we discuss below.

III. EFFECTS OF VAN DER WAALS INTERACTION ON TRAJECTORY

While detailed growth simulations are needed to determine the effects of the van der Waals attraction on the surface morphology in epitaxial growth, we can estimate the general dependence on the incidence angle by considering the trajectory of an atom approaching a flat substrate (see Fig. 2). Using Eq. (2) along with conservation of energy we have derived an expression for the deviation Δx from a ballistic trajectory of an incident atom (see Fig. 2) as a function of C_3, the incident kinetic energy K_i, the angle of incidence θ with respect to the substrate normal, and the height z above the surface,

$$\Delta x = (1/3) \, tan\theta \, B^{1/3} \int_0^{B/(z-z_0)^3} [1 - \frac{1}{(1+u)^{1/2}}] \frac{du}{u^{4/3}} \tag{13}$$

where $B = C_3/K_i cos^2\theta$.

In order to study the effects of the van der Waals attraction on the trajectory in Cu/Cu(100) deposition, we have numerically integrated Eq. 13 for the deviation $\Delta x/\sigma$ at a height $z = 2.5 \, \sigma$ above the Cu(100) substrate (corresponding to $z - z_0 \simeq 2\sigma$ where the short-range interaction becomes important) of a Cu atom with typical incident thermal kinetic energy $K_i \simeq 0.23$ eV, as a function of deposition angle θ. For comparison, our calculations were carried out using both the calculated value $C_3 \simeq 2.1$ eV-$\mathring{A}^3$ given by Eq. 12 (solid symbols) as well as the effective LJ Cu potential prediction $C_3^{LJ} \simeq 11.9$ eV-$\mathring{A}^3$ with $z_0 = 0$. We note that a recent comparison with density functional calculations [23] indicates that

in some cases Eq. 5 may slightly overestimate (by approximately 20% - 30%) the shift in the reference plane. Therefore, the deviation $\Delta x/\sigma$ was calculated both for the case of no shift in the reference plane ($z_0 = 0$) as well as using our calculated value $z_0 \simeq 1.4 \mathring{A}$.

As can be seen in Fig. 3, using the calculated value for C_3 given by Eq. 12, we find that significant deviations from a ballistic trajectory (i.e. $\Delta x/\sigma \simeq 0.1$ or larger) occur near the surface for angles of incidence larger than approximately 50°, while for smaller angles of incidence the deviations are negligible. These results are in good qualitative agreement with the experimental observation [1], [2] that the mound slope is relatively unaffected by the deposition angle for deposition angles less than 55° but increases continuously for deposition angles between 55° and 70°. In contrast, the corresponding results obtained using the significantly larger value $C_3^{LJ} \simeq 11.9$ eV-$\mathring{A}^3$ predicted by the LJ Cu potential (open symbols), indicate a significant deviation at much lower angles ($\theta \simeq 30^o$) for which deviations in the experimental mound slope due to oblique incidence are not observed. Thus, a comparison between our Cu/Cu(100) trajectory results and experiments [1] appears to support our prediction that the van der Waals constant C_3 is significantly smaller than predicted by the LJ Cu potential (1). These results also indicate that for small angles of incidence, the dominant effects of attraction at step-edges are due to the short-range attraction [24].

IV. CONCLUSIONS

Our results for the van der Waals constants C_3 and z_0 for Cu/Cu(100) and Ag/Ag(100) indicate that for the case of normal incidence, the dominant contribution to steering effects during growth is due to the short-range interaction. This supports recent results we have obtained [24] for the effects of short-range attraction on the surface morphology in Cu/Cu(100) and Ag/Ag(100) growth at normal incidence and we expect that this will be the case generally in metal epitaxial growth. However, as observed experimentally, at high angles of incidence the long-range attraction may play an important role since in this case the van der Waals energy near the surface becomes comparable to (or even larger than) the component of incident kinetic energy normal to the surface. In particular, our trajectory calculations for Cu/Cu(100) indicate that, in agreement with experiment, the effects of the long-range attraction on the trajectory will become particularly important for $\theta > 55^o$, while for smaller angles of incidence such effects may be neglected. Our calculated values for C_3 and z_0 for Ag/Ag(100) are close to those obtained for Cu/Cu(100). Therefore, we expect that similar behavior will also be observed for Ag/Ag(100) deposition. Finally, we note that while density-functional theory calculations may provide improved estimates for the van der Waals constants, we expect that the results presented here al-

ready provide reasonable estimates, especially for the van der Waals constant C_3. In the future we plan to carry out multiscale simulations of growth at high angles of incidence in order to study the combined effects of both short-range and long-range interactions on the surface morphology.

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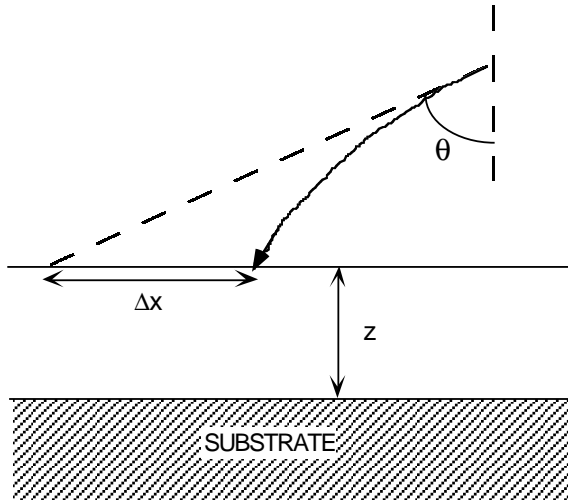FIG. 2: Schematic showing deviation Δx from a ballistic trajectory due to van der Waals attraction at a height z above the substrate.
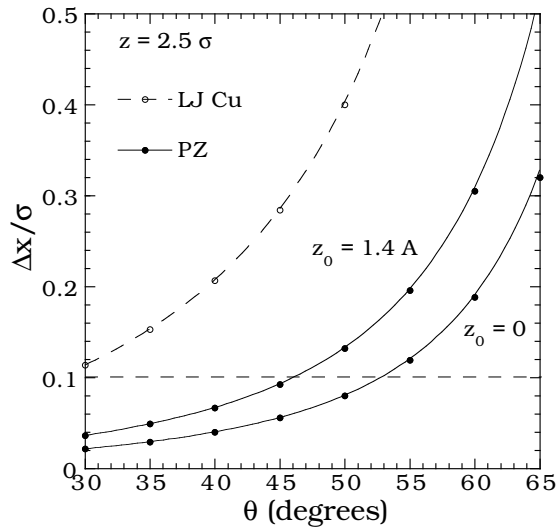

FIG. 3: Deviation from a ballistic trajectory at height $z = 2.5\ \sigma$ obtained by numerically integrating (13) for an atom with $K_i = 0.23$ eV as a function of incidence angle θ. PZ refers to results obtained using Eq. 5 while LJ Cu refers to results obtained using (1).