

Temperature dependence of the step free energy

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We have derived an expression for the step free energy that includes the usual thermally induced step meandering term and a vibrational entropy term related to the step edge atoms. The latter term results from the reduced local coordination of the step atoms with respect to the terrace atoms and was introduced recently by Frenken and Stoltze as well as by Bonzel and Emundts. Additionally, we have added third and fourth terms that deal with the vibrational entropy contribution of the thermally generated step and kink atoms. At elevated temperatures the two latter vibrational entropy terms are of the same order of magnitude. Incorporation of these vibrational entropy terms results in a faster decrease of the step free energy with increasing temperature than anticipated previously. This enhanced temperature dependence of the step free energy results in a lower thermal roughening temperature of the facet.

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The surface free energy of a surface of a solid is an important parameter that is needed for a proper understanding of many surface processes such as crystal growth, faceting, and etching. Experimental determination of the surface free energy is, however, far from trivial and only a very limited data set exists. The surface free energy $\gamma(\alpha, T)$ of a vicinal surface, misoriented with respect to a low-index orientation by an angle α at a temperature T , is usually expanded as¹

$$\gamma(\alpha, T) = \gamma(0, T) + \frac{f(T)}{d} |\tan \alpha| + q(T) |\tan \alpha|^3, \quad (1)$$

where $\gamma(0, T)$ refers to the surface free energy per unit area for the low-index Miller index surface, d is the step height, $f(T)$ is the step free energy per unit length (a) for forming a step of height d , and finally $q(T) |\tan \alpha|^3$ corresponds to the energy cost per unit area due to step-step interactions. The average spacing between the steps is $L = d / \tan \alpha$. Since steps are not allowed to cross, there is a temperature-dependent entropic repulsion between them, falling off as L^{-2} . In general, the energetic step-step interaction exhibits a similar behavior, i.e., $\sim L^{-2}$. Here we focus our attention on only one of the parameters from Eq. (1), namely, the step free energy $f(T)$. The step free energy itself is an important quantity too. For example, the thermal roughening transition of the facet can be extracted from the temperature dependence of the step free energy [by requiring that $f(T) = 0$]. At the roughening temperature (T_r) steps are spontaneously generated on the facet because there is no additional free energy required for their formation.

It is the aim of the present paper to show that the step free energy exhibits a faster decrease with increasing temperature than anticipated previously. As well as including step meandering and the vibrational entropy of the step atoms,^{3,4} we have also included the vibrational entropy of the *extra* step and kink atoms that are thermally generated at elevated temperatures. We will show that at elevated temperatures both vibrational entropy terms are of the same order of magnitude. Incorporation of both vibrational entropy terms results in a significant lower thermal roughening temperature of the facet.

As a model system we consider the (001) surface of a simple cubic lattice (Kossel crystal) with lattice parameter a . Furthermore, we take only an isotropic nearest-neighbor interaction energy ϕ into account and we consider only steps running along the high-symmetry [110] direction. The formation of kinks allows the step to wander, increasing the entropy and thus decreasing the free energy for step formation. At zero temperature the step free energy becomes equal to the step edge formation energy. If we assume that the creation of a kink with unit length a costs energy $\varepsilon (= \phi/2)$, a double kink costs energy 2ε , etc., and the step edge formation energy per unit length (a) requires an energy $\phi/2$, then the step free energy can be calculated using the partition function Z :²

$$\begin{aligned} f(T) &= -kT \ln Z = -kT \ln \left[e^{-\varepsilon/kT} \left(1 + 2 \sum_{n=1}^{\infty} e^{-n\varepsilon/kT} \right) \right] \\ &= \varepsilon - kT \ln \left[\frac{1 + e^{-\varepsilon/kT}}{1 - e^{-\varepsilon/kT}} \right], \end{aligned} \quad (2)$$

where k is Boltzmann's constant. Frenken and Stoltze³ as well as Bonzel and Emundts⁴ pointed out that thermal vibrations of the step atoms form another source of entropy that should be included in Eq. (2). The reduced coordination of the step atoms versus the normal terrace atoms lowers the typical vibration frequency of the step atoms versus the terrace atoms³⁻⁸ and therefore lowers the step edge free energy. To account for this effect, both groups^{3,4} added an additional term to Eq. (2). They both assumed that the step and terrace atoms are harmonic, isotropically vibrating Einstein oscillators, i.e., only one single mode ω was considered. Determination of the density of states $D(\omega)$ reveals that this assumption is reasonable for several materials.^{5,6,9} The vibration frequency of the step atoms ω_s is lower than that of the normal terrace atoms ω_t , due to the reduced local coordination (four nearest neighbors for the step atom versus five nearest neighbors for the terrace atoms). An approximate relationship is

$$\omega_s = \sqrt{\frac{4}{5}} \omega_t. \quad (3)$$

The free energy of an isotropic Einstein oscillator is given by

$$f = -3kT \ln Z = -3kT \ln \left[\sum_{n=0}^{\infty} e^{-n\hbar\omega/kT} e^{-\hbar\omega/2kT} \right] \\ = \frac{3}{2}\hbar\omega + 3kT \ln(1 - e^{-\hbar\omega/kT}). \quad (4)$$

The factor of 3 in Eq. (4) accounts for the three orthogonal directions of vibration. The additional vibrational free energy of a step atom versus a terrace atom is then

$$\Delta f(T) = f_s - f_t = 3kT \ln \left(\frac{1 - e^{-\hbar\omega_s/kT}}{1 - e^{-\hbar\omega_t/kT}} \right) + \frac{3}{2}\hbar(\omega_s - \omega_t). \quad (5)$$

Substituting $k\theta_{t,s} = \hbar\omega_{t,s}$, where $\theta_{t,s}$ is the Einstein temperature of the terrace (step) atom, yields for the total step free energy⁴

$$f(T) = \varepsilon - kT \ln \left[\frac{1 + e^{-\varepsilon/kT}}{1 - e^{-\varepsilon/kT}} \right] + 3kT \ln \left(\frac{1 - e^{-\theta_s/T}}{1 - e^{-\theta_t/T}} \right) \\ + \frac{3}{2}k(\theta_s - \theta_t) \quad (6)$$

where $\theta_s = \sqrt{\frac{4}{3}}\theta_t$.

Equation (6) is precisely the result obtained by Bonzel and Emundts.⁴ Frenken and Stoltze³ found an expression that is similar in spirit to Eq. (6). Rather than assuming different vibration frequencies for step and terrace atoms, respectively, they assumed that the vibration amplitude of step edge atoms (σ_s) is higher than that of the terrace atoms (σ_t) resulting in an entropy difference per step atom of $3kT \ln(\sigma_s/\sigma_t)$. We will use Eq. (6) as a starting point and consider additional contributions to the step free energy as well. The main contribution that we add to Eq. (6) stems from the fact that, with increasing temperature the total step edge length increases. Due to this increase in the total step edge length, the total number of step atoms increase with increasing T . If λ_0 is the total step edge length at zero temperature then the total step edge length $\lambda(T)$ is given by

$$\lambda(T) = \lambda_0 \left(1 + 2 \sum_{n=1}^{\infty} nP(n) \right) = \lambda_0 \left(1 + \frac{2e^{-\varepsilon/kT}}{1 - e^{-2\varepsilon/kT}} \right), \quad (7)$$

$$P(n) = \frac{1 - e^{-\varepsilon/kT}}{1 + e^{-\varepsilon/kT}} e^{-|n|\varepsilon/kT},$$

where n is the kink length measured in units of a and $P(n)$ the probability of finding a kink with length n .¹⁰ The factor of 2 in Eq. (7) originates from the fact that both positive and negative kinks can occur in a step. The total step free energy (per unit length of the step at $T=0$ K) thus becomes

$$f(T) = \varepsilon - kT \ln \left[\frac{1 + e^{-\varepsilon/kT}}{1 - e^{-\varepsilon/kT}} \right] + \left[3kT \ln \left(\frac{1 - e^{-\theta_s/T}}{1 - e^{-\theta_t/T}} \right) \right. \\ \left. + \frac{3}{2}k(\theta_s - \theta_t) \right] \left(1 + \frac{2e^{-\varepsilon/kT}}{1 - e^{-2\varepsilon/kT}} \right). \quad (8)$$

However, it is more appropriate to discriminate between kink and step atoms, because kink atoms have an even lower coordination than step atoms (in our case three nearest-neighbor bonds versus four nearest-neighbor bonds). The corresponding Einstein temperature of the kink atoms is $\theta_k = \sqrt{\frac{3}{5}}\theta_t$. The probability of finding a kink site in the step edge, $P(k)$, and the probability of finding no kink in the step edge, $P(0)$, are, respectively,

$$P(k) = 2 \sum_{n=1}^{\infty} P(n) = \frac{2e^{-\varepsilon/kT}}{1 + e^{-\varepsilon/kT}}, \quad (9)$$

$$P(0) = 1 - P(k) = \frac{1 - e^{-\varepsilon/kT}}{1 + e^{-\varepsilon/kT}}. \quad (10)$$

Furthermore, the increase in the number of step atoms (ΔN_s) due to the thermal generation of kinks with an absolute length of 2 or more is given by

$$\Delta N_s = \left(\frac{\lambda_0}{a} \right) 2 \sum_{n=2}^{\infty} (n-1)P(n) = \left(\frac{\lambda_0}{a} \right) \left(\frac{2e^{-2\varepsilon/kT}}{1 - e^{-2\varepsilon/kT}} \right). \quad (11)$$

Averaged per original step edge site at $T=0$ K one finds a fraction of $2e^{-2\varepsilon/kT}/(1 - e^{-2\varepsilon/kT})$ additional step atoms.

Finally, we arrive at the following expression for the step free energy:

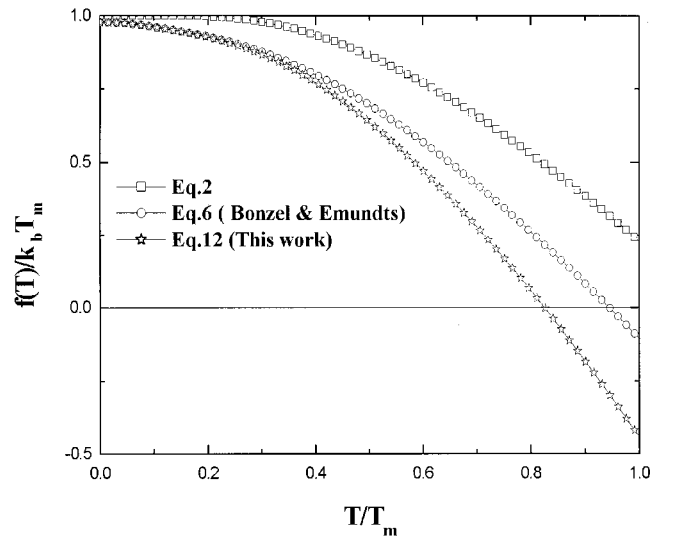


FIG. 1. Plot of the relative step free energy f/kT_m versus relative temperature T/T_m for Eqs. (2), (6), and (12). Equation (2) includes only thermally induced step meandering, Eq. (6) refers to the step free energy as determined by Frenken and Stoltze (Ref. 3) and Bonzel and Emundts (Ref. 4) and includes the vibrational entropy of the step atoms as well. Finally, Eq. (12) includes thermally induced step meandering and the vibrational entropy term from Eq. (6) as well as the vibrational entropy of the additional step and kink atoms which are thermally generated at elevated temperatures. We have assumed a kink energy $\varepsilon = kT_m$ and an Einstein temperature of a terrace atom $\theta = 0.15T_m$.

$$\begin{aligned}
f(T) = & \varepsilon - kT \ln \left(\frac{1 + e^{-\varepsilon/kT}}{1 - e^{-\varepsilon/kT}} \right) + \left[3kT \ln \left(\frac{1 - e^{-\theta_s/T}}{1 - e^{-\theta_t/T}} \right) \right. \\
& + \left. \frac{3}{2} k(\theta_s - \theta_t) \right] \left(\frac{1 - e^{-\varepsilon/kT}}{1 + e^{-\varepsilon/kT}} \right) + \left(\frac{2e^{-2\varepsilon/kT}}{1 - e^{-2\varepsilon/kT}} \right) \\
& \times \left[3kT \ln \left(\frac{1 - e^{-\theta_s/T}}{1 - e^{-\theta_t/T}} \right) + \frac{3}{2} k(\theta_s - \theta_t) \right] + \left(\frac{2e^{-\varepsilon/kT}}{1 + e^{-\varepsilon/kT}} \right) \\
& \times \left[3kT \ln \left(\frac{1 - e^{-\theta_k/T}}{1 - e^{-\theta_t/T}} \right) + \frac{3}{2} k(\theta_k - \theta_t) \right]. \quad (12)
\end{aligned}$$

The difference between this equation and Eq. (8) is quite small, indicating that the main effect stems from the creation of additional step edge length at elevated temperatures rather than an increase in the total number of kinks.

In order to visualize the effect of the additional vibrational entropy contribution of the kinks atoms and the additional step edge atoms we have plotted Eqs. (2), (6), and (12) in Fig. 1. Equation (2) includes only step meandering, whereas Eq. (6) refers to the equation derived by Bonzel and Emundts.⁴ In order to obtain a plot of f/kT_m versus T/T_m we have assumed that $\varepsilon = kT_m$ and $\theta = 0.15T_m$ (T_m is the melting point of the crystal and θ refers to the Einstein temperature of a terrace atom). As is evident from our plot the addi-

tional vibrational entropy contribution of the kink and extra step edge atoms that are thermally generated at elevated temperatures cannot be neglected.

The importance of our analysis is evident since the step free energy is a key parameter in many equilibrium surface processes (e.g., faceting and thermal roughening) as well as nonequilibrium processes (e.g., crystal growth and etching). For example, incorporation of vibrational entropy terms in the step free energy results in a thermal roughening temperature of the corresponding facet that is much lower than anticipated before. Moreover, the importance of considering vibrational entropy contributions extends beyond steps. Recently, Bonzel and Emundts⁴ have shown explicitly that for the surface free energy of low-index facets vibrational entropy cannot be ignored.

In conclusion, we have shown that the incorporation of the vibrational entropy of additional step and kink atoms that are generated at elevated temperatures results in a significant reduction of the step free energy.

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¹⁰The probability of finding a kink with positive length n (outward kink) is given by $P(n) = P(0)e^{-n\varepsilon/kT}$, whereas the probability of finding a negative kink with length n (inward kink) is given by $P(-n) = P(0)e^{-n\varepsilon/kT}$. By requiring that $\sum_{n=-\infty}^{\infty} P(n) = 1$ one can easily find that $P(0) = (1 - e^{-\varepsilon/kT}) / (1 + e^{-\varepsilon/kT})$.