# Evolution of Two-Dimensional Wormlike Nanoclusters on Metal Surfaces

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A pinch-off phenomenon is discovered in the evolution of 2D wormlike nanoclusters formed in homoepitaxial adlayers. This feature is shown to distinguish mass transport via periphery diffusion from other mechanisms. Continuum modeling of such evolution accurately describes experimental observations, particularly if one incorporates the anisotropy in step-edge line tension.

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Propagation of boundaries and interfaces is central to a broad range of problems in classical fluid mechanics and materials science (especially metallurgy). Two long-studied phenomena have generated much interest recently, due to newly acquired experimental and theoretical techniques. One is the sintering of many clusters into an aggregate [1]; the other is the "breakup" of fluid flow into drops due to an instability first analyzed theoretically by Rayleigh, Plateau, and Maxwell [2]. These two seemingly opposite phenomena are sometimes intertwined in a single physical system and process [3], and are traditionally tackled by a continuum equation (e.g., the Navier-Stokes equation). From a mathematical perspective, there are extensive investigations of the simplest boundary propagation problem of the shortening of a curve (embedded in two-dimensional space), with the normal velocity proportional to the local curvature. Notable is Grayson's theorem, which shows that *all* simple closed curves will shrink to a point without breaking up [4]. Increasingly, there is an interest in describing such phenomena on smaller length scales to assess where continuum modeling must be aided or replaced by an atomistic description (see [5] for a study of pinch-off in nanojets). We pursue this direction here.

Evolution of structures on crystal surfaces is a variation of the situation addressed in the above mentioned fluid mechanical problems. Instead of viscous surface flow, mass transport is usually governed by diffusion of adatoms (or other species), either across the surface or along the step edges. The continuum approach was first developed by Mullins [6]. More recently the kinetic Monte Carlo (KMC) simulation of atomistic models has gained some popularity. In this Letter, we report experiments and modeling of the evolution of wormlike monolayer vacancy nanoclusters. Experiments are performed for both Cu/Cu(100) and Ag/Ag(100) adlayers using time sequenced scanning-tunneling-microscopy (STM). Specifically, we report the first observations of a pinch-off phenomenon in 2D systems. This is the counterpart of the above mentioned and extensively studied 3D pinch-off. Extending ideas from Grayson's theorem, we show that this feature implies mass transport is dominated by periphery diffusion (PD). Indeed, continuum models for evolution mediated by PD accurately describe observed pinch-off events, particularly if one accounts for anisotropy in the line tension of the step edge. The kinetic parameters, as well as the influence of fluctuations on evolution, are assessed using atomistic modeling and KMC simulations.

Diffusion and coarsening of adatom clusters formed by homoepitaxy on Cu(100) and Ag(100) at room temperature have been studied extensively [7,8]. Experiments show that for diffusion of clusters of sizes up to 1000 atoms, mass transport is dominated by diffusion of atoms along the cluster boundary, i.e., the PD mechanism [8]. The same mechanism is also expected to govern the evolution of far-from-equilibrium structures in these systems [9,10]. Cluster dynamics on metal(111) surfaces, including diffusion [11] and restructuring [12], has also been studied extensively. See Ref. [13] for a review of this subject.

In continuum models, the morphology of a two-dimensional cluster is described by a closed plane curve, represented parametrically as $\mathbf{r}(s) = [x(s), y(s)]$. Its evolution is determined by specifying its normal velocity. For PD, it is given by

$$v_n(s,t) = \Omega \nabla_\tau J_{\mathrm{PD}}(s,t) \tag{1a}$$

from local mass conservation. Here $J_{\mathrm{PD}}$ is the atomic flux along the periphery, $\nabla_\tau = (x_s^2 + y_s^2)^{-1/2} \partial/\partial s$ is the derivative with respect to the arc length $\tau$ along the periphery, and $\Omega$ is the area of a unit cell. From the linear response theory, one can write

$$J_{\mathrm{PD}} = -(k_B T)^{-1} \sigma_{\mathrm{PD}} \nabla_\tau \mu\,, \tag{1b}$$

where $\mu$ is the step-edge atom chemical potential measuring the energy cost for attaching atoms to the step, and

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$\sigma_{\rm PD}$ is a coefficient measuring the mobility of step edge atoms. In the continuum model, $\sigma_{\rm PD}$ and $\mu$ depend only on the local configuration. Specifically, one can write

$$\mu = \Omega\tilde{\beta}(\theta)\kappa(s), \tag{1c}$$

where $\theta = \theta(s)$ is the local azimuthal angle of the step edge, and $\kappa$ is the local curvature. The stiffness of the step edge, $\tilde{\beta}$, is related to step-edge energy $\beta(\theta)$ through $\tilde{\beta} = \beta(\theta) + \beta''(\theta)$ [1]. Similarly, $\sigma_{\rm PD} = \sigma_{\rm PD}(\theta)$ is in general a function of the local azimuthal angle. The detailed forms of $\beta(\theta)$ and $\sigma_{\rm PD}(\theta)$ depend on the microscopic energetic and dynamical properties of the step edge. One important simplification is to assume that both $\sigma_{\rm PD}$ and $\beta$ are constant (the *isotropic continuum model*), where

$$v_n = -(k_B T)^{-1}\Omega^2\sigma_{\rm PD}\tilde{\beta}\nabla_\tau^2\kappa(s). \tag{2}$$

Then, aside from a constant prefactor, Eq. (2) represents a purely geometry-driven reshaping problem. In our formalism, $J_{\rm PD}$ has the dimension of (atoms)/s, $v_n$ and $\sigma_{\rm PD}$ of Å/s, and $\beta$ (or $\tilde{\beta}$) of eV/Å.

The experimental procedures for the Cu/Cu(100) and Ag/Ag(100) systems are quite similar. A submonolayer film is deposited at room temperature with an $e^-$-beam (for Cu) or a thermal (for Ag) evaporator. Post deposition evolution is monitored by a commercial room temperature (Omicron) STM with a scanning rate of about 0.5 frames per minute (voltage = 0.5–1.5 V, current = 0.5–0.7 nA). The mean island separation is in the range of 10–20 nm for Cu and Ag. At low coverages (≤0.3 ML), the surface is mainly covered by isolated adatom islands. Subsequent evolution of the surface consists of mainly island diffusion, coalescence, and coarsening of islands. This regime has been studied previously [7,8].

At a coverage of about 0.6 ML, the surface is covered by an incomplete layer with percolated vacancy clusters. Slightly above this coverage, there is a fairly sharp transition from percolating vacancy regions to nonpercolating wormlike vacancy clusters [14]. Such wormlike vacancies are highly irregular; therefore, their reshaping processes yield extra insight as compared to the reshaping of adatom clusters with simpler geometries [10]. We note that adatom clusters cannot be readily prepared with these wormlike shapes. Figure 1 shows examples for Cu/Cu(100) and Ag/Ag(100). The characteristic length scale of the adlayers is controlled by island separation at lower coverages.

Figure 2 presents a sequence of composite images showing the experimental data for vacancy evolution in Cu(100) overlapped with prediction of the isotropic continuum model, Eq. (2). Dark areas are monolayer deep vacancies and bright areas are monolayer high adatom clusters. The two main parameters used in the model are obtained as follows. The typical line tension of Cu(100), $\beta \approx 0.11$ eV/$a$ (where $a$ is the lattice spacing), is based on *ab initio* calculation and experiment [15]. The mobility coefficient $\sigma_{\rm PD}$ is estimated from a previous island diffusion study [8] as $\sigma_{\rm PD} \approx 70$ Å$s^{-1}$. We solve the partial differential equation numerically by discretizing the curve into a set of markers and derive a set of ordinary differential equations (ODE) for the markers. The isotropic continuum model predicts the reshaping process fairly well.

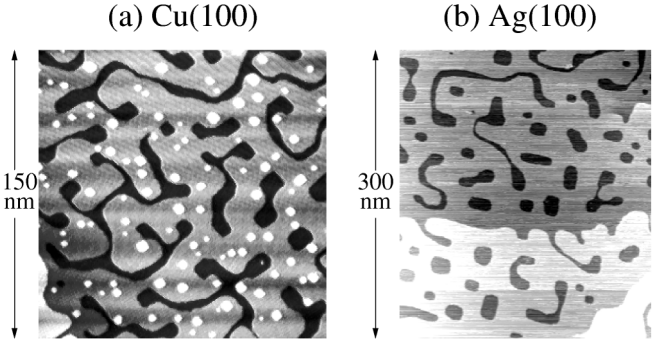


FIG. 1. Wormlike vacancy nanoclusters formed after deposition of ~0.6 ml of film on the surfaces of (a) Cu(100); (b) Ag(100).

In Fig. 2 and several other cases, vacancy clusters with long and narrow necks eventually break into disconnected vacancy clusters. STM tip effects can be dismissed since they were previously assessed to be negligible in island diffusion and restructuring studies [8,9], and the breaking up occurs in all directions with respect to the scanning direction. Effects from adatom clusters can also be discounted. Therefore what we observed is a phenomenon inherent in the curve reshaping problem driven by curvature *gradients.* As mentioned in the introduction, Grayson's theorem shows that for $v_n \propto \kappa$, *all* simple closed curves must shrink to a round point, without breaking up. Here we

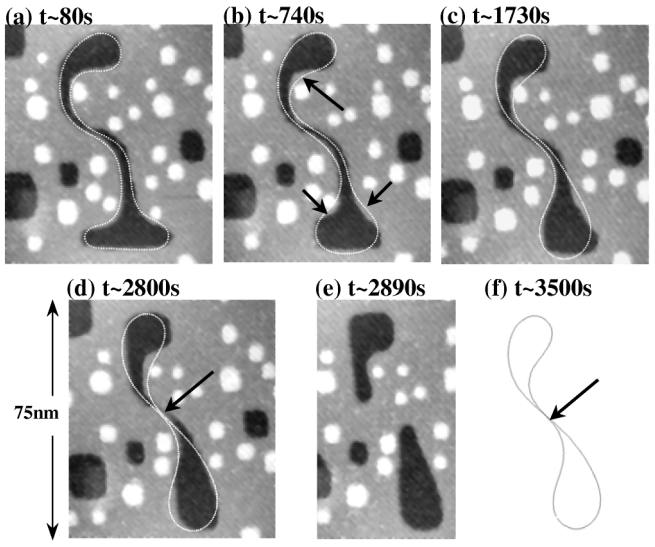


FIG. 2. A sequence of STM images showing the reshaping of a wormlike vacancy cluster. An earlier STM image (not shown) is used to produce the initial conditions at $t = 0$. (a) $t \approx 80$ s; (b) $t \approx 740$ s; (c) $t \approx 1730$ s; (d) $t \approx 2800$ s, the neck becomes very thin as pointed by the arrow; (e) $t \approx 2890$ s, the vacancy breaks into two separate vacancies. Predictions of the isotropic continuum model are shown in (a)–(d) overlapping the STM images, and in (f) where the curve crosses itself (thus develops a singularity) at $t \approx 3500$ s. In (b), subtle differences between the model and experiment are indicated by arrows.

give a heuristic argument that breakup is also *not* possible for evolution under the so-called evaporation-condensation (EC) mechanism [16], where the normal velocity of the curve is determined by the local curvature, i.e.,

$$v_n = (k_B T)^{-1} \Omega \sigma_{\mathrm{EC}}(\theta) \tilde{\beta}(\theta) (\kappa - \kappa_0). \quad (3)$$

Here $\sigma_{\mathrm{EC}}$ is the step-edge mobility due to the EC mechanism, and $\kappa_0$ is a critical curvature beyond which the islands will shrink. Just before a simple curve breaks into two parts, two points have to contact each other first, each having the same azimuthal angle $\theta$. Since both $\tilde{\beta}$ and $\sigma_{\mathrm{EC}}$ are functions of $\theta$ only, the difference between the normal velocities of the two points is proportional to the difference between the curvatures. It can be shown that the effect of any curvature difference is to make the two points move away from each other, rather than cross.

For the so-called terrace diffusion (TD) mechanism [16], the motion of the step edge is influenced by its surroundings and it is mathematically possible to have breakup. However, as EC evolution is often a very good approximation to TD evolution, we argue that breakup should be a very rare event for the TD mechanism. Experiments show that pinch-off of a wormlike vacancy cluster is a rather common phenomenon, thus supporting the view that PD is the dominant mass transport mechanism.

Comparison of several pinch-off events with simulations reconfirms that reshaping is mainly geometry driven. This is reflected both in the consistency in shape evolution and the absolute pinch-off times. Three cases of vacancy breakups with significantly different initial shapes in the Cu(100) system were examined. We found the experimentally observed pinch-off times (typically around 1 h) agree reasonably well with the isotropic continuum model (within 10 to 20 min). However, atomic scale fluctuations will inevitably introduce a stochastic nature to the reshaping process. Their importance will increase as the cluster size further decreases [5,10].

In Fig. 2(b), we also point out subtle differences between the experimental observation and the isotropic model. The discrepancies occur at the corners of the vacancy where the normal velocity in the isotropic model is overestimated. This is partly due to an overestimation of step stiffness at the corners, where $\tilde{\beta}$ is actually smaller due to the openness of step structures. By incorporating the $\theta$ dependence of $\tilde{\beta}$ (and possibly $\sigma_{\mathrm{PD}}$) in the continuum model, the agreement of simulation can be substantially improved. Here, we first deal with the implementation of the anisotropy in $\tilde{\beta}$. For simplicity, we model the vacancy cluster (or adatom island) energetics via nearest-neighbor (NN) attractive interactions $\phi$ on a square lattice for Cu(100) and Ag(100). The line tension has been solved analytically for this 2D Ising problem as [17]:

$$\beta(\theta) = k_B T[|\cos\theta| \sinh^{-1}(\alpha|\cos\theta|) + |\sin\theta| \sinh^{-1}(\alpha|\sin\theta|)], \quad (4)$$

where $\alpha \sim \frac{1}{2} e^{(\phi/2k_BT)}(1 + |\sin 2\theta|)^{-1/2}$, and so $\beta(\theta) \sim \frac{\phi}{2}(|\cos\theta| + |\sin\theta|)$, as $k_B T/\phi \to 0$. The result of incorporating energetic anisotropy with $\phi = 0.24$ eV for Cu [15] into our analysis is shown in Fig. 3. The improvement in agreement with experiment (cf. Fig. 2) is evident.

In the last part of this Letter, we examine the extent (and influence) of anisotropy in $\sigma_{\mathrm{PD}}$ based on analysis of atomistic PD models. Furthermore, we use KMC simulations of these models to explore *fluctuations* from deterministic continuum model predictions. The form of $\sigma_{\mathrm{PD}}$ depends on the rates of all hopping processes that contribute to periphery diffusion in the atomistic model. Ideally, the rates would be chosen based on precise *ab initio* calculations of the associated activation barriers, but these are rarely available. Instead, KMC studies often include reasonable choices based on semiempirical studies and detailed-balance constraints [10,18,19].

We assume that the effective barrier for an atom to detach from a cluster is prohibitively high so that this process can be neglected. A single atom attached to a close-packed step edge (with only one NN in-plane bond) can hop along the step with rate $h_e$, or hop around a kink (or corner) with rate $h_r$. Rates of other processes can be deduced from those two rates by requiring detailed balance. For example, the rate for a kink atom to "escape" along the step is $h_e \exp[-\phi/(k_B T)]$.

If $h_e = h_r$, we find that $\sigma_{\mathrm{PD}}/a \approx h_e \exp[-\phi/(k_B T)]$ is roughly independent of $\theta$ [20]. Consequently, this choice will correspond to the continuum model using the Ising line tension and an isotropic mobility coefficient. Figure 4 shows corresponding KMC simulations of the evolution of a Ag(100) vacancy cluster consisting of about 8000 vacancy sites. We choose $\phi = 0.26$ eV [10,21]. Figure 4(a) shows the initial configuration, and Fig. 4(b) shows the simulated configuration just after the cluster pinch-off. Figure 4(c) is the corresponding prediction of the continuum model with corresponding anisotropic $\beta(\theta)$.

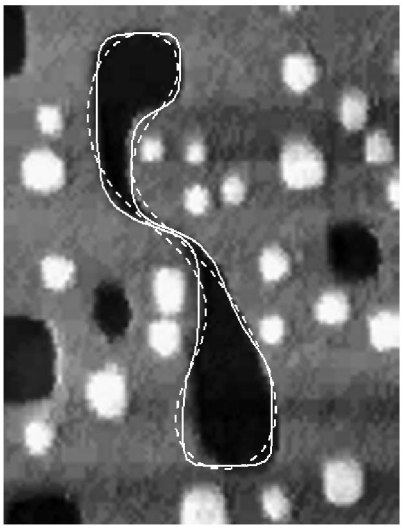

FIG. 3. Comparison between the vacancy cluster from experiment (gray-scale image), the isotropic continuum model (dashed line), and the continuum model with Ising line tension and constant $\sigma_{\mathrm{PD}}$ (solid line).

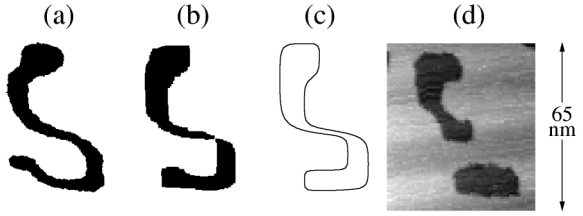


FIG. 4. (a) Initial configuration of a vacancy cluster on Ag(100); (b) Result of a Kinetic Monte Carlo simulation showing a pinch-off; (c) The prediction of the corresponding continuum model; (d) STM measurement after 38 min from (a).

It has a very thin neck (seven atoms wide), which becomes even thinner and eventually pinches off as the system evolves under the continuum model. We performed 10 MC simulations starting from the same initial configuration. The pinch-off times have a standard deviation of about 30%. Fluctuations thus play an important role for features of this size and shape. Furthermore, it seems reasonable to suggest that fluctuations tend to break up the cluster "prematurely," thus the pinch-off time predicted by the deterministic continuum model might be longer than in the real system, where fluctuations are present.

If $h_r \ll h_e$ (corresponding to an extra barrier for corner rounding at island edges or kinks), our simulations show that the overall mobility decreases, and $\sigma_{\rm PD}$ also exhibits strong anisotropy in its $\theta$ dependence. For the cluster reshaping problem, the main effect of a lower $h_r$ is the overall slowing down of the process. The effect of an anisotropy in $\sigma_{\rm PD}$ on the reshaping process is not very significant compared with the amount of fluctuations inherent in the system and the experimental sensitivity. As an aside, we note that such anisotropy may have a more dramatic effect in a system that is being driven out of equilibrium [22].

Figure 4(d) is the STM measurement about 38 min after Fig. 4(a), which shows a snapshot after the cluster pinch-off. Using $h_r = h_e$ and $h_e = \nu \exp(-E_e/k_BT)$, where $\nu = 3 \times 10^{12}$ s$^{-1}$ and the edge diffusion barrier $E_e = 0.26$ eV (and $\phi = 0.26$ eV) [21,23], the physical pinch-off time for our KMC simulations is far shorter (10 s). One way to account for the discrepancy in the pinch-off time between the experiment and the model with $h_e = h_r$, i.e., model with isotropic mobility, is to increase the barrier for kink escape, $E_e + \phi$, from 0.52 eV used above to 0.66 eV. Another way is to retain $E_e = 0.26$ eV and $\phi = 0.26$ eV, while decreasing $h_r$ by introducing an extra corner rounding barrier about 0.16 eV. The first model is consistent with a recent STM experiment by Hoogeman *et al.* [24], and the second model is more consistent with *ab initio* and semiempirical calculations.

In summary, we have demonstrated the capabilities of a continuum model to describe reshaping of nanoclusters with wormlike shapes. Behavior in the Cu(100) and Ag(100) systems is similar. The best match to experimental pinchoff times in isotropic models is obtained by choosing $\sigma_{\rm PD}/a = 34/$s for Cu and $17/$s for Ag (for similar $\phi$), consistent with the 2–3 times faster diffusion of large Cu clusters [8]. A geometry driven pinch-off phenomenon, which is a signature of the periphery diffusion mechanism, is observed. More accurate description is achieved by considering the underlying microscopic properties. Although we cannot extract a unique set of microscopic parameters, some constraints in various combinations of parameters can be established.

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