Stochastic Mullins-Herring equation for a solid-on-solid crystal

C. N. Luse and A. Zangwill
School of Physics, Georgia Institute of Technology, Atlanta, Georgia 30332
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We derive a stochastic version of the Mullins-Herring equation—a continuum equation of motion for the relaxation of a solid surface to morphological equilibrium—for a two-dimensional solid-on-solid crystal. For Arrhenius-type desorption and surface diffusion kinetics, a *linear* Langevin equation describes the scaling behavior of the surface width. The final equation of motion is interpreted in terms of effective, macroscopic desorption and surface-diffusion parameters that reflect the full chemical activity of the surface.

Thirty-five years ago, Mullins[1] studied the capillary flattening of a perturbed crystal surface to its equilibrium form. Using phenomenological arguments from kinetic theory, he derived a morphological equation of motion in the form

$$\frac{\partial h}{\partial t}=aD_S\nabla^2\Lambda-a\Omega\Lambda+a^2F \;, \tag{1}$$

where a is the lattice constant, D_S is the surface diffusion constant, Ω is the mean desorption rate, F is the mean deposition flux, and

$$\Lambda(\mathbf{x})=\exp[(\mu(\mathbf{x})-\mu_B)/k_BT] \tag{2}$$

is the thermodynamic *activity*. The latter is defined in terms of the local surface chemical potential $\mu(\mathbf{x})$ and the chemical potential of the bulk μ_B. The connection to the surface profile $h(\mathbf{x},t)$ is made by use of a celebrated formula due to Herring[2] for the local chemical potential of a nonplanar solid surface,

$$\mu(\mathbf{x})=\mu_B+a^2\tilde{\gamma}(\hat{\mathbf{n}})\mathcal{K}(\mathbf{x}) \;, \tag{3}$$

where $\tilde{\gamma}(\hat{\mathbf{n}})$ is the orientation-dependent surface stiffness[3] and $\mathcal{K}(\mathbf{x})$ is the local surface curvature.

The results of Herring and Mullins were derived from a macroscopic point of view that neglects both fluctuations and possible subtleties associated with lattice anisotropy. Recently, however, the problem has been reexamined in $1+1$ dimensions, with special emphasis on the statistical properties of the surface roughness at long length and time scales.[4,5] In particular, one inquires whether the interface width W exhibits dynamic scaling behavior,[6]

$$W(L,t)=[\langle h^2\rangle-\langle h\rangle^2]^{1/2}\sim L^{\alpha}f(t/L^{\alpha/\beta}) \;, \tag{4}$$

where L is the linear distance along the surface, and the scaling function $f(x)\sim x^{\beta}$ for $x\ll 1$ and $f(x)\rightarrow$const for $x\gg 1$. Such behavior arises naturally from *stochastic* partial differential equations of motion for the surface profile,[7,8] and Plischke and co-workers[4,5] sought to infer the relevant equation by analyzing various microscopic kinetic schemes with master equation and Monte Carlo techniques. Although the Mullins-Herring analysis is not cited explicitly, a symmetry argument was introduced that recovers their results—but only when surface-diffusion transition rates depend on total-energy differences computed from a quadratic solid-on-solid Hamiltonian.

The present paper addresses the problem of surface morphological equilibration in $1+1$ dimensions as well. Our results complement and extend the work noted above in that we (i) derive the governing stochastic equation of motion directly, beginning from a previous master-equation analysis of the problem by us; (ii) make use of physically well-motivated Arrhenius-type surface kinetics for which the symmetry argument used in Ref. 5 does not apply; and (iii) make direct contact with the classic Mullins-Herring theory and thus extract explicit expressions for macroscopic rate constants in terms of microscopic parameters.

We consider a conventional two-dimensional (2D) solid-on-solid (SOS) crystal,[9] where a column height h_i is associated with each site of a simple square lattice. No vacancies or overhangs are permitted. We associate a bond energy $-E_S$ with each pair of vertical nearest neighbors and a bond energy $-E_N$ with each pair of lateral nearest neighbors. The dynamical processes we consider are deposition, desorption, and surface diffusion. Particles are deposited $(h_i\rightarrow h_i+a)$ randomly with a mean arrival rate of aF. In accord with simple chemical intuition and universal experience in the surface science literature,[10] the transition rates for desorption and diffusion are chosen to have configuration-dependent Arrhenius-type forms. Desorption events $(h_i\rightarrow h_i-a)$ occur at a rate $k_0\exp[-\beta(E_S+nE_N)]$, where k_0 is an attempt frequency, n is the number of *lateral* nearest neighbors, and $\beta=1/k_BT$. Surface diffusion is limited to nearest neighbors (e.g., $h_i,h_{i+1}\rightarrow h_i-a,h_{i+1}+a$) and proceeds at a rate similar to the desorption rate except that, again in accord with common experience,[10] E_S is replaced by a smaller energy barrier U_S. These choices manifestly satisfy detailed balance.

In recent work,[11] the present authors employed standard techniques from the theory of stochastic processes to derive a set of Langevin equations (one for each column height variable) that collectively describe the morphological evolution of a SOS crystal surface with these dynamics. The equations turn out to be *linear* both

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in the column height variables and in the variables $c_n(i)$ ($n=0,1,2$), i.e., the probabilities that the "atom" at the top of column i has n lateral nearest neighbors. It then is straightforward to perform a coarse-grain spatial average and derive a single equivalent stochastic differential equation for the macroscopic variable $h(x,t)$ as a linear function of the concentration per site $c_n(x)$ of surface atoms with n lateral nearest neighbors. The final equation takes the form[11]

$$\frac{\partial h(x)}{\partial t}=aD_0\nabla^2\lambda(x)-a\Omega_0\lambda(x)+a^2F+\eta(x)\ , \tag{5}$$

where $D_0=(a^2k_0/2)\exp(-\beta U_S)$, $\Omega_0=k_0\exp(-\beta E_S)$, and

$$\lambda(x)=\sum_{n=0}^{2}c_n(x)\exp(-n\beta E_N)\ . \tag{6}$$

The Gaussian random variable $\eta(\mathbf{x})$ has zero mean and covariance

$$\langle\eta(x,t)\eta(x',t')\rangle=(D_0\{\delta(x-x')\nabla^2\lambda(x)-[\lambda(x)+\lambda(x')]\nabla^2\delta(x-x')\}+[\Omega_0\lambda(x)+aF]\delta(x-x'))a^3\delta(t-t')\ . \tag{7}$$

The physical content of (5) is easy to appreciate. The desorption terms are simply concentrations of surface species multiplied by the desorption rate appropriate to that species. This is a simple generalization of the typical situation where one considers desorption of noninteracting adatoms. Similarly, the diffusion terms make explicit the fact that adatoms are not the only source of the instantaneous surface current. An additional contribution arises from atoms that detach from kink sites and in-surface atoms that succeed in breaking two lateral bonds.

The equation of motion (5) is valid quite generally. But to make the connection with (1), it is necessary to assume (as did Mullins and Herring) that the surface is in *local* equilibrium. Our task then is to express the right-hand side of (5) in terms of the surface chemical potential. The situation is slightly complicated by the presence of several different surface species that are both diffusing and undergoing attachment and detachment reactions, e.g., adatoms attaching and detaching from step edges. But one readily checks that all relevant stoichiometric factors are unity so that, in equilibrium, the chemical potentials of the individual surface species satisfy

$$\mu_0=\mu_1=\mu_2\ . \tag{8}$$

We now specialize to low temperature and small slopes, so that the concentrations of adatoms ($n=0$) and kinks ($n=1$) are both small. In this dilute limit, the concentrations are related to the chemical potentials by[12]

$$c_n=\exp[\beta(\mu_n-\mu_n^0)]\quad \text{for } n=0,1\ , \tag{9}$$

where μ_n^0 is a reference constant for the species in question. Normalization determines the concentration of doubly coordinated species as $c_2=1-c_0-c_1$, so that all that remains is to determine the reference constants.

To do so, consider the special case where the surface is in true global equilibrium with macroscopic slope Δ. In this state, the probability that a kink is present at any site is independent of position, i.e., the surface executes a random walk in one dimension. From this, one easily derives a mass action formula[13] valid for this SOS model that relates the number density of up kinks n_+ (where "up" is defined relative to increasing x) to the number density of down kinks n_-. When (9) is valid, this formula reads

$$n_+n_-=\exp[-\beta E_N]\equiv K\ . \tag{10}$$

Using this and the geometrical relation $n_+-n_-=\Delta$, it follows that

$$\begin{aligned}c_0&=n_+n_-=K\ ,\\ c_1&=n_++n_--2n_+n_-=\sqrt{4K+\Delta^2}-2K\ .\end{aligned} \tag{11}$$

In global equilibrium, the chemical potential of the surface species must equal the chemical potential of the bulk $\mu_B=-E_S-E_N$. Inserting this value in (9), and using (11), we conclude that

$$\mu_0^0=-E_S$$

and

$$\mu_1^0=\mu_B-k_BT\ln[\sqrt{4K+\Delta^2}-2K]\ , \tag{12}$$

so that

$$\lambda(x)=K[1+\sqrt{4K+\Delta^2}]\Lambda(x)\equiv\mathcal{G}(\Delta)\Lambda(x)\ . \tag{13}$$

Inserting (13) into (5) yields precisely (1) with the three identifications

$$\Omega=\Omega_0\mathcal{G}(\Delta)\ , \tag{14}$$

$$D_S=D_0\mathcal{G}(\Delta)\ , \tag{15}$$

$$F=a^{-1}\Omega\ . \tag{16}$$

Equation (14) reflects the dependence of the desorption rate on the kink density of a surface inclined with respect to a high-symmetry crystallographic direction. Similarly, the surface-diffusion constant predicted by (15) takes explicit account of the fact that the identity of a particle that diffuses over a macroscopic distance varies, being at times an adatom, an atom with one lateral bond, and an atom with two lateral bonds. Finally, (16) guarantees that the mean velocity of the surface is zero at equilibrium.

To complete our program, we need only note that (3) is valid for our SOS model because $\tilde{\gamma}$ is an analytic function when $T>0$.[14] Hence, combining all the foregoing and noting that small slopes imply small curvatures, the final stochastic equation and its noise characteristics become (to lowest order in L^{-1})

$$\frac{\partial h}{\partial t}=\sigma\Omega\nabla^2 h-\sigma D_S\nabla^4 h+\eta , \quad (17)$$

$$\langle \eta(x,t)\rangle=0 , \quad (18)$$

$$\langle \eta(x,t)\eta(x',t')\rangle =2a^3[\Omega\delta(x-x')-D_S\nabla^2\delta(x-x')]\delta(t-t') , \quad (19)$$

where $\sigma=a^3\beta\tilde{\gamma}$.

Absent the noise, (17) is precisely the small slope equation of motion obtained by Mullins.[1] In particular, there are no low-order nonlinear terms such as those that appear in the theory of kinetic roughening.[15] For our present purposes, it is useful to discuss the desorption-only and surface-diffusion-only limits of (17) and (19) separately. When surface diffusion is absent, $D_S=0$, and the resulting linear Langevin equation is identical to one proposed by Edwards and Wilkinson[16] for a different problem. The scaling exponents are $\alpha=\frac{1}{2}$ and $\beta=\frac{1}{4}$. The former is characteristic of random-walk behavior and thus demonstrates that our analysis is self-consistent. This conclusion agrees with the results of Monte Carlo simulations using Arrhenius desorption kinetics,[17] and remains correct if surface diffusion and desorption operate simultaneously.

When desorption is negligible ($E_S \gg U_S$), the evolution of the surface is determined by the equation of motion with $\Omega=0$. The scaling exponents predicted by the resulting linear, fourth-order Langevin equation with conserved noise are $\alpha=\frac{1}{2}$ and $\beta=\frac{1}{8}$. Again, the surface properly relaxes to its thermally rough equilibrium state. Monte Carlo simulations using Arrhenius surface-diffusion kinetics confirm this result as well.[17]

In summary, we have derived a stochastic version of the classic Mullins-Herring equation that describes the morphological equilibration of a crystal surface above its roughening temperature. The calculation makes use of a previously derived lattice Langevin equation for the time evolution of the surface of a two-dimensional solid-on-solid crystal. Explicit expressions were obtained for a macroscopic surface-diffusion constant and an average desorption rate in terms of microscopic parameters. Sufficiently close to equilibrium, the final Langevin equation contains no low-order nonlinear terms apart from those already present in the Euclidean curvature. Accordingly, the scaling behavior of the interface width is characteristic of an appropriate linear equation of motion. Although formally derived only for a $1+1$ dimensional system, we note that (17)–(19) produce the correct equilibrium state above the roughening transition in $2+1$ dimensions ($\alpha=0$) as well for both limiting cases described above.

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[1]W. W. Mullins, J. Appl. Phys. **28**, 333 (1957); in *Metal Surfaces: Structure, Energetics and Kinetics,* edited by W. D. Robertson and N. A. Gjostein (American Society of Metals, Metals Park, OH, 1963), pp. 17–66.

[2]C. Herring, in *The Physics of Powder Metallurgy,* edited by W. E. Kingston (McGraw-Hill, New York, 1951), pp. 143–179.

[3]See, e.g., P. Nozières, in *Solids Far From Equilibrium,* edited by C. Godrèche (Cambridge University Press, Cambridge, England, 1992), pp. 1–154.

[4]M. Plischke, Z. Racz, and D. Liu, Phys. Rev. B **35**, 3485 (1987).

[5]Z. Rácz, M. Siegert, D. Liu, and M. Plischke, Phys. Rev. A **43**, 5275 (1991).

[6]F. Family, Physica A **168**, 561 (1990).

[7]M. Kardar, G. Parisi, and Y. C. Zhang, Phys. Rev. Lett. **56**, 889 (1986).

[8]T. Sun, H. Guo, and M. Grant, Phys. Rev. A **40**, 6763 (1989).

[9]J. D. Weeks and G. H. Gilmer, Adv. Chem. Phys. **40**, 157 (1979).

[10]See, e.g., A. Zangwill, *Physics at Surfaces* (Cambridge University Press, Cambridge, England, 1988); V. Bortolani, N. H. March, and M. P. Tosi, *Interaction of Atoms and Molecules with Solid Surfaces* (Plenum, New York, 1990).

[11]A. Zangwill, C. N. Luse, D. D. Vvedensky, and M. R. Wilby, Surf. Sci. **274**, L529 (1992); C. N. Luse, A. Zangwill, D. D. Vvedensky and M. R. Wilby, *ibid.* **274**, L535 (1992).

[12]J. Keizer, *Statistical Thermodynamics of Nonequilibrium Processes* (Springer-Verlag, New York, 1987).

[13]W. K. Burton, N. Cabrera, and F. C. Frank, Philos. Trans. R. Soc. London Ser. A **243**, 299 (1951).

[14]See, e.g., J. De Connick and F. Dunlop, Europhys. Lett. **4**, 1291 (1987).

[15]J. Villain, J. Phys. I **1**, 19 (1991).

[16]S. F. Edwards and D. R. Wilkinson, Proc. R. Soc. London Ser. A **381**, 17 (1982).

[17]For desorption, see M. R. Wilby (unpublished); for surface diffusion, see M. Plischke (unpublished).