Nonequilibrium free energy and kinetic roughening of steps on the Kossel(001) surface

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This paper studies the nonequilibrium energetics of growth steps. It discusses the energy and free energy of a [100] step on a Kossel(001) crystal surface as a function of the driving force in the case that two-dimensional nucleation is not active. Theoretical expressions for these energies are derived and are found to agree with data obtained from Monte Carlo simulations of step flow. The nonequilibrium expressions allow us to propose that the vanishing of the step free energy beyond a critical value of the driving force defines the onset of the kinetic roughening regime. This is found to agree with the earlier phenomenological criteria for this transition.

I. INTRODUCTION

The step free energy γ is the key parameter for describing the growth and roughening behavior of crystal surfaces.[1] It has therefore received considerable attention in the literature.[2–9] Much effort has been put into deriving an expression for the free energy of an infinitely long step on the Kossel(001) surface as a function of the step orientation at equilibrium conditions. This Kossel step is often referred to as the terrace-ledge-kink model. Some of these expressions were verified using Monte Carlo simulations.[5,6] On the other hand, almost no attention has been given to the step free energy at nonequilibrium conditions. Such conditions are highly relevant for a more precise understanding of two-dimensional (2D) nucleation growth and the phenomenon of kinetic roughening, which results in the disappearance of the nucleation barrier.[10–12]

In the nonequilibrium case, surfaces and steps under a driving force for crystallization always become rough at a sufficiently large time and length scale leading to a rounding of the roughening transition as is found explicitly in the Kardar-Parisi-Zhang (KPZ)[13] theory. Nevertheless, growth experiments[14,15] and Monte Carlo simulations[12,16,17] show a qualitative difference in the growth velocity versus driving force characteristics as the driving force $\Delta\mu$ increases above a threshold $\Delta\mu_c(T)$ at a temperature T below the equilibrium roughening temperature T_c. It is this point that one refers to as the onset of kinetic roughening. A theoretical evaluation of this transition is far from trivial. Most studies use the dynamical renormalization group[18] which extends the usual Kosterlitz-Thouless renormalization theory for equilibrium roughening. A disadvantage is that these theories use a mesoscopic description (the sine-Gordon model) of the system as a starting point. Hence there is no prediction of the critical driving force $\Delta\mu_c$ in terms of the microscopic parameters of the model.

In the present paper we want to propose a simple rule of thumb for such a prediction. To this end, we derive expressions for the step energy and free energy of the [100] step on a Kossel(001) face as a function of the driving force assuming that the step is in its steady state configuration. Our re-sults are compared with Monte Carlo data of growing steps. In the Monte Carlo simulations the step has a finite length with periodic boundary conditions to reduce edge effects. After an equilibration period the step reaches its steady-state configuration in which all kink densities remain constant even though the step is moving across the surface at a constant velocity. Both our theoretical model and the simulations are limited to the step and do not include the interaction between 2D nucleation and step flow. Also overhangs in the step direction are not allowed. Section II gives all details concerning the Monte Carlo simulations reported in this paper. At some critical driving force, the step free energy is found to become zero. At this driving force, steps can be formed at zero free-energy cost and the crystal surface becomes rough. We propose to extend the zero step free-energy criterion, which is used for defining the onset of thermal roughening, to the nonequilibrium case, i.e., that of kinetic roughening.

II. MONTE CARLO METHOD

We compare the theoretical results for the step free energy with step free energies directly obtained from step energies measured in Monte Carlo simulations. A program, which simulates the growth of a [100] step on a Kossel(001) face, measures the step energies and determines the step free energies as explained in the following section. This program was also used in two previous papers.[19,20]

The n-fold way Monte Carlo algorithm[21] is used to get acceptable simulation times and periodic boundary conditions are imposed to reduce edge effects. All simulations are performed using the "random rain" probability scheme,[22] which ensures microscopic reversibility.[16,23] In a previous paper we have shown that this scheme gives a good description of solution growth.[20] Since diffusion along the step and the surface is not included in the model, only creation and annihilation probabilities are relevant. The annihilation frequency/probability for a growth unit using the random rain model is given by

$$P^i = \frac{kT}{h} \exp\left(-\frac{2\phi_v}{kT}\right) \exp\left(-\frac{2i\phi}{kT}\right),$$ (1)

where i is the number of horizontal neighbors, and ϕ and ϕ_v are, respectively, the bond strengths of the horizontal and vertical bonds. kT/h has the usual meaning. The creation probability is site independent and is only determined by the driving force $\Delta\mu/kT$:

$$P^+ = P^{2-} \exp\left(\frac{\Delta\mu}{kT}\right).$$ (2)

III. THE STEP FREE ENERGY WITHOUT THE PRESENCE OF 2D NUCLEATION

A. Determining the free energy of a step

The step free energy is an important parameter for the step and surface roughness. If the step free energy approaches zero the nucleation barrier vanishes and the surface becomes rough. Since the free energy contains an entropy term, it cannot be obtained directly from the simulations, if the equation of state is not known. The step free energy at equilibrium conditions can, however, be determined from the integration over a number of simulations as a function of the temperature via

$$F(T) = U(0) - T\int_0^T \frac{U(T') - U(0)}{T'^2} dT'$$ (3)

as can be derived from the Gibbs-Helmholtz equation for the Helmholtz free energy F of the step.[24]

By determining the step energy for a range of temperatures at a fixed bond strength ϕ, the step free energy can be obtained directly from the step energies. In the literature, the step free energy at nonequilibrium conditions is usually obtained indirectly by fitting an expression for birth-and-spread growth to growth rate curves[14,16] or from the critical driving force for kinetic roughening.[15]

B. The step free energy at equilibrium

Theoretically, the step free energy can be obtained in two ways: using the partition function of the step, q, according to

$$\gamma_{step} = \phi - kT\ln(q)$$ (4)

or by using the integration of the step energy. In equilibrium, both approaches are feasible and result in the expression

$$\gamma_{step} = \phi - kT\ln\left(\frac{1 + \exp\left(-\frac{\phi}{kT}\right)}{1 - \exp\left(-\frac{\phi}{kT}\right)}\right).$$ (5)

Bennema and Meekes[25] also derived this expression for the equilibrium step free energy, which becomes zero at $\phi/kT = \ln(1+\sqrt{2}) \approx 0.881$. This is close to but, due to the neglect of step-step interactions, not equal to the critical bond

strength for thermal (equilibrium) roughening. It happens to be precisely the critical coupling for an Ising model as derived by Onsager.[26]

C. The step free energy at nonequilibrium

For nonequilibrium conditions, the concept of a step free energy is not so well defined. We propose a rather pragmatic construction for $\gamma_{step}(\Delta\mu)$ satisfying (i) $\gamma_{step}(\Delta\mu=0)$ reduces to the equilibrium result [Eq. (5)], (ii) setting $\gamma_{step}(\Delta\mu)=0$ gives an estimate for the kinetic roughening point in reasonable agreement with growth experiments. The more obvious choice is $\gamma = U - TS(\Delta\mu)$. As it turns out, this choice using Shannon's expression for calculating the entropy[27,28]

$$\gamma = \epsilon_{step} - Tk\left(\sum_{n=-\infty}^{\infty} -P_n\ln(P_n)\right)$$ (6)

with $P_n = \frac{1}{2}\Gamma_{k,|n|}$ and $P_0 = 1 - \sum_{n=1}^{\infty}\Gamma_{k,n}$, where $\Gamma_{k,n}$ is the density of kinks of height n, does (of course) satisfy criterion (i) but not (ii). Instead, we construct $\gamma_{step}(\Delta\mu)$ by assuming that Eq. (3) is still valid for nonequilibrium stationary conditions provided that the driving force is kept constant. We use this expression to derive the step free energy from the step energy. In order to obtain the nonequilibrium step energy, we express it in terms of $\Gamma_{k,n}$ according to

$$\epsilon_{step} = \phi + \sum_{n=1}^{\infty} n\phi\Gamma_{k,n}.$$ (7)

References 29 and 19 derive the kink density neglecting kink-kink correlations as a function of the driving force:

$$\Gamma_{k,n} = 2\Delta^n \frac{1-\Delta}{1+\Delta};$$ (8)

with

$$\Delta = \sqrt{\frac{\exp\left(-2\frac{\phi}{kT}\right) + \exp\left(\frac{\Delta\mu}{kT}\right)}{\exp\left(\frac{\Delta\mu}{kT}\right) + \exp\left(2\frac{\phi}{kT}\right)}}.$$ (9)

This expression is derived assuming adjacent sites to be statistically independent. Appendix A briefly explains its derivation and discusses the kink-kink interactions. Using Eq. (8), the step energy becomes

$$\epsilon_{step} = \phi + \frac{2\Delta\phi}{1-\Delta^2}$$ (10)

for values $\Delta < 1$. If $\Delta = 1$, $\epsilon_{step} = \phi$. The integral in the equation for the step free energy according to Eq. (3),

$$\gamma_{step} = \phi - T\int_0^T \frac{2\Delta\phi}{(1-\Delta^2)T'^2} dT'.$$ (11)

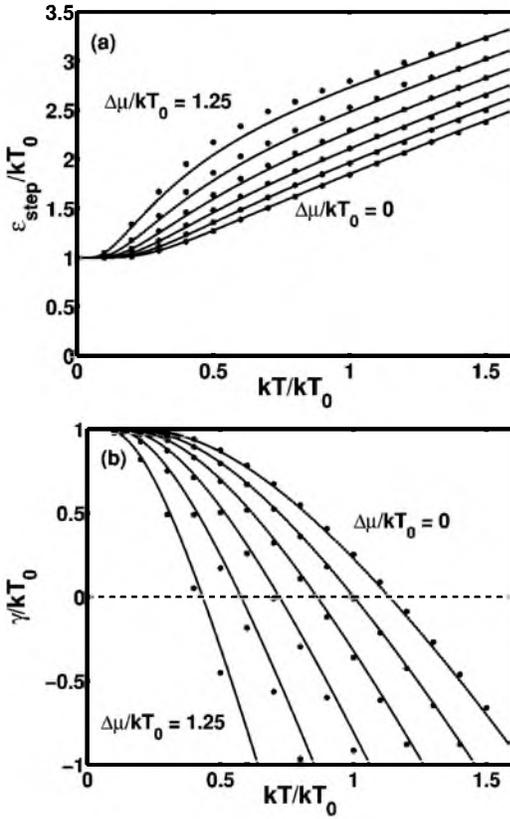cannot be solved analytically and is therefore determined numerically.

FIG. 1. The step energy (a) and the step free energy (b) as a function of the temperature for six different driving forces, $\Delta\mu$ $=0, 0.25, 0.5, 0.75, 1$, and $1.25 kT_0$, at a constant bond strength of $\phi = kT_0$, where T_0 is an arbitrary constant temperature. The dots represent the Monte Carlo measurements and the curves the theoretical models according to Eqs. (10) and (11), respectively.

In the following, we express all energies in units of kT_0, where T_0 is an arbitrary constant temperature, which we use for normalization. Figure 1(a) shows the step energy as a function of the temperature according to Eq. (10) for six different driving forces at a constant bond strength of $\phi = kT_0$, Fig. 1(b) presents the step free energy according to Eq. (11). The curves are the result of a numerical integration starting at $T=0$ K, where $\epsilon_{step} = \phi$. These theoretical values agree well with results obtained from Monte Carlo simulations. In Fig. 1(a) the dots represent the step energies measured in the simulations. The deviation of the theoretical curve from the Monte Carlo simulations at higher driving forces is due to the expression for the kink density, which does not describe the kink density for large kink heights very accurately.[19] This does not cause a problem in determining the total kink density, since the density of kinks with large heights is small. For the step energy, however, these small values are multiplied with the kink height and cause a slight deviation. The step free energies obtained from the Monte Carlo data [dots in Fig. 1(b)] are determined by a trapezoidal numerical integration of the step energy using Eq. (3). At each point, the integration includes all measured step energies at lower temperatures as well as the value $\gamma_{step} = \phi$ at $T=0$ K. Since both Eq. (11) and the Monte Carlo simulations use the same method to come to the step free energy,

the agreement between the curves and the Monte Carlo results only confirms the correct temperature dependence of the step energy in Eq. (10) and does not conform the validity of the method to calculate the step free energy from the step energy.

Because of the large contribution of the entropy, the step free energy becomes zero or negative at some temperature. For growth of a crystal surface, this would result in a transition to rough growth, since at this transition, steps can be formed at no free-energy cost. For our single step model, this is not the case, because no extra steps are allowed to be formed; the step can only get more and higher kinks. We can nevertheless use this result to derive a nonequilibrium condition for roughening.

D. The step free energy as a function of the driving force

The preceding section discusses the step free energy for a constant, nonzero driving force, and for a constant bond strength as a function of the temperature. From an experimental point of view, the driving force dependence of the step free energy is equally important in understanding 2D nucleation and kinetic roughening. By combining results for constant $\Delta\mu$ also this dependence can be found. Figure 2(a) shows the step free energy as a function of $\Delta\mu/kT$ for 11 different bond strengths ranging from $\phi/kT=1.5$ to 2.5. Each data point on the curves is obtained by an integration at constant ϕ and $\Delta\mu$ using Eq. (11).

Figure 2(b) shows, as a function of the bond strength, the critical driving force, $\Delta\mu_c$, at which the step free energy becomes zero. This is done both using Eq. (11) (solid line) and using Monte Carlo data shown in Fig. 1(b) and some additional simulations. Again the Monte Carlo data and theoretical curves are in good agreement. The critical driving force is zero till $\phi/kT=0.88$, which is the critical bond strength for thermal roughening as determined earlier. Above this bond strength, surfaces need a threshold driving force to become kinetically rough. Gilmer and Bennema[16] were the first to observe this roughening behavior by means of Monte Carlo simulations. They observed a transition from exponential to linear growth.

van Veenendaal et al.[12] argued that, in contrast with thermal roughening, kinetic roughening is not a phase transition and it lacks a well-defined transition point. They proposed eight criteria to mark the onset of the kinetical roughening. Their criterion $E2b$, which indicates the change in growth behavior from exponential to linear growth, is generally seen as the most reliable one. The dashed line in Fig. 2 represents this criterion. Our $\gamma_{step}=0$ line is in excellent agreement with this macroscopic description of the kinetic roughening regime for high bond strengths. We therefore propose to extend the $\gamma_{step}=0$ criterion for thermal roughening to the kinetic roughening regime.

Close to the critical bond strength for thermal roughening $\phi/kT=0.88$, our $\gamma_{step}=0$ line deviates from the macroscopic description, which approaches zero more smoothly. A similar behavior is predicted from the dynamical renormalization group analysis.[18] The fact that our rather heuristic construction misses these finer details, is not too surprising.
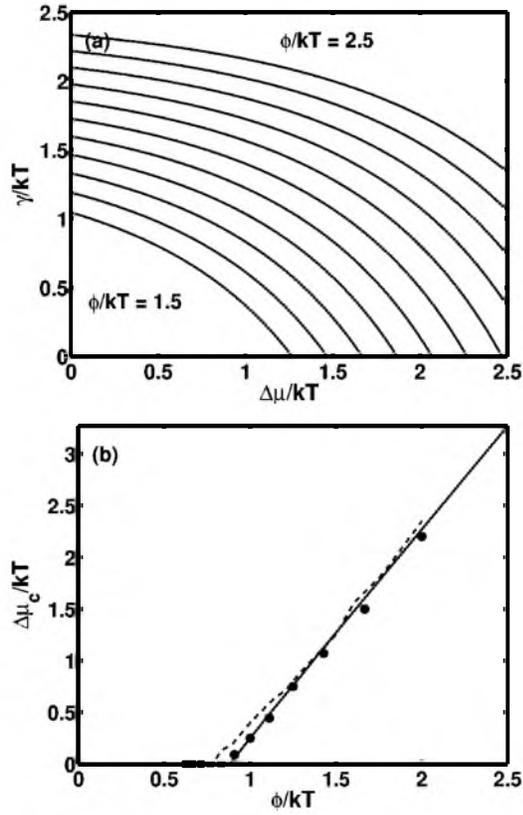
FIG. 2. (a) The step free energy as a function of $\Delta\mu/kT$ for 11 different bond strengths ranging from $\phi/kT = 1.5$ to 2.5 with intervals 0.1. Each curve is obtained using Eq. (11). The integration is performed at $\phi = kT_0$ and constant $\Delta\mu$. (b) The critical driving force at which $\gamma_{step} = 0$ as a function of the bond strength. The dots represent Monte Carlo results obtained from Fig. 1(b) with some additional simulations, the solid line is obtained using Eq. (11) and the dashed line represents the transition from exponential to linear growth as described by van Veenendaal et al.[12]

To start with: even in equilibrium our Eq. (5) does not accurately describe the vanishing of the step free energy as T approaches the roughening temperature[30] due to the neglect of step-step interactions. Moreover, taking these interactions into account in a nonequilibrium situation involves an even deeper analysis like the dynamical renormalization group.

IV. CONCLUSIONS

The present paper discusses the step energy and free energy of an infinitely long [100] step on the Kossel(001) surface as a function of the driving force without the presence of 2D nucleation. Analytical expressions for both quantities are derived and compared with step free energies determined in Monte Carlo simulations. The expression for the step energy is obtained using the nonequilibrium expression for the kink density. This gives a good agreement with the Monte Carlo simulations especially in the low driving force regime. The expression for the nonequilibrium step free energy is obtained via the Gibbs-Helmholtz equation using the step energy as a starting point. Again a nice agreement with the Monte Carlo simulations is found. The critical driving force,
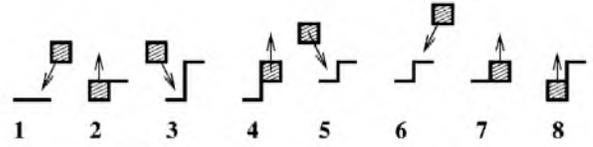

FIG. 3. Elementary events leading to an increase (1–4) or decrease (5–8) of the kink density of single height kinks. Only kinks up are considered here. For the total kink density also kinks down should be included.

at which the step free energy becomes zero, is used to find a new criterion for the transition from smooth growth to the kinetically rough regime. This is in good agreement with the kinetic roughening behavior as observed macroscopically.

Our determinations of the nonequilibrium free energy, both theoretically and in the Monte Carlo simulations, are based on the assumption that Eq. (3) is still valid at nonequilibrium conditions. This approach is able to describe the kinetic roughening behavior as observed macroscopically and therefore appears to be a good description for this application.

APPENDIX: KINK DENSITY

This expression for the kink density is obtained by constructing dynamical equations for all possible kink configurations using the frequencies of elementary events at different step sites and assuming adjacent sites to be statistically independent. This gives a change in the density of single height kinks of

$$a\frac{d}{dt}\Gamma_{k,1} = 2(1 - a\Gamma_k)\left[\exp\left(\frac{\Delta\mu}{kT}\right) + \left(1 - \frac{a}{2}\Gamma_k\right)\exp\left(-\frac{2\phi}{kT}\right)\right.$$
$$\left. + \frac{a}{2}\Gamma_k\right] + 2\left(\frac{a}{2}\Gamma_{k,2}\right)\left[\exp\left(\frac{\Delta\mu}{kT}\right) + \left(1 - \frac{a}{2}\Gamma_k\right)\right.$$
$$\left. + \frac{a}{2}\Gamma_k\exp\left(\frac{2\phi}{kT}\right)\right] - 2\left(\frac{a}{2}\Gamma_{k,1}\right)\left[2\exp\left(\frac{\Delta\mu}{kT}\right)\right.$$
$$\left. + \left(1 - \frac{a}{2}\Gamma_k\right)\exp\left(-\frac{2\phi}{kT}\right) + 1 + \frac{a}{2}\Gamma_k\exp\left(\frac{2\phi}{kT}\right)\right]$$

(A1)

with

$$\Gamma_k = \sum_{n=1}^{\infty}\Gamma_{k,n}.$$

(A2)

Equation (A1) can be understood as follows: the first term represents the increase in kink density due to the adding and removal of growth units at sites without a kink as drawn in Fig. 3 as events 1 and 2. The second term indicates the creation of single kinks from kinks of height 2 (events 3 and 4)

and the last term represents the decrease in kink density due to the vanishing of single kinks (events 5–8). Figure 3 only gives the change in kink density due to changes in kink density of kinks up. Equation (A1) accounts for both kinks up and kinks down by the factor 2 in each term.

Analogous to the change in the density of single kinks the change in kink density of height n with $n \neq 1$, $a \, d/dt \Gamma_{k,n}$, can be determined. If a steady state for all kink densities is assumed

$$a\frac{d}{dt}\Gamma_{k,n}=0 \qquad (A3)$$

for all n, solving these equations results in Eq. (8).

Neglecting the kink-kink interactions was proven to be justified for growth conditions within the random rain model.[20] Figure 4 shows two correlation factors, α_{ad} and α_{vac}, as a function of the driving force at a bond strength of $\phi/kT = 2$ obtained using Monte Carlo simulations. These factors represent the correlation between a kink up followed by a kink down and a kink down followed by a kink up, respectively, and are obtained as follows:

$$\alpha_{ad}=\frac{\displaystyle\sum_{n=1}^{5}\sum_{m=-5}^{-1}P_{unc}(n,m)}{\displaystyle\sum_{n=1}^{5}\sum_{m=-5}^{-1}P(n,m)} \qquad (A4)$$

and

$$\alpha_{vac}=\frac{\displaystyle\sum_{n=-5}^{-1}\sum_{m=1}^{5}P_{unc}(n,m)}{\displaystyle\sum_{n=-5}^{-1}\sum_{m=1}^{5}P(n,m)}. \qquad (A5)$$

$P_{unc}(n,m)$ is the probability of finding two adjacent kinks of height n and m if they are not correlated,
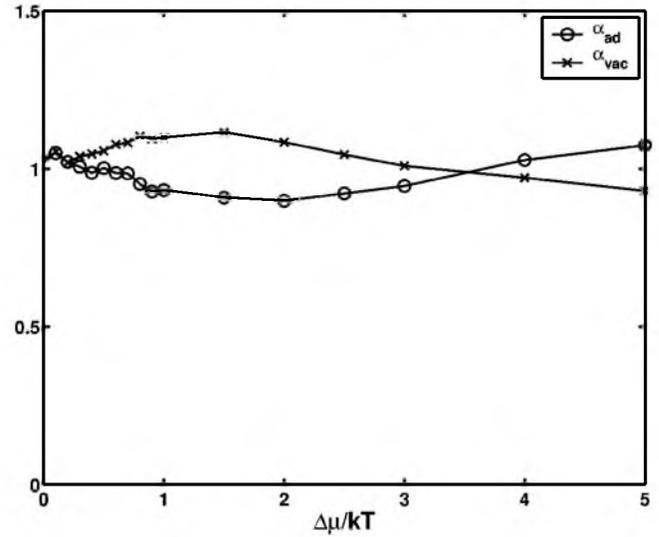

FIG. 4. The two α factors describing the kink-kink correlation obtained by Monte Carlo simulations for a bond strength of $\phi/kT = 2$; a value of $\alpha = 1$ corresponds to the absence of a correlation.

$$P_{unc}(n,m)=\tfrac{1}{4}a\Gamma_{k,|n|}a\Gamma_{k,|m|}, \qquad (A6)$$

and $P(n,m)$ is the actual probability of finding a kink combination (n,m). A positive value of n and m indicates a kink up and a negative value a kink down. The factors are, for simplicity, assumed to be independent of the height of the adatom and the depth of the vacancy and are limited to kink densities with heights up to 5, since these forms are by far the largest contribution. If both α factors are one, the kinks are not correlated. Since the factors presented in Fig. 4 are approximately one, the kink density as derived above is assumed to be a good description for a large range of driving forces including the kinetic roughening regime.

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