ROUGHENING OF THE Cu(110) SURFACE

J. Merikoski, H. Häkkinen, M. Manninen and J. Timonen

Department of Physics, University of Jyväskylä, P.O. Box 35
FIN-40351 Jyväskylä, Finland

K. Kaski

Tampere University of Technology, P.O. Box 692
FIN-33101 Tampere, Finland

and

Research Institute for Theoretical Physics, P.O. Box 9
FIN-00014 University of Helsinki, Finland

Abstract

The structure of the Cu(110) surface is studied at high temperatures using a combination of lattice-gas Monte Carlo and molecular dynamics methods with identical many-atom interactions derived from the effective medium theory. The anisotropic six-vertex model is used in the interpretation of the lattice-gas results. We find a clear roughening transition around $T_R = 1000$ K, and $T_R/T_M = 0.81$. Molecular dynamics reveals the clustering of surface defects as the atomistic mechanism of the transition and allows us to estimate characteristic time scales. For the system of size 50x50, the time scale of the local roughening at 1150 K of an initially smooth surface is of the order of 100 ps.
I. INTRODUCTION

Thermal disorder of fcc(110) metal surfaces has attracted considerable theoretical and experimental interest during the past few years. Due to its high structural and energetic anisotropy, this surface provides an intriguing case where a number of competing disordering mechanisms can be found. Roughly speaking, the (110) surfaces can be divided into two categories. Metals such as Cu and Ni preserve their bulk-terminated (1x1) structure as the ground state, consisting of nearest neighbour chains separated by the conventional fcc lattice constant. On the other hand, 5d metals Ir, Pt and Au have the tendency of forming the so-called (1x2) missing-row reconstructed structure or even further a (1xn) micro-faceted structure, where only every n:th chain is left in the first crystal layer, and the surface profile has (111) facets in the atomic scale. For the non-reconstructed case, we can choose copper as the prototype.

Anomalous increase of disorder has been observed at Cu(110) between 500 K and 1000 K by using X-ray and helium diffraction methods, low-energy ion scattering and inverse photoemission (IPE), low-energy electron diffraction (LEED), high-resolution electron-energy-loss spectroscopy (HREELS) and, most recently, the impact-collision ion-scattering spectroscopy (ICISS). It is now generally accepted that strongly anharmonic vibrations of surface atoms (anomalous Debye-Waller effect) are responsible for the increase of disorder at the surface above 550 K. It has been conjectured that these vibrations induce a roughening transition where the lattice structure of the surface is preserved, while the height-height correlations between the surface atoms diverge logarithmically. This was the initial conclusion from the X-ray diffraction experiments by Mochrie, who estimated the lower bound of the transition temperature $T_R$ to be 870 K. This result was later criticized by Zeppenfeld et al. who showed that the line shape of the specularly reflected thermal helium beam is not consistent with a rough surface with logarithmic height-height correlations up to 900 K. By extending the measurements recently up to 1200 K, they find in fact that $T_R = 1070$ K. Also Dürr et al. have recently observed structural changes above 1000 K, the nature of
which remains unclear. It has been known for a long time that the (110) surface is missing from the equilibrium crystal shape of copper just below the melting temperature \( T_M \) but the nature of the disordering mechanism has not been known for the temperature range of 1000 K up to \( T_M \). Specifically, the possible existence of both the roughening and the surface premelting transitions,\(^1\) as well as their possible mutual interactions, have not been resolved.

The fcc(110) face is the most open one among the low-index faces of fcc lattice, with a structure resembling the (more open) stepped (113),(115),... surfaces. The basic excitation of a stepped surface is a kink on the step edge, whereas at a low-index face, roughening is induced by formation of vacancies and adatoms or excitations with a still higher energy.\(^2\) In the limit of very large anisotropy, the anisotropic BCSOS (body-centered solid-on-solid) model of the fcc(110) face and the terrace-step-kink model of high-index surfaces become equivalent.\(^3\) In the case of copper (110) surface, anisotropy is not very large, and its roughening is best described by that of a low-index face. This kind of roughening has been described by various Monte Carlo simulations on lattice-gas and solid-on-solid models.\(^4\) Recently, molecular dynamics simulations using many-atom interactions have shown pronounced disorder and finally premelting of the (110) surface of Al, Ni, Au and Cu.\(^5\) Identification of the rough phase is difficult in the molecular dynamics simulations, however, because tractable sample sizes and simulation times preclude the identification of a logarithmic behaviour of the height-height correlation function.

In this paper we use a new theoretical approach to investigate the roughening of the Cu(110) surface. By extracting the interatomic interactions from the well-tested effective-medium theory,\(^6\) the structure of the Cu(110) surface at high temperatures is studied by means of both the lattice-gas Monte Carlo (LGMC) and molecular dynamics (MD) simulations with comparable system sizes.\(^7\) A brief account of the results was already given in Ref.\(^8\) but here we shall give a detailed description of the method and of the various results it can provide.

In the LGMC simulations we identify the rough phase from the behaviour of the height-
height correlation function

\[ G(\vec{r}) = \langle (h(\vec{0}) - h(\vec{r}))^2 \rangle , \quad (1.1) \]

where \( h(\vec{r}) \) is the height of the surface at point \( \vec{r}=(x,y) \). Below the roughening temperature \( T_R \), the interface width is finite with a finite correlation length, while at and above \( T_R \) the correlation function diverges logarithmically,

\[ G(\vec{r}) \sim 2A(T) \ln r + c ; \quad T \geq T_R . \quad (1.2) \]

At the transition point the coefficient \( A \) has the universal value \( A(T_R)=1/\pi^2 \).

Using the LGMC model we find a clear roughening transition around 1000 K. The dynamics of the rough surface is studied via MD simulations employing the same interactions as used in the LGMC method. The LGMC results are qualitatively similar to the MD results which include the effects of lattice vibrations and relaxation. Furthermore, the atomistic mechanism of the roughening is found through MD to be the creation of defect clusters of vacancy and adatom type, and the relevant time scales can also be estimated. It is noteworthy that the estimated \( T_R \) is, for the first time, in a realistic temperature range in comparison with the previously calculated (by MD) surface premelting and bulk melting temperatures for the same interatomic potential.

The paper is organized as follows. Section II describes the models which have been employed, and gives a technical description of our simulations, including also a discussion of the effects of the inherent differences between our LGMC and MD models. The determination of the roughening temperature by LGMC simulations is described in Section III. In Section IV we discuss the results of the MD simulations, found by following the evolution of the surface from a smooth to a locally rough phase. We follow in particular the time evolution of the occupation numbers of the surface layers and of the cluster distributions, and atomic diffusion. Our conclusions are given in Section V.
II. MODELS AND METHODS

The effective medium theory (EMT) is an approximative method for calculating the total energy of an arbitrary arrangement of metal atoms. EMT relates the energy of an atom in metal to the local electron density and, therefore, implicitly includes many-atom effects. It gives a reasonable description of a number of surface properties including surface relaxation, reconstruction and phonon spectra. We have extended the interaction range in EMT to the third nearest neighbours in the fcc copper lattice as outlined in Ref. 16. These interactions have been used in both the lattice-gas Monte Carlo and the molecular dynamics simulations.

A. Lattice-gas Monte Carlo simulations

In our Monte Carlo simulations we use a face-centered cubic lattice-gas model with many body interactions derived from EMT in the form of a function \( E = E(C_1, C_2, C_3) \), where \( C_j \) is the number of the \( j^{th} \) neighbours for an atom in the lattice. In Fig. 1 we show \( E \) as a function of \( C_1 \) and \( C_2 \) with \( C_3 = 2C_1 \). The broken curve is the derivative \( dE/dC_1 \) or the energy cost of a broken nearest neighbour bond. We also show in this figure the simplest possible pair interaction model (dotted line) that is normalized such as to produce the right cohesive energy in a perfect lattice and zero energy at zero coordination. The basic excitation energies at Cu(110) are about 2.5 times higher in the pair interaction model than in the EMT.

The EMT lattice-gas Hamiltonian can be written in the form

\[
H - \mu N = \sum_i n_i [E(C_{1i}, C_{2i}, C_{3i}) - v_i - \mu],
\]

where \( n_i = 0, 1 \) is the occupation number of the lattice site \( i \), \( C_{ji} \) is the number of its \( j^{th} \) neighbours and \( \mu \) is the chemical potential. The external potential \( v \) is needed for the formation of an interface in the lattice-gas model. We have assumed the form \( v_i = a \) for the first layer, and \( v_i = bz_i^{-3} \) for the other layers, where \( z_i \) is the distance of the lattice site \( i \) from
the ‘substrate’ or, equivalently, the layer number \( z_i = 1, 2, \ldots \). With our choice \( a = 6000 \text{ K} \) and \( b = 9000 \text{ K} \) the formation of the first ‘adsorption layer’ is essentially two-dimensional and the bulk limit is reached for \( z_i \approx 10 \).

For comparison with our lattice gas results, we have also mapped the lattice gas interface to an anisotropic six-vertex solid-on-solid model or the BCSOS model. A schematic picture of the fcc(110) face seen from above, and its mapping to the six-vertex model, are shown in Fig. 2. In Fig. 2a, the black dots denote surface atoms at level 0 and the open symbols with + and − are surface atoms at levels +1 and −1, respectively. The corresponding vertex configuration is also shown. The energy parameters of this model are determined from the surface excitation energies of EMT. The energy cost of broken bonds, \( \epsilon_1 = \epsilon_2 \) in the nearest neighbour direction and \( \epsilon_3 = \epsilon_4 \) in the next nearest neighbour direction, are found from the energy function \( E = E(C_1, C_2, C_3) \) for a coordination corresponding to the uppermost atom layer for which \( C_1 \approx 7 \) and \( C_2 \approx 4 \). These energies are then scaled such as to reproduce the right energy for an adatom-vacancy pair on an otherwise flat face. In this way we find for the vertex energies: \( \epsilon_1 = \epsilon_2 = 1485 \text{ K} \) (the derivative of \( E \) with respect to \( C_1 \)), \( \epsilon_3 = \epsilon_4 = 322.5 \text{ K} \) (the distance between the curves for different \( C_2 \) in Fig. 1), and \( \epsilon_5 = \epsilon_6 = 0 \). The model is in fact a pair potential model with an energy scale derived from a many-atom model. Notice that no external potential is needed here to define the location of the interface.

The exact transition temperature \( T_R \) in the thermodynamical limit of the six-vertex model is given by

\[
\Delta(T_R) = -1; \quad \Delta(T) = (a^2 + b^2 - c^2)/2ab,
\]

where \( a = \exp(-\epsilon_1/kT), \ b = \exp(-\epsilon_3/kT) \) and \( c = \exp(-\epsilon_5/kT) \). Using the energy parameters given above, the roughening temperature of the EMT six-vertex model in the thermodynamical limit is \( T_R^{6v}(L \to \infty) = 1090 \text{ K} \). The behaviour of the coefficient \( A \) defined in Eq. (1.2) is also known exactly as a function of temperature,

\[
A(T) = \left[ \frac{1}{2} \pi^2 - \pi \arcsin \Delta(T) \right]^{-1}
\]
\[ = \frac{1}{\pi^2} + (T - T_R)^{1/2}[a_1 + a_2(T - T_R) + ...] . \]

In Eq. (2.3), the value of \( A \) at the transition point, \( A(T_R) = \frac{1}{\pi^2} \), is universal. We will use the leading square root (Kosterlitz-Thouless) behaviour near \( T_R \) of coefficient \( A \) in interpreting the results of our many-body-lattice-gas Monte Carlo calculations.

It is evident from Eq. (2.2) that the critical temperature of the six-vertex model depends on two parameters, the energy scale parameter \( \epsilon = \epsilon_1 - \epsilon_5 \), and the anisotropy of vertex energies \( \nu = (\epsilon_3 - \epsilon_5)/(\epsilon_1 - \epsilon_5) \). In our parametrization the anisotropy ratio is \( \nu = 0.217 \).

In Ref. [27] the vertex energies were determined from surface energies \( \sigma_{110}, \sigma_{100}, \sigma_{111} \), and the anisotropy ratio was found to be \( \nu = (\sigma_{111}\sqrt{3/2} - \sigma_{110})/(\sigma_{100}\sqrt{2} - \sigma_{110}) \). In our EMT lattice-gas model this method of defining the vertex energies would give \( \nu = 0.141 \). This value is still much higher than the value \( \nu = 0.080 \) obtained in Ref. [27] from the relaxed surface energies of the embedded atom method. In that work the low \( \nu \) value leads to a much lower estimate for the critical temperature. This discrepancy is mainly caused by the difficulty in including in the energy scales of a pair interaction model the many-body effects of the true interactions. Simulations with realistic many-atom interactions are thus really needed to settle this question. We shall show below that, just above \( T_R \), typical excitations at the Cu(110) surface are not large (100) or (111) facets, but monoatomic steps with a temperature dependent kink density. This behaviour indicates that the effects on the surface excitation energies of both many-atom forces and relaxation are very complicated.

We use the method of equilibrium Monte Carlo simulations, which is known\textsuperscript{28} to be suitable for lattice-gas and solid-on-solid models. The many-body nature of the Hamiltonian Eq. (2.1), and the extension of the interactions up to third neighbours in the lattice-gas model, increases the computation time by approximately a factor of 20 in comparison with the pair potential model we have also used. The lengths of the runs varied from a few thousand (for isotherms) to 500000 Monte Carlo steps per lattice site, for systems of size \( L^2 \) with \( 12 \leq L \leq 196 \).
B. Molecular dynamics simulations

The lattice-gas model discussed above lacks two major physical features. First, there is no real physical time connected with the evolution in the lattice. Second, the effects of lattice vibrations and surface relaxation are ignored. To study these effects we have performed large-scale molecular dynamics simulations employing the same interaction potential from which the site-site interaction energies are calculated for the LGMC model. This potential is fully documented in a previous work on surface premelting.\textsuperscript{16}

Our sample consists of 8 dynamical (110) layers on top of 4 static substrate layers, with either 30 close-packed [110] rows of 30 atoms or 50 rows of 50 atoms. The number of dynamical atoms is then 7200 and 20000 in the smaller and the larger sample, respectively. The dynamics is realized by the Nosé-Hoover canonical thermostat.\textsuperscript{29} This method is a natural choice in our simulations since, throughout this work, we wish to compare the molecular dynamics results with those of the LGMC model, the lattice configurations of which are generated at constant temperature. The lattice parameter of the substrate is adjusted such as to correspond to the simulated temperature as defined from the thermal expansion produced by the interaction potential. The equations of motion are integrated by using the velocity-Verlet algorithm,\textsuperscript{30} which has been modified to handle the thermostat equations.\textsuperscript{16} Due to the good stability of the algorithm, we have been able to use a large time step of 14 fs, which is roughly a tenth of the Debye period for copper. The large number of atoms in MD requires special methods for selecting the pairs of atoms for which the interactions are calculated. The method we have used is described in the Appendix.

The results which we shall report in this paper are those for temperatures $T = 1100$ K and $T = 1150$ K. In the $T = 1150$ K case we shall analyse a pair of runs, one initiated from a rough lattice-gas configuration generated by the LGMC model with a number of atoms corresponding to full layers (run A, 30x30 sample, length 406 ps), and the other initiated from an undefected smooth surface (run B, 50x50 sample, length 616 ps). At $T = 1100$ K we have made only a single run (run C, 50x50 sample, length 560 ps), initiated from the
undefected smooth surface. The reason for studying these temperatures is that, according to the LGMC results, they are within the range where the surface is rough but not yet premelted (the surface premelting of Cu(110) occurs in our MD model at $T \geq 1200 \text{ K}$). We have also made some simulations at lower temperatures, but due to the slowing down of diffusion, the statistics for the defect clusters becomes poor.

C. Inherent differences of the LGMC and MD models

In our LGMC simulations the energy function $E$ is derived from the effective medium theory by using the bulk lattice constant at zero temperature. In the lattice-gas model there is no surface relaxation, but its effect on the transition temperature can easily be estimated by comparing the energy of the basic excitation of the unrelaxed lattice-gas model with that at the relaxed surface. The inward relaxation means higher electron density or effectively higher coordination, and thus decrease in the slope of the energy function of Fig. 1. In our lattice-gas model we therefore overestimate the excitation energies and, consequently, the roughening temperature of Cu(110), by about 5%. This estimate will be used in determining our final estimate for $T_R$.

In the LGMC energy function the effect of thermal expansion is not included, but this effect is in most part included in our estimate of the relaxation effects on the roughening temperature given above. A more fundamental difference between the two models is the fluctuating particle number in the LGMC simulations vs. the fixed particle number in the MD simulations. In practice this difference leads to a much slower sampling of uncorrelated lattice configurations in the MD simulations. In the MD simulations the interaction potential has been smoothened at the cutoff radius (between the 3$^{rd}$ and 4$^{th}$ neighbours) as described in the Appendix of Ref. 16. This has been done in such a way that effectively (through indirect interactions) increases the anisotropy, and thus lowers the roughening temperature of our MD model. We only note here that the way of cutting the interaction range in MD simulations can have a considerable effect on such surface properties that are very sensitive
to the strength of the interaction beyond the nearest neighbours. This is evident from the
discussion of the missing-row reconstruction given in Ref. 21.

III. MC RESULTS

Calculated height-height correlation functions for the lattice-gas system with \( L = 96 \) and
for the six-vertex system with \( L = 50 \) are shown in Fig. 3. Indicated symbols denote the
Monte Carlo results and solid lines are best logarithmic fits to the data points. The distance
\( r \) is in the direction of the next-nearest neighbours in the surface plane. In the lattice-gas
model the value of the chemical potential was chosen such as to produce an interface at a
level \( z_i > 10 \), i.e. \( v_i < 10 \) K. For temperatures above \( T = 1000 \) K, the effect on the surface
structure of the substrate potential difference between adjacent layers is negligible. As noted
in Ref. 31, finite size effects become significant for \( r \sim L/5 \). On the other hand, a few lowest
values of \( r \) have been discarded in the fits because Eq. (1.2) becomes exact only at large
\( r \). We have also done simulations for bigger systems, but increasing computational cost makes
it impossible to sample the long-wavelength fluctuations properly. This finite time effect
prevents us from being able to make fits to the correlation functions at larger values of \( r \).

From the logarithmic fits to the correlation functions we can infer the value of the
coefficient \( A \) defined in Eq. (1.2). The result is shown in Figs. 4a and 4b as a function
of temperature for the EMT lattice-gas model and for the six-vertex model, respectively.
A square root fit of Eq. (2.3) to the Monte Carlo data is shown by the solid line. From
these fits we find \( T_{R}^{lg} = 1000 \) K and \( T_{R}^{6v} = 1030 \) K. It is evident that the dependence on the
system size of the transition temperature is beyond our accuracy. The difference between
the exact value in the thermodynamic limit of the six-vertex model \( (T_{R}^{6v}(L \to \infty) = 1090 \) K)
and our numerical result \( (T_{R}^{6v} = 1030 \) K) is caused by two effects, the effect of finite size and
(mainly) the relatively short distances over which the fitting of the correlation function has
been made. A systematic deviation of similar magnitude \( (\sim 60 \) K) is expected to be present
also in our lattice-gas result, where MC runs of comparable length have been performed,
and logarithmic fits to the correlation functions have been made in a similar way. Thus we can conclude that $T_{lg}^{R}(L\to\infty) \approx 1060$ K.

For comparison we have also determined the $T_R$ of our lattice-gas model by studying the finite size behaviour of the interfacial width, $\delta h^2 = \langle (\bar{h} - h(\vec{r}))^2 \rangle_{\vec{r},t}$, where $\bar{h}$ is the nominal surface height for a given configuration. Above the transition temperature, $\delta h^2$ diverges logarithmically as a function of the linear size of the system size, $L$, or $\delta h^2 \sim A(T) \ln L$ for large $L$. In Fig. 4c we show the result for the transition temperature as determined from the coefficient $A(T)$ for the interfacial width. Here data for $L = 12, 18, 24$ and 30 has been used. The result is found to be consistent with that obtained from the correlation functions.

The Hamiltonian Eq. (2.1), leads us to still another way of deducing the roughening transition, namely through layering transitions in an adsorption system. For a thickening adsorption film the critical points of the layering transitions approach the bulk roughening temperature. In Fig. 4 we show a few adsorption isotherms corresponding to the formation of the first 'adsorption layer' and the inverse slope of the adsorption isotherms at the layering transition point, $\mu = \mu_1$, as a function of temperature. The solid line in Fig. 4b is a fit with the two-dimensional critical exponent of the susceptibility, $\gamma = 7/4$, and with a critical temperature $T_1 = 845$ K. A similar analysis for the next layer gives $T_2 = 870$ K. We do not intend to determine $T_R$ by repeating this procedure for further layers; we only note here that these critical layering points, $T_k$, are lower bounds for the roughening temperature. In our lattice-gas model the first adlayer grows essentially two-dimensionally (the second layer is almost unoccupied), which means that $T_1 \approx T_{lg}^{d=2}$ and we have $T_{lg}^{d=2}/T_{lg}^{R} = 0.80$. By using vertex energies $\epsilon_1$ and $\epsilon_3$ as the energy parameters in the two-dimensional Ising model we obtain $T_{C,Ising}^{lg}/T_{lg}^{R} = 0.80$. Besides being a further confirmation of our estimate of the roughening temperature in the lattice-gas model, this result shows that a simple pair-potential model with relatively short-range interactions (such as the six-vertex model) can be used to describe the roughening transition of a metallic system, provided the values of the energy parameters of the model are determined in an appropriate way. The effect on the roughening transition of the broken particle-hole (adatom-vacancy) symmetry is too small to be detected in
our lattice-gas model: the energy difference between convex and concave corners on Cu(110) is less than 10 K.

In Fig. 6 snapshots of typical configurations of a lattice-gas system with $L = 30$ are shown for two temperatures. Atoms in the lowermost odd layers are coloured black to guide the eye. Below $T = 1000$ K excitations are mainly single adatoms and vacancies at the surface. Around $T = T_R$ the connectivity of the adatom and vacancy clusters increases, and at higher temperatures the surface is clearly ‘rough’. The anisotropy of the clusters reflects the high anisotropy of the excitation energies in the surface plane, but there is no clear indication of (111)-type facetting since the anisotropy in our model is not very large. In the snapshot at $T = 1100$ K two overhangs can be seen: in both cases one of the four nearest neighbours at the next atom layer below is missing. Near $T = T_R$ the overhang density is very low ($<0.001$), and the solid-on-solid approximation of the six-vertex model is valid.

We conclude that the roughening temperature of our EMT lattice-gas model is $T_{\text{lg}} = 1060$ K. Considering the effect on the energy scale of surface excitations of relaxation (see Sec. II C), our best estimate for the roughening temperature of Cu(110) is $T_R \approx 1000$ K. Comparing this with the bulk melting point for the same potential, $T_M = 1240$ K we find $T_R/T_M = 0.81$.

### IV. MD RESULTS

We shall first compare the runs A (rough initial configuration) and B (smooth initial configuration) by studying the occupation numbers of the surface layers as a function of time. Atoms are attached to layers according to their z-coordinate by dividing the z-dimension of the sample in slices of thickness $\Delta z = a/2\sqrt{2}$, where $a$ is the conventional fcc cubic lattice constant. $\Delta z$ then corresponds to the distance between adjacent (110) planes in the bulk. We adopt hereafter the convention of ‘crystal’ and ‘adatom’ layers. The crystal layer $c_1$ is the uppermost full layer of the undefected surface at $T = 0$, and the adatom layer $a_1$ is the first unoccupied layer at $T = 0$. The other crystal and adatom layers are numbered from
the $T = 0$ interface into the bulk and into the vacuum, respectively.

The occupation numbers of the surface layers in runs A and B for $T = 1150$ K are plotted in Fig. 7 as a function of time. We can extract from Fig. 7 several important features of surface roughness. First, the initial roughness (i.e. occupation numbers) of the LGMC surface in the run A remains essentially the same also during the MD phase. The width of the interface seems to slightly increase after the MD simulation is started, which can be seen from the systematic increase in the occupation of the two adatom layers. The rough initial LGMC configuration is thus stable against the lattice vibrations and relaxation effects, i.e., it has no tendency of smoothing during the MD simulations. Second, we can reach the roughness of the run A during the first 150 ps of run B, which is initiated from the smooth surface. Notice that this is directly an estimate for the physical time needed for the surface to ‘roughen’ locally via its intrinsic dynamics. Third, one can see irregular fluctuations of a few tens of ps, on top of the normal statistical fluctuations. These long-wavelength fluctuations can especially be seen in the run A, which is made for the smaller, 30x30, sample. These fluctuations are connected with the diffusion dynamics of adatom and vacancy clusters. They show that, during our simulation time, it is possible to produce at least a few uncorrelated lattice configurations, i.e., we are able to travel through the configuration space of the rough surface.

At $T = 1100$ K (run C) the behaviour of the occupation numbers is qualitatively similar to that shown in Fig. 7. However, it takes much more time (about 300 ps) to reach the average LGMC level. We can interpret this as a ‘critical slowing down’ effect, which makes the observation times for the cluster dynamics in MD simulations extremely long when the transition temperature is approached. Some snapshots of two-dimensional adatom clusters in layer $a_1$ at 1150 K (run B) are shown in Fig. 8. The configurations in the first two snapshots (with a time interval of 14 ps or 1000 MD time steps) are clearly strongly correlated. In the third snapshot we obviously see a new lattice configuration. Despite the large vibrations and atomic diffusion, the clusters have a well-defined (110) surface symmetry.

In order to study atomic mobility we have calculated the probability distributions
\( p(x,y,z;t) \) for the surface layers, where \( p \) is the probability that an atom is in the position \((x,y,z)\) at time \( t \), when it is at the origin at \( t = 0 \). The function \( p(z;t) \) for layer \( a_1 \) shown in Fig. 9 illustrates the large number of layer changes during the simulations: After the observation time of 70 ps it is about equally probable to find the atom in layer \( c_1 \) as in layer \( a_1 \). This result is be related to the initial rising time of the occupation of the layer \( a_1 \) shown in Fig. 7. The \( p(x;t) \) distribution for the cross-channel [001] direction is shown in Fig. 10. The spacing between the maxima in \( p(x;t) \) corresponds to a half of the lattice constant, which indicates that the cross-channel [001] diffusion is the main mechanism of layer changes. This result has also been found from previous MD simulations of the fcc(110) surface diffusion.

We have studied the residence time of an atom at the lattice sites of each surface layer by analyzing the atomic displacements during the last 42 ps of the run B (\( T = 1150 \) K), and by collecting the statistics of jumps from one lattice site to another. The collected distributions of the residence times for the surface layers are shown in a semilogarithmic scale in Fig. 11. After an initial rise all distributions seem to obey an exponential law, \( p \propto e^{-t/\tau} \), from which the mean residence times, \( \tau \), for the diffusing atoms can be estimated to be 1.5 ps, 2.2 ps, 3.5 ps and 4.5 ps for \( a_2 \), \( a_1 \), \( c_1 \), and \( c_2 \), respectively. These residence times correspond to 10-30 lattice vibrations. Notice, however, that in layer \( c_2 \) 27% of the atoms are not diffusing at all during our observation time. The 'true' residence time for that layer must therefore be longer than the 4.5 ps quoted above. The corresponding fraction of immobile atoms in \( c_1 \) is only 2%, and practically all atoms in layers \( a_2 \) and \( a_1 \) have made at least one jump during our observation time.

The diffusion constants \( D_x, D_y \) for the surface layers are determined from the time-dependent mean-squared atomic displacements (msd) \( r^2(t) = \langle (r(t) - r(t_0))^2 \rangle \), where the brackets mean averages taken over 20 initial times \( t_0 \) and over atoms belonging initially to a given layer. \( D_\nu \), \( \nu = x, y \), can be obtained from the Einstein relation as, for \( t \to \infty \), \( r_\nu = 2D_\nu t + \text{const.} \) We find that \((D_x, D_y)\) for \( a_2, ..., c_2 \) are \((1.80, 4.13)\), \((2.05, 2.69)\), \((1.71, 2.77)\), and \((0.88, 1.24) \times 10^{-5} \) cm\(^2\)/s, respectively. It is evident that the calculated surface
mobility is high, near the mobility level in the bulk liquid at the melting point. However, the persistence of the lattice structure makes the diffusion clearly anisotropic. We emphasize that what has been considered here is the intrinsic (tracer) diffusion constant, not the mass transport constant which is expected to become isotropic at $T = T_R$ due to the macroscopic step diffusion.

The time scale of the roughening of a smooth surface can also be measured by studying the time evolution of cluster size distributions. In Fig. 12a we show the size distribution at $T = 1100$ K of adatom clusters in layer $a_1$ as a function of time (MD run C). After a simulation of 0.56 ns we are still far from the equilibrium distribution for clusters of size $N > 60$. At $T = 1150$ K the size distribution is stable (within our statistical accuracy) after 0.16 ns for $N$ up to $N \approx 120$. The result for the time interval 160 ps to 616 ps (run B) is shown in Fig. 12b. The dotted line is the behaviour of the lattice-gas system with of same size and at the same temperature. The results for the vacancy clusters in layer $c_1$ are similar. The height-height correlation function $G$ (not shown here) of Eq. (1.1) as determined from the MD data for $T = 1150$ K, is an increasing function of $r$ only for $r \leq 5$. With $r$ taken to be in the direction of the next-nearest neighbours (the direction of weaker bonds), this result reflects the fact that, during this simulation of length 0.6 ns and well above the roughening temperature, we have been able to collect reasonable statistics for defect clusters only for $N \leq 100$. The dynamics of the cluster size distributions in our MD simulations is consistent with the results for the kinetics of the roughening of a stepped surface discussed in Ref. 40: roughness sets in over short distances and then spreads asymptotically as $t^{1/3}$. The time scale of roughening, 100 ps (Fig. 7) at $T = 1150$ K and 300 ps at $T = 1100$ K, defined here as the time required for the occupation numbers of the innermost layers to saturate to their 'rough' values, clearly describes the local behaviour. For systems of size $L^2$ with $L \geq 50$, this quantity should depend only weakly on $L$. We have not tried to determine the asymptotic behaviour for late times.

Based on the calculated diffusion constants in the surface region, we can conclude that for an atom found initially in layer $c_1$, it takes at $T = 1150$ K about 30 ns ($50 \times$ our
simulation time) to travel through a distance similar to the length of the simulation box in the shorter y-direction. The corresponding time for diffusion across the box in the x-direction is about 90 ns. These characteristic times provide an order-of-magnitude estimate for the amount of computation time needed for a reliable calculation of the height-height correlation function at one temperature by the MD method. In order to be able to determine $T_R$, a few temperatures below 1150 K should be studied. The computation time required by the present MD model, with the EMT interactions for Cu(110), would be of the order of one year of Cray X-MP CPU time.

V. CONCLUSIONS

We have studied the roughening of the Cu(110) surface via atomistic simulations using both the Monte Carlo and molecular dynamics methods which employ the effective-medium theory as the interaction potential. The Monte Carlo simulations made for our lattice-gas model, adjusted by corrections arising from relaxation and finite size effects, show clearly that the Cu(110) surface has a roughening transition around $T = 1000$ K, about 200 K below the surface premelting temperature determined for the same potential. The rough phase has been identified from the logarithmic behaviour of the height-height correlation function and of the interface width. The transition temperature is obtained from the temperature-dependent coefficient of the logarithmic term. The finite size effects have been estimated by mapping the lattice-gas interface to an anisotropic six-vertex model, for which the behaviour in the thermodynamical limit is known exactly. Knowing the bulk melting point for the same potential, we find $T_R / T_M = 0.81$. This is in excellent agreement with the experimental result $T_R / T_M = 0.79$ given in Ref. Molecular dynamics simulations of the same surface cannot produce statistics enough for the height-height correlation function, but they show the stability of the LGMC surface against lattice vibrations and relaxation, i.e., the rough LGMC surface shows no tendency of smoothing when used as an initial configuration for MD simulations. Furthermore, MD simulations show that the roughening mechanism is
connected with the dynamics of diffusive adatom and vacancy clusters and gives information about the corresponding time scales. For the system of size 50x50 studied in this work, an initially smooth surface ‘roughens’ locally in the time scale of about 100 ps at $T = 1150$ K, and of about 300 ps at $T = 1100$ K. The time interval between two uncorrelated rough configurations in MD simulations is found to be of the same order.

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APPENDIX: CELL METHOD AND NEIGHBOUR LIST

A well-known problem in MD simulations with short-range interactions is the question of how to select only those pairs of atoms which are within the range of the potential. The brute-force testing of all the $1/2N(N-1)$ pairs at each time step is a prohibitive waste of time even in supercomputers, if $N$ is of the order of few thousands atoms. In our simulations, we have constructed the so-called neighbour list, which includes the indices $j$ of all neighbours of atom $i$ for which $r_{ij} < r_L$, $r_L$ the list radius. By using this list, only $1/2NN_L$ interactions have to be calculated, where $N_L$ is the average number of neighbours for a given atom. The cutoff $r_C$ in the EMT interaction potential is between the third and fourth nearest neighbours in the $T = 0$ fcc copper lattice. We have set $r_L$ to correspond to the distance to the middle of the sixth and seventh neighbours, which means that $N_L$ falls within the range of 80-90. In order to minimize the frequency of the updating of the list, we study at each time step the displacements of atoms from the previous updating step. The list is updated whenever the maximum displacement exceeds half of the list ‘skin’, $r_L - r_C$. 

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For the sample sizes used in this work, also the $N^2$ computations needed for updatings become significant. We have managed to speed up the updating using the following method. We divide the sample into $n_x \times n_y$ subcells according to the number of the 2D lattice sites, i.e., 30x30 or 50x50 for the samples studied in this work. For each subcell $c_i$, the indices of neighbouring subcells $c_j$ are stored in a map in the beginning of the simulation. After attaching a given atom to its subcell, it is sufficient to go through its own subcell and (in our case) only 15 neighbouring subcells to construct its neighbour list. This method, being linear with the system size, clearly overrides the $N^2$ searches over all pairs, and brings the time needed for updating comparable to that needed in the calculation of the EMT interactions. Our method can be regarded as a 2D modification of the so-called linked-cell method\textsuperscript{41} with the important difference that the size of the subcell is chosen to accommodate only one lattice site in two dimensions. In the present method - remember that we also use a stable integration algorithm which allows a large time step - we have been able to perform MD simulations for 30000 atoms (20000 of which dynamical) on a Decstation 5000/200 (3.7 Mflops) scalar machine at a rate of about 20 ps/day.
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* Present address: School of Physics, Georgia Institute of Technology, Atlanta, GA 30332, USA.

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FIGURES

FIG. 1. Energy of an atom in EMT lattice-gas (full curves). The broken curve is the derivative of \( E \) with respect to \( C_1 \), and the dotted line is the energy in a simple pair potential model.

FIG. 2. Mapping of the Cu(110) surface to the six-vertex model. (a) Correspondence between the fcc(110) face and the six-vertex model (a model configuration with a vacancy on an otherwise flat surface), and (b) energies of the six vertices allowed by the solid-on-solid restriction.

FIG. 3. Height-height correlation functions for (a) lattice-gas model and (b) six-vertex model.

FIG. 4. Coefficient \( A \) as a function of temperature (a) from the correlation functions of the lattice-gas model, (b) from the correlation functions of the six-vertex model and (c) from the interfacial width of the lattice-gas model.

FIG. 5. (a) Formation of the first 'adsorption layer' in the lattice-gas model and (b) inverse slope of the adsorption isotherms at the layering transition point.

FIG. 6. Snapshots of lattice-gas configurations for two temperatures.

FIG. 7. The occupation of surface layers \( a_2, \ldots, c_2 \) as a function of simulation time in MD runs A and B for \( T = 1150 \) K. Run A was initiated from a rough lattice configuration and run B from an undefected smooth surface.

FIG. 8. Snapshots of two-dimensional clusters in layer \( a_1 \) in MD for \( T = 1150 \) K.

FIG. 9. The probability distribution \( p(z;t) \) showing the atomic mobility perpendicular to the (110) surface.

FIG. 10. The probability distribution \( p(x;t) \) showing the atomic mobility in the [001] direction parallel to the (110) surface.
FIG. 11. The natural logarithm of the residence time distribution for the surface layers. Shown also are the linear fits, from which the mean residence times $\tau$ for each layer have been estimated.

FIG. 12. Size distribution of two-dimensional clusters in layer $a_1$ (a) as a function of time in the MD run C for $T = 1100$ K and (b) in the MD run B for $T = 1150$ K. The dotted line in (b) is the LGMC behaviour at the same temperature.