Local electromigration model for crystal surfaces

O. Pierre-Louis
CNRS/Laboratoire de Spectrométrie Physique, UJF-Grenoble 1, BP87, F38402 Saint Martin d’Hères, France
(Dated: March 23, 2022)

We analyze the dynamics of crystal surfaces in the presence of electromigration. From a phase field model with a migration force which depends on the local geometry, we derive a step model with additional contributions in the kinetic boundary conditions. These contributions trigger various surface instabilities, such as step meandering, bunching and pairing on vicinal surfaces. Experiments are discussed.

In the presence of an electric current, mobile atoms experience a diffusion bias, which is called electromigration. Surface electromigration is known as major source of rupture of microstructures, and is also an interesting tool for spontaneous nano-structure formation. In the past 15 years, kinetic instabilities at the micro, or nanometer scales, such as step bunching, meandering, and pairing, on stepped surfaces under electromigration have been the focus of a large literature. In the usual model for step motion under electromigration, mobile atoms between steps experience a constant drift force, while kinetic boundary conditions at steps are not affected by migration. It was first suggested in Ref. [2] that migration could lead to additional terms in step kinetic boundary conditions, and that these terms could modify the electromigration-induced drift of monolayer islands. Nevertheless, a microscopic explanation was lacking.

From the work of Rous and Bly [3] it is known that, in the vicinity of steps, the backscattering of carriers strongly alters the migration force. In the present letter, we show that the boundary conditions used previously in the literature should be modified to account for the variations of the migration force in the step region. To do so, we derive a step model from a phase field model with a non-constant migration force. The analysis of this step model reveals that the new contributions may produce all the instabilities known so far on vicinal surfaces. We finally discuss the relevance of our results for experimental observations on various surfaces.

We start with a microscopic description in terms of a phase field model [4]. We use the simplest model, where the surface is described by two fields \( \phi \) and \( c \), which respectively represent the normalized height of the surface, and the local concentration of mobile atoms. More sophisticated models, which may account for arbitrary kinetics at the steps are not considered here for the sake of simplicity [4]. The dynamics of the phase field \( \phi \) is such that \( \phi \) relaxes to a step and terrace structure. Terraces are wide regions where \( \phi \) is constant, and steps have a typical width \( W \), as shown in Fig.1. The motion of the steps is driven by the departure from equilibrium in the step region, measured by the concentration variations: \( c - c_{eq} \), where \( c_{eq} \) is the equilibrium concentration. The dynamics of \( \phi \) is a relaxation with time-scale \( \tau_\phi \):

\[
\tau_\phi \partial_t \phi = -\partial_c f + W^2 \nabla^2 \phi + \lambda (c - c_{eq}) \partial_\phi g \tag{1}
\]

The free energy density \( f \) is a periodic function of \( \phi \) with minima for the values of \( \phi \) corresponding to the terraces. The coupling function \( g \) is also a function of \( \phi \), with \( \partial_\phi g > 0 \), and \( g_+ - g_- = 1 \), where \( \pm \) indicate the lower or upper side of the step respectively. The constant \( \lambda \) controls the strength of the coupling between mobile atoms and steps.

A global external force is present, related to the macroscopic current in the bulk of the crystal. This current induces a local surface migration force \( \mathbf{M} \) on mobile atoms. The force \( \mathbf{M} \) depends on the surface local geometry via the phase field \( \phi \). The resulting mass flux, oriented in the direction \( \mathbf{n}_c = \mathbf{M}/|\mathbf{M}| \), reads:

\[
\dot{c}_c = Dc \frac{\mathbf{M}}{k_B T} = \frac{Dc}{\xi} \mathbf{n}_c \tag{2}
\]

where \( D \) is the local \( \phi \)-dependent diffusion constant, and \( \xi = k_B T/|\mathbf{M}| \) is a \( \phi \)-dependent lengthscale which characterizes the amplitude of the force. Local mass conservation then reads:

\[
\partial_t c = \nabla \left[ D \left( \nabla c - \frac{c}{\xi} \mathbf{n}_c \right) \right] + F - \frac{c}{\tau} - \partial_t h \tag{3}
\]

where \( h \) is the solid concentration, i.e. the number of solid atoms per unit area above a plane of arbitrary height parallel to the terraces. The variations of \( h \) are analogous to that of \( \phi \), and the jump of \( h \) across a step is constant \( h_- - h_+ = 1/\Omega \), where \( \Omega \) is the atomic area. Writing Eq. (4), we have discarded the tensorial coupling between the geometrical anisotropy of the step and the migration direction (i.e. the orientation of \( \mathbf{n}_c \)), which could change the local migration direction in the vicinity of a step. We shall rather focus on another effect which is, in our opinion, the most important one: the variation of the migration force amplitude in the step region. The phase field model presented here also neglects the dependence of the migration force on the adatom density. Indeed, this effect should occur at high densities only [5], while the adatoms densities which are relevant for the experiments mentioned below are small.
discontinuous at the step (the lower part of the figure, where the concentration may be suitable asymptotics, one obtains a step model as shown in |φ|)

and the departure from equilibrium (simplicity, we have shown a 1D cross-section, but the model shall assume that steps are slowly driven out of equilibrium, so that the smallest cut-off length is the local amplitude of the migration force. Using suitable asymptotics, one obtains a step model as shown in the lower part of the figure, where the concentration may be discontinuous at the step (c+, ≠ c−), and φ is now a Heaviside function which indicates the step position.

We now derive a step model from the phase field model. When step kinetics is fast, one may perform the thin interface asymptotics reported in Ref. [7, 10]. We assume that steps are slowly driven out of equilibrium, so that the smallest cut-off length related to the diffusion field on terraces is much larger than the step width W. We therefore define a small parameter ε ∼ W/ξc. We also take the coupling constant λ ∼ 1, and the departure from equilibrium (c − ceq) ∼ ε. The latter condition indicates that step kinetics is fast enough to keep the concentration in the step region close to ceq. Furthermore, the relaxation dynamics of the phase field itself must be fast enough so that the dynamics does not affect the step and terrace structure, and we choose τφ ∼ ε2.

From these asymptotics, the dynamics of the concentration of atoms far from the steps reduce to Eq. (1), with D → D0, and without the term ∂t h.

On the macroscopic level, and in the limit where the adatom coverage is small, mass conservation at the step reads:

$$\frac{V_n}{D_0\Omega} = n.\nabla c_+ - n.\nabla c_- + \frac{c_- - c_+}{\xi_s}$$  \hspace{1cm} (4)

where c0 and D0 are respectively the constant value of ξ and D on terraces far from steps. Performing the thin interface asymptotics, we obtain Eq. (4) to leading order. But since c ∼ ceq at the steps to leading order, the last term (c− c+)/ξs only appears to higher orders.

The additional equations obtained from the thin interface asymptotics are the kinetic boundary conditions for the concentration at the steps:

$$D_0 n.\nabla c_\pm - \frac{D_0 c_\pm}{\xi_s} = \nu_\pm \left( c_\pm - \tilde{c}_{eq} - \beta \frac{V_n}{\Omega} (1 \pm \frac{c_{eq}}{\xi_s}) \right)$$

where \(\tilde{c}_{eq} = c_{eq}(1 + \Gamma \kappa)\). These expressions involve some coefficients, the definition of which follows:

$$\Gamma c_{eq} = 2^{1/2} \frac{W}{\lambda} \int d\phi (f - f_{min})^{1/2}$$

$$\beta = 2^{1/2} \frac{2\phi}{W} \int d\phi (f - f_{min})^{1/2}$$

$$\nu_{\pm} = \pm \int dz (g_\pm - g) (D_{\pm} = D_0 - D^{-1})$$

$$Q_{\pm} = \pm \int dz (g_\pm - g)(1 - \xi_0/\xi)$$  \hspace{1cm} (7)

where fmin is the value of f at its minima. Integrals are taken through one step in the normal direction z. The constants g± are the values of g on both sides of the steps.

If we ignore the terms proportional to Q±, Eqs. (6) are equivalent to the general linear kinetic boundary condition of steps when step transparency and attachment-detachment on both sides of the steps are taken into account. Using linearized non-equilibrium thermodynamics, Eqs. (6) could have been stated directly, with the new terms proportional to Q±. Hence, Eqs. (6) are more general than the specific limit of the specific phase field model derived above. The relevance of our derivation from a phase field model comes from the explicit link between the terms of Eqs. (6) and microscopic quantities. Indeed, from Eqs. (7), Q+ or Q− account for the variations of |M| on the lower or upper side of the step respectively. Moreover, Q+ > 0 or Q− < 0 respectively account for the a decrease or an increase of |M| in the step region.

Instead of analyzing the consequences of the full boundary conditions (6), we shall now focus on a simplified limit. We define:

$$Q = Q_+ + Q_- = \int dx (1 - \xi_0/\xi).$$  \hspace{1cm} (8)

In order to grasp some of the main consequences of the new contributions, we shall focus on a simplified limit

FIG. 1: Phase field model with a non-constant migration force. The step region of width W is hatched. For the sake of simplicity, we have shown a 1D cross-section, but the model in the text is 2D. Notations: c is the mobile atom concentration, φ the phase field, D is the local diffusion constant, and |M| is the local amplitude of the migration force. Using suitable asymptotics, one obtains a step model as shown in the lower part of the figure, where the concentration may be discontinuous at the step (c+, ≠ c−), and φ is now a Heaviside function which indicates the step position.
where \( Q_+ = Q_- = Q/2 \). This may be obtained in the phase field model with an antisymmetric \( g \) and a symmetric variation of \( 1/\xi \). This assumption amounts to considering that the main effect of the force variation in the step region is an average increase, or decrease of the amplitude of the force, respectively leading to a negative or positive \( Q \). We also focus on a specific limit for step kinetics. We define:

\[
d_0 = D_0(n^+ + n^-) = \int dx \left( \frac{D_0}{D} - 1 \right) \tag{9}\]

Comparing the last term in the l.h.s. with the last term in the r.h.s. of Eqs. \( 10 \), we infer that \( Q_\pm \) will be relevant when it is of the order magnitude as \( D_0/\nu_\pm \). We therefore take the limit where \( \nu_\pm \) is large, which implies \( d_0 \) small. We also take \( D \) to be symmetric across the step so that \( \nu_+ = \nu_- \).

With these assumptions –symmetric \( 1/\xi \) and \( D \) and fast kinetics– the boundary conditions \( 11 \) read:

\[
c_\pm = c_\text{eq}(1 + \Gamma \kappa + Q^*/2\xi_s) + \beta \nu_n/\Omega \tag{10}\]

where

\[
Q^* = Q + d_0 = \int dx \left( \frac{D_0}{D} - \frac{\xi_0}{\xi} \right) \tag{11}\]

The expression \( 11 \) indicates in a remarkably compact formulation, that a single quantity \( Q^* \) accounts at the same time for the variations of the migration force, and for the variations of the diffusion constant in the step region. Eqs. \( 11 \) account for transparent steps when \( \beta \) is large, and non-transparent steps with fast attachment-detachment kinetics when \( \beta \) is small.

We shall now point out how all known elementary instabilities of vicinal surfaces are obtained from the model with kinetic boundary conditions \( 11 \). Let us analyze the stability of an array of initially straight and parallel steps separated by the same distance \( \ell \). We assume that the direction of migration is orthogonal to the average step direction. We also consider the conserved regime where \( F = 0 \) and \( 1/\tau \to 0 \). The \( m \)th step is perturbed by a small deviation

\[
\zeta_m(x, t) = \zeta_0 \phi \exp[i\omega t + im \phi + iqx] \tag{12}\]

where \( \phi \) and \( q \) are respectively the phase shift from step to step and the wavevector along the step. An instability is indicated by a positive \( \Re \{i\omega\} \). Substituting Eq. \( 12 \) in the model equations, one finds the general expression of \( i\omega \) as a function of \( \phi \) and \( q \).

In the case of in phase meandering (\( \phi = 0 \)), one finds in the long wavelength and weak electromigration limit \( (q\ell)^2 \sim \ell/\xi_0 \ll 1 \):

\[
i\omega \approx \Omega c_\text{eq} D \left[ \frac{Q^*}{\xi_0} q^2 - \Gamma \ell q^4 \right] \tag{13}\]

Therefore, the train of steps is unstable when \( Q^*/\xi > 0 \), and the most unstable wavelength is: \( \lambda_m = 2\pi(2\xi_0 \ell/Q^*)^{1/2} \).

In order to analyze step bunching, we shall introduce a repulsion between steps. If this interaction is of elastic or entropic origin, its free energy per unit step length is \( A/\ell^2 \) \( 14 \). The local equilibrium concentration is then

\[
\tilde{c}_\text{eq} = c_\text{eq} \left( 1 + \Gamma \kappa + 2A (\ell_+^3 - \ell_-^3) \right) \tag{14}\]

where we have only considered the interaction between neighboring steps, and \( A = \Omega A/k_B T \). For the sake of simplicity, we analyze the stability of the mode \( q = 0 \), which accounts for the bunching of straight steps. In the limit of weak electromigration, the linear stability analysis leads to:

\[
\frac{i\omega}{\Omega D c_\text{eq}} = \frac{2Q^*(1 - \cos(\phi)) - 12(\ell/\ell)^2[1 - \cos(\phi)]^2}{2(1 - \cos(\phi))\Omega D \beta/\ell} \tag{15}\]

Once again, an instability appears if \( Q^*/\xi > 0 \). The stability analysis thus indicates that a vicinal surface is simultaneously destabilized with respect to bunching and meandering for a downhill flux when migration or diffusion is weaker in the step region, and for an uphill migration when migration or diffusion is enhanced in the vicinity of the steps.

Let us now discuss some of the experimental results of the literature. On Si(111), atoms drift along the current direction \( 12 \). Three temperature regimes, denoted I, II, and III, with increasing temperature, were found above the \( (7 \times 7) \to (1 \times 1) \) reconstruction transition temperature \( 11 \). In regimes I and III, bunching is observed for a downhill current during both growth and sublimation \( 12 \). In regime II, bunching is observed during growth for a downhill current, and during sublimation for an uphill current \( 13 \). From the step model without the \( Q \) contribution, it was concluded that regimes I and III correspond to opaque steps \( (\beta, \nu_+, \text{ and } \nu_- \text{ small}) \), and regime II corresponds to fast step kinetics \( (\nu_+ \text{, and } \nu_- \text{ large}) \) \( 13 \).

In the case of opaque steps, the \( Q \) terms are probably only a small contribution, unless a dramatic increase of migration is observed in a large region around the step. There is no evidence of such a strong effect.

In the case of fast kinetics, the \( Q \) terms become important. From the study of step pairing \( 5 \), it was concluded that \( \beta \) is large, which means that steps are transparent. In Ref. \( 13 \), the occurrence of pairing was related to a small negative kinetic length \( d_0 \approx -0.13 \AA \). In the present analysis, this result generalizes to \( Q^* = Q + d_0 \approx -0.13 \AA \). We therefore obtain an alternative explanation for the pairing in the limit \( |Q| \gg |d_0| \) of steps on Si(111), based on \( Q < 0 \), i.e. on a stronger migration in the step regions. Quantitatively, we find \( Q \approx -0.13 \AA \). This may for example account for an increase of 1% of the migration force in a step region of width 13\AA.
Step meandering is also observed during sublimation with downhill migration in regime II [2]. If $Q < 0$, as suggested above, then $Q$ rather favors the stabilization of the meander for a downhill flux. Meandering therefore requires an extended study, which would also account for the sublimation rate, and which is beyond the scope of the present letter. A recent discussion can be found in Ref. [15].

Another system of interest is Si(100), which undergoes a dimer-row reconstruction, rotated of $\pi/2$ from one layer to the next one. We here assume that dimer rows are perpendicular $\perp$ or parallel $\parallel$ to steps, and that the current is perpendicular to the average step orientation. It was shown in Ref. [16] that the difference of diffusion constant ($D_\perp$, $D_\parallel$) perpendicularly to the step leads to pairing, and subsequent bunching of pairs [17] for both directions of the electric current. The crucial quantity on terraces is the migration induced mass flux $j \sim c_{eq} D/\xi$, which is proportional to the product of the diffusion constant with the migration force. Therefore, the phenomena that are attributed to a variation of $D$ can also be the result of a variation of $\xi$. Thus, pairing and bunching of pairs can also be the result variations of $\xi$. More precisely, stronger migration along dimer rows reproduces pairing and bunching of pairs for both directions of the current, as observed in experiments [18]. As a conclusion for Si(100), the variations of the force cannot be neglected a priori. Furthermore, following Ref. [19], one could consider pairs as effective steps, with an internal region where diffusion and the migration force may vary. We could then follow the above mentioned analysis to determine the effective value of $Q$. This would help to analyze the pair bunching dynamics.

We also expect the effect presented above to be relevant for the case of metals. Indeed, from microscopic models on metallic surfaces [4], strong variations of the migration force in the vicinity of the steps were found. Rous and Bly [20], indicate a decrease up to $\sim 50\%$ in a region $\sim 20\AA$ for Na. Using Eq. (8) with an approximate integration of the results of Ref. [19], we find $Q \approx 10\AA$. This contribution is two order of magnitude larger than that found above for Si(111), and should therefore have drastic consequences on the dynamics of metal surfaces under electromigration. Experiments on Au surfaces [21] indicate that in presence of an electric current, the Ehrlich-Schwoebel (ES) effect [19] (a decrease of interlayer mass transport related to a low value of $\nu_-$) disappears, and a significant increase of interlayer mass transport is observed. The disappearance of the ES effect is probably caused by the increase of the temperature due to the joule heating effect. Indeed, it was shown in Ref. [22], that the ES effect disappears at high temperature on Au. Therefore, kinetics is fast, and the tendency to bunching indicated in Ref. [21] could be caused by the non-constant migration scenario presented above.

Step bunching was also observed on some other metal surfaces [22]. Moreover, recent experiments [23] have shown that GaN(0001) vicinal surfaces also exhibit step bunching for a downhill electric current during epitaxial growth. The non-constant migration force scenario should also be considered in these cases. But the lack of quantitative understanding of the microscopic processes prevents a precise analysis.

In conclusion, we have shown that variations of the migration force in the vicinity of the steps may lead to step bunching, meandering, or pairing during electromigration. This mechanism defines a novel scenario for surface instabilities, which may compete or combine with the other destabilizing mechanisms analyzed in the literature. Finally, we have discussed the relevance of our results for some semiconductor and metal surfaces.

[1] A.V. Latyshev et al. Surf. Sci. 213 157 (1989).
[2] M. Degawa, H. Minoda, Y. Tanishiro, and K. Yagi Phys. Rev. B 63, 045309 (2001).
[3] O. Pierre-Louis, J.-J. Métois Phys. Rev. Lett. 93, 165901 (2004).
[4] S. Stoyanov, Jpn. J. Appl. Phys. 30 1 (1991).
[5] O. Pierre-Louis, T.L. Einstein, Phys. Rev. B, 62 13697 (2000).
[6] P.J. Rous, and D.N. Bly, Phys. Rev. B 62 8478 (2000).
[7] O. Pierre-Louis, Phys. Rev. E 68, 021604 (2003).
[8] O. Pierre-Louis, unpublished.
[9] H. Ishida, Phys. Rev. B 49 14610 (1994).
[10] A. Karma, W.-J. Rappel, Phys. Rev. E 57, 4323 (1998).
[11] P. Nozières in Solids far from Equilibrium edited by C. Godrèche (Cambridge University Press, Cambridge).
[12] M. Degawa et al Surf. Sci. 461 L528 (2000).
[13] J.-J. Métois and S. Stoyanov, Surf. Sci. 440 407 (1999).
[14] O. Pierre-Louis, Surf. Sci., 529 114 (2003).
[15] T. Zhao, J. D. Weeks, and D. Kandel Phys. Rev. B 70, 161303 (2004).
[16] L.V. Litvin, A.B. Krasilnikov, and A.V. Latyshev, Surf. Sci. Lett. 244 L121 (1991).
[17] M. Sato et al, J. Phys. Soc. Jap. 73 1827 (2004).
[18] T. Zhao, J. D. Weeks, and D. Kandel Phys. Rev. B 71, 155326 (2005).
[19] R.L. Schwoebel, J. Appl. Phys. 40 614 (1969).
[20] N. Shimoni, M. Wolovelsky, O. Biham, O. Millo, Surf. Sci. 380 100 (1997).
[21] R. Ferrando and G. Tréglia, Phys. Rev. Lett. 76, 2109 (1996).
[22] R. Johnson, Phys. Rev. 54 549 (1938).
[23] M.H. Xie et al, Phys. Rev. B 61 9983 (2000).
[24] We here ignore the terms related the interface definition mentioned in Ref. [8], which are not relevant for our purposes.
[25] Indeed, the mass flux (l.h.s. of Eqs. (5)) must be proportional to a linear combination of the 3 thermodynamic forces, which are proportional to the departure from equilibrium on both sides of the step ($c_+ - c_{eq}$) and ($c_- - c_{eq}$), and the amplitude of the migration force far from the step $1/\xi_0$. Then we follow Ref. [8] and perform a linear combination of the boundary conditions to cancel the cross concentration terms, which introduces the term $\beta V_\perp$.