Crossover between Terrace Diffusion and Diffusion Step-to-Step on Vicinal Surfaces: Scaling Function and Analytic Approximations

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Abstract

On equilibrium vicinal surfaces with mass transport dominated by terrace-diffusion (TD), there can be crossover from TD to diffusion step-to-step (DSS) behavior for fluctuation wavelength λ large compared to the step separation ℓ. We show that the temporal correlation function can be written as a function of a single dimensionless variable proportional to time/ℓ^3 and present an excellent, simple approximation for this scaling function. This formulation can be used to distinguish mass transport dominated by DSS versus evaporation-condensation (attachment-detachment) limited kinetics (for which the capillary-wave characteristic time τ has the same λ^2 behavior as DSS).

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The temporal correlation function for equilibrium fluctuations of isolated steps has received a great deal of analytical attention and has been rather thoroughly described [1–4]. It is well established that a capillary wave analysis can be used to distinguish the three limiting cases by examining the wavevector dependence of the time constant characterizing the healing of fluctuations: $\tau_q^{-1} \propto q^2, q^3$, or q^4, for evaporation-condensation (EC), terrace-diffusion (TD), or periphery-diffusion (PD) limited transport, respectively. (Here $q \equiv 2\pi/\lambda$ is the wavevector of the step fluctuation.) On a vicinal surface, other behaviors also become possible [1,5]. The crossover between these various limits is a subject of active interest. In particular, for small q (i.e. $q\langle\ell\rangle < 1$, where $\langle\ell\rangle$ is the

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mean step separation), TD can cross over into diffusion-step-to-step (DSS) behavior in which one of the q's in τ_q^{-1} is supplanted by $1/\ell$, leading to q^2/ℓ behavior [5]. While TD behavior is easy to achieve in numerical simulations [6], it has not to date (with the notable exception of Cu(111) in HCl [7]) been seen in experiments [8,10]. Moreover, to properly interpret the prefactor of q^2 seen in such measurements, it is crucial to know whether the underlying mechanism is EC or DSS.

For "pure" cases in which $\tau_q^{-1} = A_n q^n$, the temporal autocorrelation function $G_n(t)$ (or, equivalently, the mean-square width $w^2(t/2)$ of the step fluctuations[3,4]) has been shown in several papers to satisfy the following equation, arising from a capillary wave analysis:

$$G_n(t) \equiv \langle [x(t+t') - x(t')]^2 \rangle_{t'} = (2k_BT/\pi\tilde{\beta}) \int_0^\infty dq\, q^{-2}[1 - \exp(-tA_n q^n)]$$
$$= (2k_BT/\pi\tilde{\beta})(tA_n)^{1/n}\Gamma(1 - 1/n). \qquad (1)$$

We focus on the case n=3, which for an isolated step corresponds to terrace-diffusion limited (TD) fluctuations; in this case, $A_3 = 2\tilde{\beta}\Omega^2 c_t D_t / k_BT$, where $\tilde{\beta}$ is the step stiffness, Ω the atomic area, $c_t D_t$ the product of terrace atom (or vacancy) concentration and diffusion constant, and k_BT the thermal energy. Eq. (1) becomes $G_3(t) = (2k_BT/\pi\tilde{\beta})\Gamma(2/3)A_3^{1/3}t^{1/3}$.

Treatment of the crossover to DSS was discussed in Ref. [1]; for the exponent of q, the integer n should be replaced by a continuously variable exponent z_q. For the case of insignificant Ehrlich-Schwoebel asymmetry and $qd \ll 1$, where d is the "kinetic" length [9] (or $a_q \ll 1$, in the notation of Refs. [1,2]),

$$z_q = 3 - q\ell/\sinh(q\ell) \qquad (2)$$

which is 3 for large values of $q\ell$ but drops smoothly but relatively abruptly to 2 for small $q\ell$. However, that paper did not pursue the consequences in real space. Since measurements are now being made [10,11] which need to distinguish between EC and DSS behavior, it is timely to present some formal results which should be helpful in analyzing data. (Explicit, albeit preliminary, Monte Carlo studies of the crossover [12] have also been reported.) In this short communication, we point out scaling behavior that the correlation function should exhibit in DSS and present an exact expression and analytic approximants for the scaling function.

If we insert Eq. (2) into Eq. (1) in a manner that maintains proper units, we find

$$G_{3\leftarrow 2}(t) = (2k_BT/\pi\tilde{\beta})\int_0^\infty dq\, q^{-2}[1-\exp\{-tA_3q^3/(q\ell)^{q\ell/\sinh(q\ell)}\}] \tag{3}$$

It is not hard to carry out numerically the integral in Eq. (3). At early times it goes like $t^{1/3}$, then crosses over to $t^{1/2}$ (over a range of somewhat over a decade in t). To obtain an expression that is more tractable analytically and easier to interpret, we replace A_3q^3 in the argument of the exponential in Eq. (1) by $(A_3/\ell)q^2$ for $q < \varsigma/\ell$, where ς is expected to be of order unity. We then have [2] a pair of definite integrals, yielding results in terms of the error function and the incomplete gamma function [13]:

$$\int_0^{\varsigma/\ell}\frac{dq}{q^2}\left[1-\exp\left(-\frac{tAq^2}{\ell}\right)\right] = -\frac{1-\exp(-tA\varsigma^2/\ell^3)}{\varsigma/\ell} + \left(\frac{\pi tA}{\ell}\right)^{\frac{1}{2}}\mathrm{Erf}\left[\varsigma\left(\frac{tA}{\ell^3}\right)^{\frac{1}{2}}\right] \tag{4a}$$

$$\int_{\varsigma/\ell}^{\infty}\frac{dq}{q^2}[1-\exp(-tAq^3)] = \frac{1-\exp(-tA\varsigma^3/\ell^3)}{\varsigma/\ell} + (tA)^{\frac{1}{3}}\Gamma\left[\frac{2}{3}, tA\left(\frac{\varsigma}{\ell}\right)^3\right] \tag{4b}$$

Note that for $\varsigma \leq 1$, dividing the argument of the exponential by $q\ell$ (due to the replacement of q by $1/\ell$) increases its magnitude, thereby increasing the magnitude of the resulting integral relative to $G_3(t)$. In other words, $G_3(t)$ underestimates the evolution of fluctuation correlations given by $G_{3\leftarrow 2}(t)$, as we shall see again below.

Eq. (3) can be rewritten as a scaling relation involving a function g of the "temporal" dimensionless ratio tA_3/ℓ^3, involving an integration over the "spatial" dimensionless combination [3] $s \equiv q\ell$:

$$\frac{G_{3\leftarrow 2}(t)}{2k_BT\ell/\pi\tilde{\beta}} = g\left(\frac{tA_3}{\ell^3}\right); \quad g(z) \equiv \int_0^\infty ds\, s^{-2}[1-\exp(-zs^{3-s\,\mathrm{csch}(s)})]. \tag{5}$$

In Fig. 1 is a plot of $g(z)$ as well as its logarithmic derivative, $d\ln(g(z))/d\ln(z)$. The crossover from $z^{1/3}$ to $z^{1/2}$ evidently occurs between $z \sim 10^{-2}$ and 10^0. Similarly, the pair of integrals in Eq. (4) can be recast in terms of scaling functions $g_<$ and $g_>$:

$$g_<(z) \equiv -[1-\exp(-z)] + (\pi z)^{1/2}\mathrm{Erf}(z^{1/2}) \tag{6a}$$
$$g_>(z) \equiv [1-\exp(-z)] + z^{1/3}\Gamma(2/3, z) \tag{6b}$$

[2] Note that $\Gamma(1/2, x^2) = \sqrt{\pi}[1-\mathrm{Erf}(x)]$.

[3] This sort of expression might well have been anticipated since ℓ is the only characteristic length in the direction normal to the steps.

To leading order in z, $g_<(z) \sim z$ and $g_>(z) \sim \Gamma(2/3)z^{1/3}$. In the other extreme of asymptotic z, $g_<(z) \to (\pi z)^{1/2}$ and $g_>(z) \to 1$. These functions are plotted in Fig. 2 along with $g(z)$. Then

$$G_{3\leftarrow 2}(t)/[\ell(2k_BT/\pi\tilde{\beta})] \cong [g_<(\varsigma^2 tA_3/\ell^3) + g_>(\varsigma^3 tA_3/\ell^3)]/\varsigma \tag{7}$$

Hence, the problem reduces to finding the value of ς which optimizes by some criterion the correspondence of the trial function $[g_<(\varsigma^2 z) + g_>(\varsigma^3 z)]/\varsigma$ to $g(z)$. The choice adopted here is to optimize the replication of the logarithmic derivative of $g(z)$. In Fig. 3 is a contour plot of ratio of the logarithmic derivative of the trial function to that of $g(z)$: $\varsigma^{-1}[d\ln(g_<(\varsigma^2 z) + g_>(\varsigma^3 z))/dz]/[d\ln(g(z))/dz]$. By this criterion the optimal value of ς lies between 0.95 and 1.00. Sacrificing a small amount of accuracy for simplicity, we set $\varsigma = 1$, so that the $[1-\exp(-z)]$ terms cancel, giving

$$G_+(t) = \frac{2k_BT\ell}{\pi\tilde{\beta}}\left[\left(\frac{\pi tA_3}{\ell^3}\right)^{1/2}\mathrm{Erf}\left\{\left(\frac{tA_3}{\ell^3}\right)^{1/2}\right\} + \left(\frac{tA_3}{\ell^3}\right)^{1/3}\Gamma\left(\frac{2}{3},\frac{tA_3}{\ell^3}\right)\right] \tag{8}$$

for our advocated approximation for the DSS-TD crossover function $G_{3\leftarrow 2}(t)$.

In Fig. 2 we include a curve for $g_+(z)$, the scaled version of $G_+(t)$:

$$g_+(z) \equiv g_<(z) + g_>(z) = (\pi z)^{1/2}\mathrm{Erf}(z^{1/2}) + z^{1/3}\Gamma(2/3, z). \tag{9}$$

This function exceeds $g(z)$ (the scaled version of $G_{3\leftarrow 2}(t)$) by less than 9% near z $= 0.04$, in the middle of the crossover regime, and falls rapidly as z enters a "pure" region: $g_+(z)$ is less than 1% greater than $g(z)$ for $z > 2$ or $z < 2\cdot 10^{-4}$. Furthermore, approximating $g(z)$ by $g_+(z)$ is notably better than the simplest approximation of using Eq. (1) to estimate $(2k_BT/\pi\tilde{\beta})(tA_n/\ell)^{1/2}\Gamma(1/2)$, i.e. using just $g_2(z) \sim (\pi z)^{1/2}$ instead of $g_+(z)$ [10]. In contrast to $g_+(z)$, $g_2(z)$ is always less than $g(z)$. For large z, the difference between $g_2(z)$ and $g(z)$ is insignificant, but as z decreases, this difference becomes increasingly and insufferably large: by $z = 0.5$, $g_2(z)$ is 1% smaller than $g(z)$; by $z = 0.1$ it is over 10% smaller; by $z = 0.01$ (the smallest value of z displayed in Fig. 2) it is 36% too small, and it continues to fall. For most applications to experiments, use of $g_+(z)$ instead of $g(z)$ should easily be satisfactory, but use of $g_2(z)$ is questionable unless one knows in advance that z is large.

In the case studied in ref. [11], which motivated this investigation, the maximum value of z is $5\cdot 10^{-3}$. Since $g(0.001) = 0.133$, assumption of $t^{1/2}$ behavior for all times and consequent use of g_2 leads to an estimate of z as $0.133^2/\pi$, 5.6 times the true value: Assuming all other variables are known, this use of g_2 then produces an estimate of c_tD_t that is 5.6 times the true value. This situation becomes progressively worse at smaller values of z. At $z = 10^{-4}$ or 10^{-5}, e.g., g_2 overestimates by factors of 12.5 or 27.0, respectively. A more stringent test is whether experimental data can be well fit with Eq. (5), using measured values for stiffness and step spacing; for the data in Ref. [11], such was not the case, providing strong evidence that DSS was not the mode of mass transport underlying the step fluctuations.

It was originally recognized [5] that, to distinguish conclusively EC from DSS, one should analyze several values of mean step spacing of a particular vicinal surface. However, use of the scaling formulation in Eq. (5) and the analytic approximation in Eq. (9) are new. This approach should be applicable more generally in studying crossover behavior. [4] Moreover, observation of data collapse by appropriate scaling of independent variables lends confidence to theoretical understanding of the dynamics.

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[4] For example, a similar tactic could be used to distinguish TDPS, i.e. terrace diffusion with a perfect Schwoebel barrier [5], from periphery diffusion, both of which have $\tau_q^{-1} \propto q^4$. Analogous to Eq. (2) Khare and Einstein [2] found $z_q = 2+2/(1+q^2\ell d)$. The crossover behavior is more complicated since the dimensionless combinations qd and $q\ell$ are multiplied. Moreover, as noted in Appendix A of ref. [2], there is an alternative formalism which is probably more physically realistic and makes a non-trivial difference when both terrace and step-edge diffusion are important. To avoid obscuring the key ideas of this Letter and because TDPS applies only for extreme situations [2], we defer detailed discussion of this example.

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Figure Captions

FIG. 1: Plot (solid curve) of the scaling function $g(z)$, where z is the dimensionless time tA_3/ℓ^3 (solid curve, right vertical axis). Also plotted as the dashed curve is the logarithmic derivative of $g(z)$, indicating the effective exponent of $g(z)$ (left vertical axis).

FIG. 2: Comparison of scaling function $g(z)$, as in Fig. 1 and $g_<(z)$ [short dashes], $g_>(z)$ [long dashes], and their sum $g_+(z)$ [long and short dashes]. Evidently $g(z)$ is well approximated by $g_<(z) + g_>(z)$. The dotted curve is $(\pi z)^{1/2}$, the result of assuming pure q^2 behavior.

FIG. 3: Contour plot of the *ratio* of the *logarithmic derivative* of the trial approximant $([g_<(\varsigma^2 z)+g_>(\varsigma^3 z)]/\varsigma)$ of the scaling function $g(z)$ to that of $g(z)$ itself, plotted vs. the dimensionless time z and the proportionality constant ς marking the value of $q = \varsigma/\ell$ at which temporal scaling is taken to change abruptly from q^2 to q^3 behavior. The contour lines correspond to labeled values of this ratio; the darker the shading, the closer this ratio is to unity, the ideal value. The darkest region lies between 0.995 and 1.005. Although ς=1 is slightly higher than optimal, the analytic convenience makes it a convenient choice. The dips in these contour lines as functions of z correspond to the crossover region.