Mater. Res. Soc. Symp. Proc. Vol. 1318 © 2011 Materials Research Society
DOI: 10.1557/opl.2011.269

Stochastic Models of Epitaxial Growth

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ABSTRACT

We study theoretical aspects of step fluctuations on vicinal surfaces by adding conservative white noise to the Burton-Cabrera-Frank model in one spatial dimension. We consider material deposition from above, as well as entropic and elastic-dipole step repulsions. Two approaches are discussed: (i) the linearization of stochastic equations when fluctuations are small, which captures correlations; and (ii) a mean field approach, which leaves out correlations but captures nonlinearities. Comparisons to kinetic Monte-Carlo simulations are presented.

INTRODUCTION

The fluctuations of steps on surfaces of crystalline materials such as silicon have been the subject of active experimental interest. A goal is to determine dominant pathways of atomic mass transport by observing the terrace width probability density or distribution (TWD) [1, 2]. Developing a complete theory of stochastic effects on vicinal surfaces poses a challenge. Crucial, yet largely unresolved, issues include: (1) the derivation of noise models from microscopic principles, and (2) the rigorous description of statistics for terrace widths in large systems. An approach that partly circumvents issue (1) is to add *ad hoc* noise to the celebrated Burton-Cabrera-Frank (BCF) model [3, 4] of step flow. In this vein, a systematic kinetic description of terrace-width fluctuations in terms of a mean field was proposed recently [5] on the basis of hierarchies for terrace correlation functions in one space dimension (1D). This formalism was recently applied to a large system of interacting steps in the absence of material deposition under the assumption that the noise obeys a second-order conservative scheme [6]. Here, we extend the formulation of [6] to the case with material deposition of flux F from above. In addition, we discuss possible physical implications that stem from the analysis, and illustrate limitations of approximations for the (intrinsically nonlinear) stochastic equations of motion. We show *how* the step interactions and deposition flux can jointly cause narrowing of the TWD, thus enriching the recent related work by Hamouda, Pimpinelli and Einstein [2] with step energetics.

THEORY: MODELING AND ANALYSIS

The step geometry is shown in figure 1. The j-th terrace is the region $x_j<x<x_{j+1}$ which has width w_j, where $j=0, \ldots, N-1$, and N is large. We apply screw periodic boundary conditions, mapping steps to point particles on a ring [5, 6]. For a vicinal crystal, the average terrace width is fixed at a constant value, $\langle w\rangle$, and w_j equals $\langle w\rangle$ initially (at t=0).

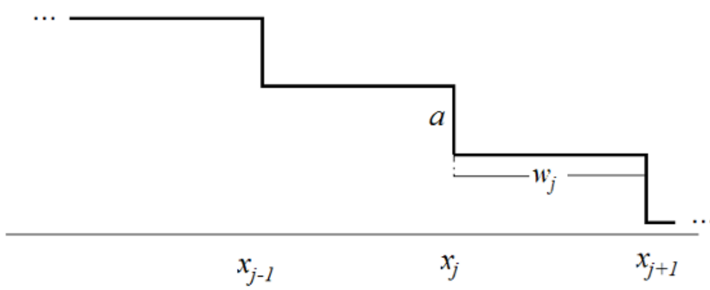

Figure 1. Schematic of a vicinal surface in 1D; x_j are step positions and a is the step height.

To formulate equations of motion for $w_j(t)$, we use the BCF theory [3, 4] with an external deposition flux, F, as well as entropic and elastic-dipole step repulsions [7]. Following [2], we apply a Galilean transformation to the co-moving frame with velocity $Fa\langle w\rangle$. We assume that step motion is slower than adatom diffusion (i.e., apply the quasistatic approximation) in this co-moving frame. Then, we add second-order conservative white noise to the equation of motion for w_j: the noise term is $-\eta_{j+1}+2\,\eta_j-\eta_{j-1}$ where $\eta_j(t)$ are independent (and identically distributed) white (delta-correlated) noises. This choice yields a *finite* variance of the TWD but is not unique. However, lower-order (non-conservative and first-order) schemes for white noise fail to yield a finite variance for long times [6]. Details of the formulation are given in [2, 5, 6, 8]. By change of variables from w_j to $w_j/\langle w\rangle$, denoted s_j, and use of non-dimensional time via scaling of t by some scale t^*, e.g., $\langle w\rangle^2/D_s$ where D_s is the terrace diffusivity, the stochastic equations are

$$\frac{ds_j}{dt} = -Fa\,\mathcal{A}(s_{j-2}, s_{j-1}, s_j, s_{j+1}, s_{j+2}) - \eta_{j+1} + 2\eta_j - \eta_{j-1}; \quad s_j = w_j\langle w\rangle^{-1}\,, \tag{1}$$

where $\mathcal{A}(\ldots,s,\ldots)$ blows up as $1/s^3$ if any terrace-width variable, s, approaches zero [6, 8].

Small fluctuations: linearization and steady-state TWD

The linearization of Eqs. (1) leads to the matrix equation

$$\frac{d\boldsymbol{s}}{dt} = -Fa\,\boldsymbol{A}\cdot\boldsymbol{s} + \boldsymbol{Q}\cdot\boldsymbol{\eta}; \qquad \boldsymbol{s} = \frac{\boldsymbol{w}}{\langle w\rangle}\,. \tag{2}$$

Here, $\boldsymbol{w}$ and $\boldsymbol{\eta}$ are N-dimensional vectors with components w_j and η_j, and $\boldsymbol{A}$ and $\boldsymbol{Q}$ are $N\times N$ circulant matrices. For example, for *diffusion-limited kinetics* these matrices have first rows [$1-2p+3g(1+2\varsigma)$, $-1+p-g(3+4\varsigma)$, $g(1+\varsigma)$, 0, …, 0, $g\varsigma$, $p-g(1+4\varsigma)$] and [2, -1, 0, …, 0, -1] where [8]

$$g = 3\frac{\tilde{g}}{k_B T} m_0{}^3 (ac_s), \qquad \varsigma = \frac{1}{2}\frac{e^{-\nu}}{\sinh\nu}, \qquad p = \frac{1}{2}\left[\frac{\nu}{(\sinh\nu)^2} - \frac{e^{-\nu}}{\sinh\nu}\right], \qquad \nu = \frac{Fa\langle w\rangle^2}{2D_s}; \quad (3)$$

$\tilde{g}$ is a typical step-step interaction energy, $k_B T$ is the Boltzmann energy, m_0 is the initial (constant) slope of the vicinal crystal, and c_s is the equilibrium adatom concentration at steps.

By basic stochastic calculus, we assert that the solution to Eq. (2) is a (vector) Gaussian random variable for every time $t>0$. Thus, the corresponding TWD turns out to be the Gaussian

$$P^{\mathrm{lin}}(s,t) = \frac{1}{\sqrt{2\pi\sigma_N(t)^2}} \exp\left[-\frac{(s-1)^2}{2\sigma_N(t)^2}\right]. \qquad (4)$$

For a finite number, N, of steps, the variance, $\sigma_N(t)^2$, of this TWD can be expressed exactly in terms of a discrete sum involving the eigenvalues of the matrices $\boldsymbol{QQ}^T$ and $\boldsymbol{A}+\boldsymbol{A}^T$ (where the superscript T denotes the matrix transpose) [5, 6]. Each set of eigenvalues is the discrete Fourier transform of the first row of the corresponding matrix [5]. In the macroscopic limit, $N\to\infty$, the discrete sum is replaced by an integral [5, 6]. The respective *steady-state* variance is found to be

$$\sigma_{\mathrm{st}}{}^2 = \sigma_\infty(t\to\infty)^2 = \frac{4}{Fa}\frac{1}{\sqrt{1-2p+4g(1+2\varsigma)}}\frac{1}{\sqrt{1-2p+4g(1+2\varsigma)}+\sqrt{1-2p}}, \qquad (5)$$

which accounts for terrace correlations (but not for nonlinearities). For zero deposition rate (i.e., as $F\to 0$), Eq. (5) yields $(2g)^{-1}\langle w\rangle^2/(D_s t^*)$, in agreement with [6]. In figure 2, we plot $\sigma_{\mathrm{st}}{}^2$ versus p for different values of the interaction parameter, g. Note that Eq. (4) predicts a nonzero probability for negative terrace widths, which amounts to step crossing. If $\sigma_{\mathrm{st}}{}^2$ is small enough, this likelihood of step crossing can be ignored. In [8], the variance of the TWD was computed for *flux-induced*, first-order conservative noise, whose coefficient depends linearly on p and stems from the asymmetric attachment of atoms at steps.

Mean field approach and decorrelation hypothesis

An alternate approach, in which nonlinearities are retained, is to fix the value of the neighboring terrace widths in each of Eqs. (1) to an *a priori unknown* mean field, $f(s,t)$. This field must be determined self-consistently [2, 5]. Seeds of this approach can be traced in the classic work by Gruber and Mullins [9]. Recently, the underlying kinetic framework was formulated systematically via appropriate hierarchies for terrace-terrace correlation functions [5].

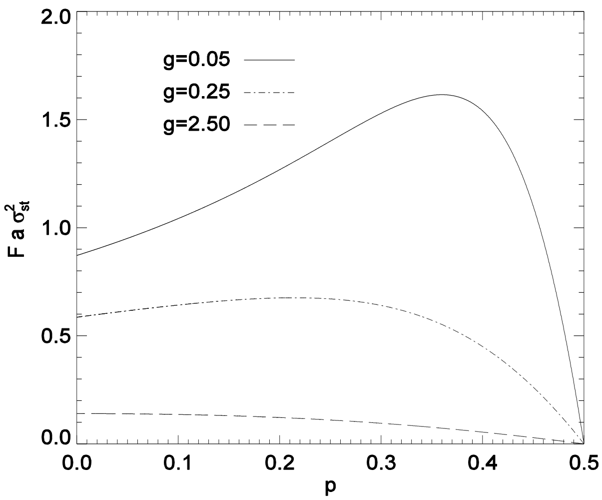

Figure 2. Plot of steady-state variance of the TWD as a function of parameter *p* by Eq. (5).

A goal is to reduce the system of Eqs. (1) to a single, tractable Langevin-type equation for an effective terrace width, $\hat{s}$ [5, 6]. This goal is achieved in three stages. *First*, the variables $s_{j\pm1}$ and $s_{j\pm2}$ are replaced by $f(\hat{s})$ and s_j is replaced by $\hat{s}$; and the noise term is replaced by $q\eta$, where q^2 equals 6 (the sum of squares of elements in the first row of matrix $\boldsymbol{Q}$) and η is the usual white noise. *Second*, we require that $\hat{s}$ produces the *same* TWD, $P(s)$, as the one from the starting system, Eqs. (1). Alas, the ensuing consistency formula for f turns out to be unwieldy: f is given in terms of the 5-terrace correlation function, $p^{(5)}$. *Third*, to enable analytical progress, we assume that the terrace widths are decorrelated, viz., $p^{(5)}$ is expressed as the product of the TWD's. By comparing the equations for the decorrelated s_j with the Langevin equation for $\hat{s}$, we derive an approximate formula for the self-consistent f. In the steady state, this formula reads [6]

$$\mathcal{A}\big(f(s), f(s), s, f(s), f(s)\big) \approx \iint_{-\infty}^{+\infty} \mathcal{A}(y_1, y_2, s, y_2, y_1) P(y_1) P(y_2)\, dy_1 dy_2. \tag{6}$$

For example, consider *diffusion-limited kinetics* without deposition [6]. For *large g*, Eq. (6) yields f approximately equal to unity (average s_j). The respective, "zeroth-order" TWD is

$$P_0^{\mathrm{mf}}(s) \propto s^{-\frac{4\breve{g}}{3}} \exp\left(-\frac{2\breve{g}s}{3} - \frac{\breve{g}}{3s^2} - \frac{4\breve{g}}{9s^3}\right), \quad \breve{g} = \frac{1}{3}\frac{t^* D_s}{\langle w\rangle^2}\, g, \quad s > 0; \quad P_0^{\mathrm{mf}}(s) \equiv 0, \ \ s < 0. \tag{7}$$

By deriving an asymptotic expansion for f in powers of g^{-1}, we can obtain a more accurate, "composite expression" for the TWD that involves a single integral of $\mathcal{A}$ [6].

DISCUSSION

The analysis of stochastic effects in 1D reveals certain advantages of the mean field approximation over the small-fluctuation limit of the linearized model. Recall that the linearization of the governing equations of motion captures certain correlations (but cannot account for nonlinearities). In contrast, the mean field approach under the decorrelation ansatz captures nonlinearities but leaves out correlations. Thus, the question naturally arises as to which approximation is more reliable in the present setting of vicinal surfaces. To address this issue, we resort to comparing the TWD's predicted by the mean field and linearization approaches to the TWD produced via kinetic Monte Carlo simulations; see figure 3 [6]. This comparison indicates that the mean field approach, with a higher-order correction for *f*, reproduces accurately the essential features of our simulations for the steady-state TWD. A noteworthy feature is the *asymmetry* of the TWD, which should arise physically from the non-crossing condition for steps and is more pronounced as the step repulsion decreases. This asymmetry *cannot* be predicted by the linearized model, but is captured within the mean field approximation. Hence, in this vein, nonlinearities of step interactions tend to be more significant than terrace-terrace correlations. A similar observation can be made for the time-dependent TWD, although terrace correlations are stronger for finite times, and the above mean field approximation needs to be improved [6].

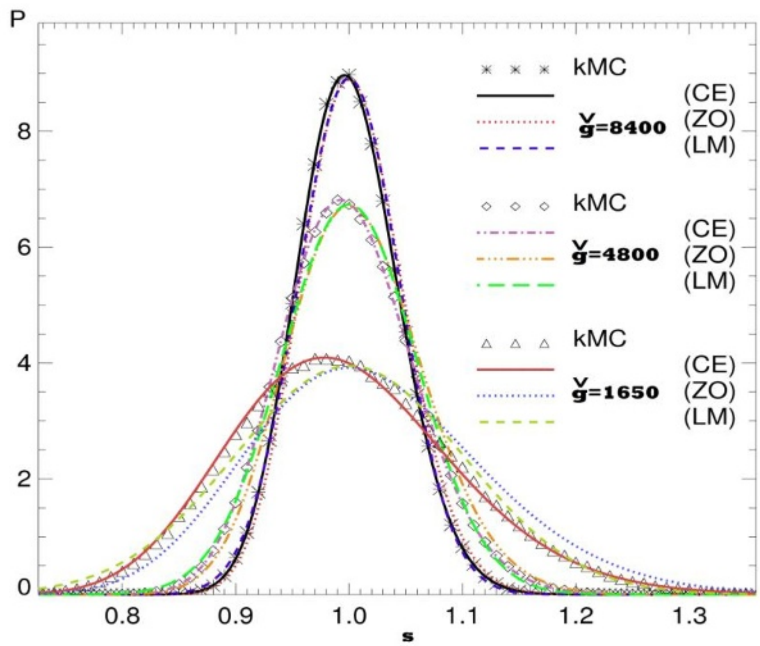

Figure 3. Steady-state TWD for F=0 and attachment-detachment limited kinetics, reproduced from figure 2 of [6]: (i) kinetic Monte Carlo simulations (kMC); (ii) linearized model (LM); and (iii) mean field approach by a zeroth-order (ZO) formula in which f is approximated by the average normalized terrace width ($f \approx 1$), and a composite expression (CE) in which f acquires a higher-order correction of the order of g^{-1}. The parameter $\breve{g}$ is defined in Eq. (7).

Our analysis predicts the *narrowing* of the steady-state TWD under the combined effects of step repulsions and deposition flux, F. For example, consider diffusion-limited kinetics with recourse to Eqs. (4) and (5) as $N \to \infty$. For small F, the steady-state variance approaches a value that scales as g^{-1}. As F becomes large (i.e., $p \to 0$), the steady-state variance decreases according to the asymptotic formula

$$\sigma_{\mathrm{st}}^2 \approx (Fa)^{-1}(1+4g)^{-\frac{1}{2}}\left(\sqrt{1+4g}+1\right)^{-1}. \qquad (8)$$

Results of the present study are limited in their applicability because of the assumed (one-dimensional) geometry. We expect that the detailed form of the TWD, especially for small values of the terrace width, can be distinctly different in two spatial dimensions (2D) where steps meander. For example, Eq. (7) reveals a singularity of the TWD at s=0. We believe that this type of singularity is an artifact of 1D. However, some of our results, e.g., the narrowing of the TWD with the step interaction strength, should hold for quasi-1D step systems.

CONCLUSIONS

This study explores the advantages, predictions and limitations of analytical approximation theories for terrace fluctuations on vicinal crystals in 1D. The mean field approach under a decorrelation hypothesis captures the asymmetry of the steady-state TWD, in contrast to the small-fluctuation limit of a linearized model. Both theories predict narrowing of the steady-state TWD with increasing deposition rate or step-repulsion strength. A limitation of the present study is due to the one-dimensional geometry. However, it is expected that some results, such as the scaling of the TWD with the deposition rate or the step-repulsion strength, should be applicable to quasi-1D systems.

ACKNOWLEDGMENTS

Research by the first author (DM) was supported by NSF under grant DMS 08-47587. Work by the other two authors (PP and TLE) was supported by the NSF MRSEC under grant DMR 05-20471 at the University of Maryland, with ancillary support from CNAM.

REFERENCES

1. S. D. Cohen, R. D. Schroll, T. L. Einstein, J. J. Métois, H. Gebremariam, H. L. Richards, and E. D. Williams, *Phys. Rev. B* **66**, 115310 (2002).
2. A. BH. Hamouda, A. Pimpinelli, and T. L. Einstein, *Europhys. Lett.* **88**, 26005 (2009).
3. W. K. Burton, N. Cabrera, and F. Frank, *Phil. Trans. Roy. Soc.* **243**, 299 (1951).
4. H. C. Jeong and E. D. Williams, *Surf. Sci. Rep.* **34**, 171 (1999).
5. D. Margetis, *J. Phys. A: Math. Theor*. **43**, 065003 (2010).
6. P. N. Patrone, T. L. Einstein, and D. Margetis, *Phys. Rev. E*, accepted for publication.
7. V. I. Marchenko and A. Ya. Parshin, *Sov. Phys. JETP* **52**, 129 (1980).
8. P. N. Patrone, R. Wang, and D. Margetis (unpublished).
9. E. E. Gruber and W. W. Mullins, *J. Phys. Chem. Solids* **28**, 875 (1967).