Roughening of close-packed singular surfaces

Federica Trudu,[1] Vincenzo Fiorentini,[1,2] Paolo Ruggerone,[1] and Uwe Hansen[2,*]
[1]*Istituto Nazionale per la Fisica della Materia and Dipartimento di Fisica, Università di Cagliari, Italy*
[2]*Walter Schottky Institut, TU München, Garching, Germany*
(Received 19 October 2000; published 26 March 2001)

An upper bound to the roughening temperature of a close-packed singular surface, fcc Al (111), is obtained via free-energy calculations based on thermodynamic integration using the embedded-atom interaction model. Roughening of Al (111) is predicted to occur at around 890 K, well below bulk melting (933 K), and it should therefore be observable, save for possible kinetic hindering.

DOI: 10.1103/PhysRevB.63.153402 PACS number(s): 68.35.Bs, 68.35.Md, 68.35.Rh

Roughening[1–3] is one of the most fundamental phase transitions at surfaces, yet probably the most elusive. The roughening of vicinal surfaces[2,3] is generally accepted to be a transition of infinite order of the Kosterlitz-Thouless[4] class. The extremely weak free-energy divergence at the critical point implies frustratingly slow variations in space and time of whatever order parameter is chosen to characterize the transition. This makes predictions on roughening a challenge for atomistic simulation techniques, this being not the least of the reasons why statistical mechanics models[5] have traditionally been the dominant approach to this problem.

The roughening of singular faces poses additional problems. Vicinal surfaces roughen as the (mostly configurational) entropic free energy related to step meandering prevails over the cost of step and kink formation; on vicinals, where steps already exist by construction, this occurs generally at temperatures well below melting. Singular-face roughening, on the other hand, requires step formation to begin with. Singular faces, therefore, roughen at much higher temperatures, so much so that roughening is thought to be preempted by melting in most cases, especially on close-packed faces.

Here we use a simple approach to predict the roughening transition temperature of a singular surface, based on free-energy calculations performed with an atomic-level finite-temperature simulation technique (the embedded-atom method coupled with Monte Carlo thermodynamic integration). We calculate the free energies of several vicinals to the singular face, and estimate the temperatures at which the free energy of each vicinal becomes lower than that of the singular. Since roughening is phenomenologically identified with the appearance of hills and valleys of arbitrary height on the surface, we assume that roughening will be fully developed at the temperature at which the steepest and most costly vicinal is favored over the low-index face. To obtain an internally consistent and low-error-bar estimate, we calculate the crossing temperatures with the free energy of the singular surface of the free energies of several vicinals with progressively shorter terraces; we then obtain T_R as the extrapolated crossing temperature of the shortest/most costly vicinal. To be definite, here we estimate an upper bound to T_R for any Al surface, and find it to be $\sim$890 K, well below the bulk melting temperature of 933 K.

To obtain such an upper bound, we study Al (111), which is expected to have the highest roughening temperature among the low-index faces, being the most closely packed. Also, it is stable[6] up to the bulk melting temperature, and predicted to sustain overheating.[7] The vicinals of Al (111) we consider here are Al (88 10), Al (557), and Al (335), obtained by miscut of the (111) plane at angles of $\sim 1°$, 9°, and 14°, respectively. There exist two kinds of step on Al (111), namely, the 111 faceted and the 100 facetted. The latter are energetically more costly, and our vicinals belong to this second class. In the notation of Lang, Joyner, and Somorjai,[13] bearing out directly the interstep distance, these faces are denoted as $[9(111)\times(100)]$, $[6(111)\times(100)]$, and $[4(111)\times(100)]$, respectively, meaning (say) six rows of a (111) face separated by a (100)-faceted step. These vicinals lie on the (111)-(100) line of the stereographic map of the fcc lattice.[8] The steepest vicinal on this line is Al (113), or $[2(111)\times(100)]$: its appearance should set the occurrence of fully developed roughening. Here we first simulate straight-step vicinals, and then estimate the correction due to kink formation by simulating one kinked vicinal.

Free energies are calculated via the embedded-atom method and thermodynamic integration. The embedded-atom method[9] is a fairly reliable method of predicting structural and thermal properties of metals. Its main advantage is its moderate computational cost and ensuing high numerical accuracy achievable within the method's bounds. The disadvantages are essentially that the choice of materials to be simulated is restricted by the availability of accurate potentials (constructing which is a science in itself), and that the embedded-atom method, being based on an effective interatomic potential, is not as accurate as first principles methods. This inherent inaccuracy is attenuated for Al by the highly refined parametrization of Ercolessi and Adams,[10] built to reproduce a large database of *ab initio* energy and force calculations. Recently[11] the Ercolessi-Adams model has been further refined to correct minor inaccuracies in the description of surface diffusion and high-energy scattering.

Thermodynamic integration is adopted because the roughening transition occurs (if at all) well above the Debye temperature ($\sim$400 K for Al bulk), and it is therefore imperative to properly include anharmonic effects in the free energy of the relevant surfaces. While useful at lower temperatures, the commonly adopted quasiharmonic approximation is not very reliable at high temperature, as shown by recent simulations[11] on Al (100). In thermodynamic integration,[12]

the potential energy of the system is progressively switched on, through a parameter λ, starting from a reference system whose free energy is known:

$$V(\lambda)=\lambda\, W-(1-\lambda)\, U_h, \tag{1}$$

with W and U_h the potentials of the actual system and of a harmonic crystal. Since[12]

$$\frac{\partial F}{\partial \lambda}=\langle U_h-W\rangle_\lambda, \tag{2}$$

the free energy at a fixed temperature $T_{\rm ref}$ is

$$F_{\rm ref}=F_{\lambda=1}=F_{\lambda=0}+\int_0^1 \langle U_h-W\rangle_\lambda\, d\lambda. \tag{3}$$

The integrand is calculated by Metropolis canonical Monte Carlo simulation, and the $\lambda=0$ value is known by construction. By the thermodynamical free-energy–enthalpy relation

$$\frac{d}{d\,T}\left(\frac{F}{T}\right)=-\frac{H}{T^2}, \tag{4}$$

the free energy in the interval $[T_{\rm ref},T]$ is

$$F(T)=T\left[\frac{F_{\rm ref}}{T_{\rm ref}}-\int_{T_{\rm ref}}^{T}\frac{H}{T^2}dT\right]. \tag{5}$$

The integrand is calculated again by canonical Monte Carlo simulation. The surface free energy per unit area is

$$F_{\rm surf}(T)=\frac{1}{2\,A}[F_{\rm slab}(T)-N\,F_{\rm bulk}(T)], \tag{6}$$

where $F_{\rm bulk}(T)$ is the bulk free energy per atom, $F_{\rm slab}(T)$ is the free energy of the N-atom simulation slab, and A is its surface area. Whenever appropriate, thermal expansion is accounted for with an expansion coefficient given by the ratio $a(T)/a(0)$ of the lattice constants at temperatures T and zero, obtained by NPT simulations.[11] Free energies are calculated in supercells containing 450 to 600 atoms depending on the orientation. Each Metropolis Monte Carlo run was $\sim 3\times 10^7$ steps long. We estimate error bars of 0.5% in the surface free energy, and about ± 10 K in the crossing points and T_R.

In Fig. 1 we report the free energy vs temperature for Al (111) and vicinals. At first, Al (111) is favored. At higher temperatures, vicinals with progressively shorter terraces become favored free-energy-wise. The crossing points are $T=773$ K for Al (88 10), $T=875$ K for Al (557), and $T=914$ K for Al (335).

The crossing points in Fig. 1 tend to ''accumulate'' toward a finite value as the terraces become progressively shorter. This suggests identifying T_R with the ''accumulation point'' of this sequence. To quantify it, we fit a polynomial through the crossing points just obtained as a function of interstep distance, and define T_R as the temperature value corresponding to the interstep distance on the vicinal surface with the shortest terrace within our class of (100)-faceted, straight-stepped vicinals, namely, Al (113), whereby the interstep distance is ~ 5.5 Å. At $T=T_R$ as just defined, all the vicinals (within our restricted class) are favored over Al (111), so that an arbitrarily large and composite fluctuation can appear in the surface profile. The result is displayed by the upper curve in Fig. 2: the roughening temperature estimate is 930 K, very close to the melting temperature of Al bulk (theoretical[7] 939 K; experimental[6] 933 K).

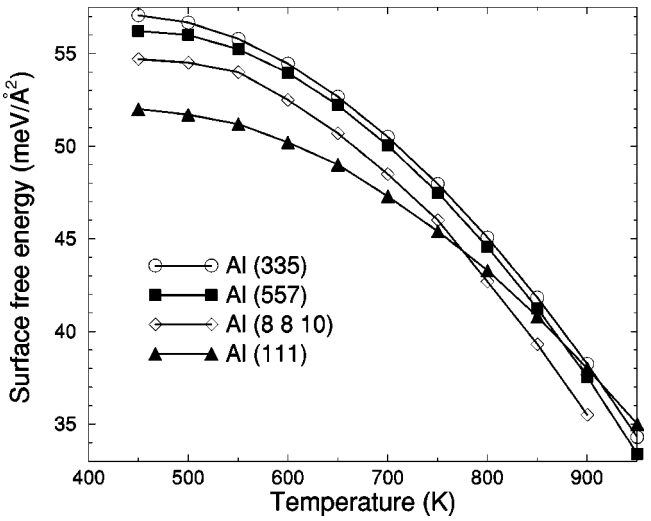

FIG. 1. Free-energy temperature dependence for Al (111) and vicinals.

To refine the prediction, we first note that only undefected straight steps have been considered so far. On the other hand, at finite temperature kinks will form on steps. Kinks affect the free energy of the stepped surface both indirectly because their very existence allows step meandering, and directly via their formation internal energy and vibrational entropy due to their vibrational modes. We consider that the latter free-energy variation will be captured accurately by a simulation. We neglect the step-meandering-related configurational entropy, based on previous work on vicinal surfaces[14] suggest-

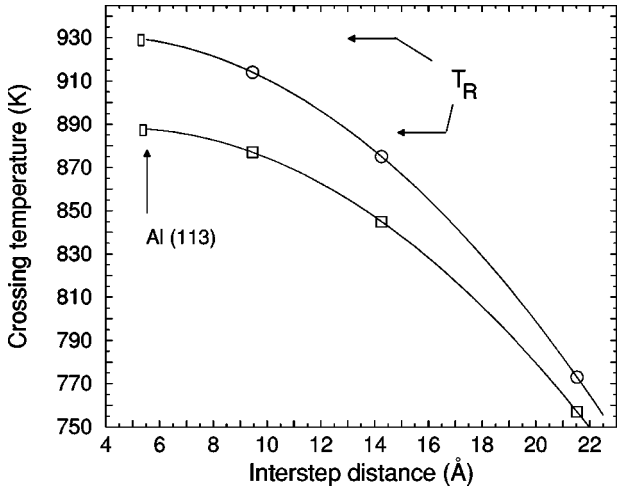

FIG. 2. Crossing points of surface free energies of vicinals and singular surface. Upper curve, straight steps; lower curve, kinked steps. T_R is defined as the temperature corresponding to the Al (113) interstep distance.

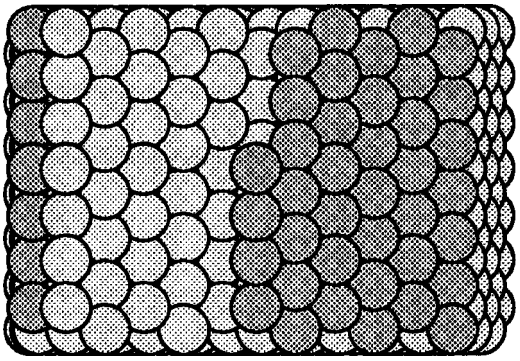

FIG. 3. Top view of kinked Al (557) as studied in free-energy calculation. Like all other cells, it contains two periodically repeated steps per side.

ing that the configurational contribution is negligible compared to the vibrational below the roughening transition.

The simulation of vicinal surfaces with kinks is demanding in periodic boundary conditions; here we restrict ourselves to a single case, kinked Al (557), chosen because of its favorable geometry. Each side of the simulation slab, depicted in Fig. 3, contains one straight and one kinked step. The latter exhibits two kinks, with a relatively low linear density of 0.05 $Å^{-1}$. The number of atoms is preserved by this procedure, as required by numerical considerations. As shown in Fig. 4, the kinked Al (557) turns out to have a crossing point with Al (111) at $T=845$ K, with a reduction of 4% over the straight-step value. Assuming that the other crossing points are lowered by about the same amount due to kinks, and applying the same procedure as before, we find $T_R=887$ K (lower-lying curve in Fig. 2). This is a strong upper bound because accounting for lower-cost (111)-faceted steps should lower this figure. In addition, taking account of meandering will also (moderately) lower our estimate.

Roughening has not been reported for any fcc (111) face so far. Our predicted T_R is rather close to, but lower than, the melting temperature, so it is quite conceivable that roughening of Al (111) could be observed. Our prediction concerns

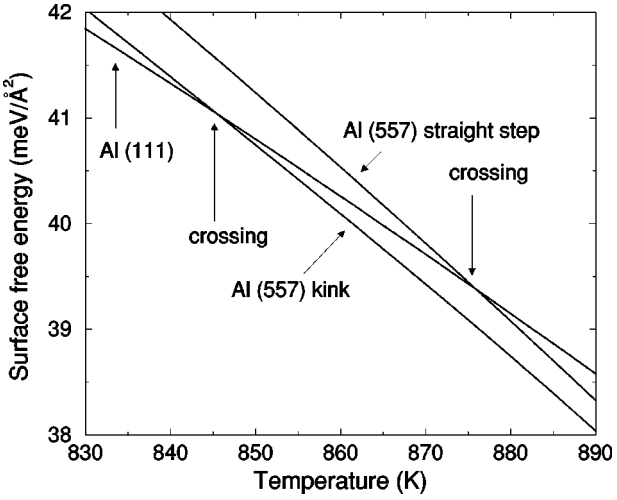

FIG. 4. Lowering of the free-energy crossing point of Al (557) with Al (111) due to the presence of kinks.

energetics, however. Kinetic effects are not considered in any way. However, Al (111) was observed[6] in medium energy ion scattering experiments to remain stable up to the melting temperature. Also, molecular dynamics simulations[7] showed Al (111) to be stable for at least 2 ns up to 1088 K, or 150 K above bulk melting. While the length and time scales accessible in simulation are not comparable with those of relevance in roughening, this is an indication that kinetics may play a role, slowing down or hindering the transformation. Thus, it is possible that experiments aiming at the observation of the roughening of Al (111) predicted here may have to observe the surface over time spans of hours, or produce ''nucleation'' defects by, e.g., nanoindentation.

As a further check on the predictions based on the embedded-atom Al potential, reinforcing the plausibility of our estimate, we calculate T_R for vicinals within the terrace-ledge-kink (TLK) model of Villain *et al.*,[15] through the relation

$$K=\frac{W_m}{k_B T_R} e^{W_0/k_B T_R}. \tag{7}$$

Here W_m is the energy needed to move a step by one row toward a neighboring step $m+1$ atomic rows away, and W_0 is the kink formation energy. This expression is valid for $W_m<T<W_0$, which is the case here. The value of K depends upon the details of the underlying theory, and it equals 2 for the original TLK model; values of 2 for Cu (113) (Ref. 16) and 2.1 for Ag (115) (Ref. 3) have been suggested based on experiments or Monte Carlo simulations on vicinals. We evaluate these parameters from total energy calculations on slabs containing at least five steps per slab side, and comprising from 1700 to 4000 atoms depending on orientation. The parameter W_m is calculated removing one complete atomic row of step-edge atoms. If N is the total number of atoms and L that of step-edge atoms, the total energy for row removal is

$$L\,W_m=E_{N-L}-[E_N-LE_b], \tag{8}$$

with E_{N-L} and E_N the internal energy of the system after and before row removal, and E_b the bulk energy per atom. W_m is thus defined per atom. For a kink we remove only half a row, creating two kinks:

$$2\,W_0=E_{N-L/2}-[E_N-(L/2)\,E_b]-W_m \tag{9}$$

with $E_{N-L/2}$ the internal energy of the slab after half-row removal.

For Al (335) we find $W_m=3$ meV, $W_0=112$ meV, $T_R=411$ K; for Al (557) we find $W_m=1$ meV, $W_0=108$ meV, $T_R=314$ K; for Al (88 10) we find $W_m=0.1$ meV, $W_0=106$ meV, and $T_R=209$ K. These values are quite comparable with results of previous investigations on stepped metal surfaces.[17,18] Our numbers for Al (335) are compatible with those inferred from scanning tunneling microscopy measurements on Ag (115),[19] which has the same step-step separation: $W_m=3$ meV, $W_0=114$ meV, and $T_R=427$ K. [The (115) face consists of (111)-faceted steps separated by a (100) terrace four atomic rows wide, whereas the (335) has (100) steps and (111) terraces.] Concerning T_R of Al (111),

den Nijs *et al.* observed[20] roughening of Ni (115) at about 200 K, and estimated 420 K for the roughening of Ni (100), the nearest singular face on the stereographic plot. Our value of 412 K for Al (335) similarly suggests that our upper bound of 890 K for the associated singular (111) is quite plausible. Our predictions for both singular and vicinal faces await experimental verification.

In summary, we have calculated an upper bound to the roughening temperature of a singular metal surface using an atomistic simulation method. Our results for Al (111) suggest that roughening may occur appreciably below melting, and therefore be observable, save for kinetic hindering.

V.F. thanks the Alexander von Humboldt–Stiftung for supporting his stays at the Walter Schottky Institut.

*Present address: Bosch AG, Stuttgart, Germany.

[1] W. K. Burton, N. Cabrera, and F. C. Frank, Philos. Trans. R. Soc. London, Ser. A **243**, 299 (1951); J. Lapoujoulade, Surf. Sci. Rep. **20**, 191 (1994).
[2] M. S. Hoogeman, M. A. J. Klik, D. C. Schler, L. Kuipers, and J. W. M. Frenken, Surf. Sci. **448**, 142 (2000).
[3] M. S. Hoogeman and J. W. M. Frenken, Surf. Sci. **448**, 155 (2000).
[4] J. M. Kosterlitz and D. J. Thouless, J. Phys. C **6**, 1181 (1973).
[5] S. T. Chui and J. D. Weeks, Phys. Rev. B **14**, 4978 (1976); J. D. Weeks, in *Ordering in Strongly Fluctuating Condensed Matter Systems*, edited by T. Riste (Plenum Press, New York, 1980).
[6] A. W. Denier van der Gon, R. J. Smith, J. M. Gay, and D. J. O'Connor, Surf. Sci. **227**, 143 (1990).
[7] F. D. Di Tolla, F. Ercolessi, and E. Tosatti, Phys. Rev. Lett. **74**, 3201 (1995).
[8] http://www.fysik.dtu.dk/~stoltze/cryst/fcc.html
[9] M. S. Daw and M. I. Baskes, Phys. Rev. B **29**, 6443 (1984).
[10] F. Ercolessi and J. B. Adams, Europhys. Lett. **26**, 583 (1994).
[11] U. Hansen, P. Vogl, and V. Fiorentini, Phys. Rev. B **60**, 5055 (1999).
[12] D. Frenkel and B. Smit, *Understanding Molecular Simulations* (Academic Press, New York, 1996).
[13] B. Lang, R. W. Joyner, and G. A. Somorjai, Surf. Sci. **30**, 440 (1972).
[14] J. W. M. Frenken and P. Stoltze, Phys. Rev. Lett. **82**, 3500 (1999).
[15] J. Villain, D. R. Grempel, and J. Lapujoulade, J. Phys. F: Met. Phys. **15**, 890 (1985).
[16] W. Selke and A. M. Szpilka, Z. Phys. B: Condens. Matter **62**, 381 (1986).
[17] P. A. Gravil and S. Holloway, Phys. Rev. B **53**, 11 128 (1996).
[18] K. D. Hammonds and R. M. Lynden-Bell, Surf. Sci. **278**, 437 (1992).
[19] M. S. Hoogeman, M. A. J. Klik, D. C. Schlösser, L. Kuipers, and J. W. M. Frenken, Phys. Rev. Lett. **82**, 1728 (1999); M. S. Hoogeman, D. C. Schlösser, J. B. Sanders, L. Kuipers, and J. W. M. Frenken, Phys. Rev. B **53**, 13 299 (1996).
[20] M. den Nijs, E. Riedel, E. H. Conrad, and T. Engel, Phys. Rev. Lett. **55**, 1689 (1985).