Roughening of close-packed singular surfaces

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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.

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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 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 will be favored over the low-index face. To obtain an internally consistent and low-error-bar estimate, we calculate the crossing temperatures of the free energies of several vicinals with progressively shorter terraces, with the free energy of the singular surface; 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 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 up to the bulk melting temperature, and predicted to sustain overheating. The vicinals of Al (111) we consider here are Al (8 8 10), Al (557) and Al (335), obtained by miscut of the (111) plane at an angle of \( \sim 1, 9, \) and 14 degrees respectively. There exist two kind of steps on Al (111), namely the 111-faceted and the 100-faceted. The latter are energetically more costly, and our vicinals belong to this second class. In the notation of Lang, 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) 6 rows of a (111) face separated by a (100)-faceted step. These vicinals lay on the (111)-(100) line of the stereographic map of the fcc lattice. 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 is a fairly reliable method to predict 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, by its nature of effective interatomic potential, is not as accurate as first principles methods. This inherent inaccuracy is attenuated for Al by the highly refined parameterization of Ercolessi and Adams, built to reproduce a large database of ab initio energy and force calculations. Recently the Ercolessi-Adams model has been further refined to cure 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 quasi-harmonic 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 $\lambda$, starting from a reference system whose free energy is known:

$$V(\lambda) = \lambda W - (1 - \lambda) U_h$$

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

$$\frac{\partial F}{\partial \lambda} = (U_h - W)_\lambda,$$

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

$$F_{\text{ref}} = F_{\lambda=1} = F_{\lambda=0} + \int_0^1 (U_h - W)_\lambda d\lambda. \quad (3)$$

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

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

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

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

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

$$F_{\text{surf}}(T) = \frac{1}{2A} \left[ F_{\text{slab}}(T) - NF_{\text{bulk}}(T) \right]$$

where $F_{\text{bulk}}(T)$ is the bulk free energy per atom, $F_{\text{slab}}(T)$ is the free energy of the N-atom simulation slab, and $A$ 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 an 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 $\pm 10$ 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 (8 8 10), $T=875$ K for Al (557), and $T=914$ K for Al (335).

The crossing points in Fig. 1 tend to “accumulate” towards a finite value as the terraces become progressively shorter. This suggests to identify $T_R$ with the “accumulation point” of this sequence. To quantify it, we fit a polynomial through the crossing points just obtained as 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 $\sim 5.5$ Å. At $T=T_R$ as just defined, all the vicinals (within our restricted class) are favored over Al (111), so that 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).

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 instead the step meandering-related configurational entropy, based on previous work on vicinal surfaces [14] suggesting that the configurational contribution is negligible compared to the vibrational below the roughening

![FIG. 1. Free energy temperature dependence for Al (111) and vicinals.](image-url)
The simulation of vicinal surfaces with kinks is demanding in periodic boundary conditions; here we restrict 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-laying curve in Fig. 3). This is a strong upper bound because accounting for lower-cost (111)-faceted steps should lower this figure. In addition, account for meandering will also lower (moderately) our estimate.

Roughening has not been reported for any (111) face so far. The 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 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 towards 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) [16] and 2.1 for Ag (115) [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 5 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

$$LW_m = E_{N-L} - [E_N - LE_b], \quad (8)$$

with $E_{N-L}$ and $E_N$ the internal energy of 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 only remove half a row, creating two kinks:

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

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 (8 8 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 [5,8]. Our numbers for Al (335) are compatible with those inferred from STM measurements on Ag (115) [9], 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 be therefore observable, save for kination hindering.

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