Growth enhanced surface diffusion and elastic instability on amorphous solids

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A continuum model for growth of solids is developed, considering adatom deposition, surface diffusion, and configuration dependent incorporation rate. For amorphous solids it is related to surface energy densities. The high adatom density leads to growth enhanced dynamics of (a) Mullins’ classical equation [J. Appl. Phys. 28, 333 (1957)] without, and (b) of the Asaro-Tiller-Grinfeld-Srolovitz instability with lateral stress in the growing film. The latter mechanism is attributed to morphologies found in recent experiments.

The theoretical approach to kinetic roughening [1], due to its roots in Statistical Mechanics, relates various growth processes on solids to so called universality classes. Their distinction allows to identify essential properties for the large scale morphology beyond the microscopic mechanisms, say certain symmetries or conservation laws, which manifest themselves in terms of universal scaling exponents.

One such important property is mass conservation suppressing adatom loss to the surrounding space, which allows for surface relaxation only through transport along the surface. The total solid mass then is always equal to its initial value plus the integrated incoming flux.

Molecular Beam Epitaxy (MBE) guarantees such conditions, and growth parameters like for instance flux intensity, temperature, chemical composition of the adsorbate can be easily and precisely controlled [2]. It has been widely used and refined for growth of semiconductor and metal crystals. However, under typical conditions the diffusion length and average crystal step distance are quite large, imposing their own features to the morphology [3,4], such that any theoretically predicted asymptotic scaling regime lies beyond the reach of experimental observation.

On the other hand it may become observable in growing amorphous substances where it seems plausible that intrinsic lengthscales remain small. Some experiments have been performed in recent years looking for kinetic roughening on amorphous solids [3,4,5]. It turns out that their theoretical interpretation in terms of standard continuum [1] and discrete [2,3] models leaves two main open questions which are addressed in this letter. First, far from equilibrium the kinetics on the surface are different from relaxation by thermally activated adatoms leading to Mullins’ continuum equation [1]. Second, in some experiments there appears a very pronounced intermediate lateral lengthscale together with a mounding instability [3,5] whose origin was unclear. Obviously it cannot be due to step edge barriers as is the case on crystalline surfaces [3,4]. Another suggested mechanism, deflexion of incoming particle trajectories or “steering” [5], is in some cases relevant at grazing incidence but negligible for normal beams [3].

Here a new continuum approach to growth with surface diffusion is developed resulting in a flux dependent coefficient for surface evolution (see Eqs. (1) and (2)), the counterpart to equilibrium relaxation Eq. (1). The mounding instability is shown to be due to lateral elastic stress in the growing solid [3,4,5], which is responsible for the well known Asaro-Tiller-Grinfeld-Srolovitz (ATGS) instability [5,6]. Surface modulations allow for relaxation of a laterally stressed solid. For large enough wavelengths this energy gain overcomes the cost in additional capillary energy, disfavoring and destabilizing a flat surface. Due to the nonequilibrium kinetics it appears in a new light: Its driving force is an equilibrium, the dynamical evolution a nonequilibrium phenomenon. In the following calculations the surface energetics account well for the observed wavelength (the size of emerging mounds), and the nonequilibrium kinetics yield the linear growth rate of the instability.

To begin, the continuum model of equilibrium relaxation is briefly recalled [1]. Surface configurations are described by a space and time dependent height field $H(x,t)$, neglecting overhangs and voids. The driving force for equilibrium relaxation is the surface free energy, $\mathcal{F} = \int d^2x \gamma \sqrt{1 + (\nabla H)^2}$. If an atom is added somewhere at the surface this total area may change, resulting in a extra energetic contribution $\mu = -\Omega \gamma \nabla^2 H$ [5]. $\mu$ is often called chemical potential and $\Omega = a^3$ denotes the atomic volume. Spatial variations in $\mu$ bias the adatom diffusion and create a macroscopic mass exchange. Local (mass and volume) conservation impose a continuity equation for the surface dynamics, which for $|\mu| \ll k_B T$ [2a] reads

$$\partial_t H = -a \nabla \cdot \left( \frac{\Omega \gamma}{k_B T} \nabla^2 H \right) \equiv -\kappa (\nabla^2)^2 H. \quad (1)$$

A reasonable assumption for the adatom diffusion coefficient is $D = a^2/\tau_0 e^{-\varepsilon_{eff}/k_B T}$, an Arrhenius form with some activation barrier $\varepsilon_{eff}$ (which on a random surface
comes from an average over waiting times at each site \(\Xi(k)\) and an “attempt frequency” \(1/\tau_0\). Eq. (4) predicts an exponential decay with rate \(-\kappa k^4\) for fluctuations with wavenumber \(k\), which has been verified experimentally [23]. On a phenomenological basis Eq. (1) has also been applied to growth with relaxation by curvature driven surface diffusion, where under deposition (“shot”) noise it results in a power spectrum of height fluctuations \(S(k, t) \equiv \langle |H(k, t)|^2 \rangle \propto |k|^{-4}\). Of course under growth the coefficient \(\kappa\) takes a different form as above in Eq. (4) which is adressed next.

On a growing solid there is a constant supply of mobile adatoms out of the beam hitting the surface. The number of thermally activated adatoms, responsible for equilibrium relaxations, now becomes negligible. Here an ansatz is presented where the incorporation rate \(I\{H\}\) depends on the surface configuration \(H(x, t)\) and connects it thus to the adatom density \(\rho(x, t)\),

\[
\partial_t H = I\{H\} \Omega \rho \\
\partial_t \rho = \nabla \cdot D\{H, \rho\} \nabla \rho - I\{H\} \rho + F/\Omega.
\]  

(2)

Note that \(H + \Omega \rho\) is a conserved quantity, increasing by the average growth velocity \(F\). The problem is to find the dependence \(I\{H\}\), but before turning to that point its rôle in a phenomenological equation as (1) shall be worked out.

Eqs. (2) are expanded around the “flat” growing surface \(H_0(t) \equiv H_0 + Ft\), on which the incorporation rate takes some value \(I_0\), and around the average adatom density \(\rho_0 \equiv F/(\Omega I_0)\). Small deviations \(h(x, t) \equiv H(x, t) - H_0(t)\) and \(c(x, t) \equiv \Omega(\rho(x, t) - \rho_0)\) obey to linear order

\[
\partial_t h = -\frac{F}{I_0} I_1 \ast h + I_0 c \\
\partial_t c = \frac{F}{I_0} I_1 \ast h + (D \nabla^2 - I_0)c,
\]

(3)

where \(D \equiv D\{H_0(t), \rho_0\}\). \(\{H\} - I_0 \approx I_1 \ast h\) is approximated linearly (not necessarily local in space) and will be evaluated in its Fourier transform \(I_1(k)\).

In the long wavelength limit, \(Dk^2 \ll I_0\) (beyond the diffusion length \(\ell_d\), the typical distance an adatom moves before incorporation), and also \(|I_1(k)|/I_0 \ll I_0\), the eigenvalues of (3) are

\[
\lambda_1 = -\frac{DF}{I_0} k^2 I_1(k) \\
\lambda_2 = -I_0
\]

(4)

with relative errors \(O(Dk^2/I_0) + O(F|I_k(k)|/I_0^2)\). \(\lambda_2\), remaining finite in the long wavelength limit, rules the enhanced (diminished) incorporation under higher (lower) adatom density. The eigenvector of \(\lambda_1\) mainly lies in direction of \(h\), so in the considered large scale limit the linearization of Eqs. (3) turns into

\[
\partial_t h(k, t) = -\frac{DF}{I_0^2} k^2 I_1(k) h(k, t),
\]

(5)

a non-equilibrium version of Eq. (1).

On crystal surfaces \(I_1(k)\) depends essentially on the step configurations, but on amorphous solids it is proportional to variations in energy density at the surface, and can be derived in a mean field type approach. For a diffusing adatom the amorphous surface consists of potential wells of various depths. They have an average distance \(a\) from each other and a probability distribution of depths \(n(\varepsilon/\varepsilon_0)/\varepsilon_0\), where the energy scale \(\varepsilon_0\) is explicitly included in the notation. In a simple view of the nonequilibrium growth process an atom gets deposited, diffuses, and is finally incorporated into the solid in a sufficiently deep potential well. Dimer formation or other types of nucleation can be neglected if sticky sites are denser than adatoms — a condition to be verified a posteriori. An adatom “sticks” to a site, if it cannot escape until it is buried by the further growing solid. Thus the depth \(\varepsilon\) of “sticky” potential wells fulfill \(\tau_0 e^{-\varepsilon/SkBT} > a/F\). Assuming an exponential distribution of energy depths, \(n(\varepsilon/\varepsilon_0)\approx \exp(\varepsilon/\varepsilon_0)\) this yields a relative proportion of sticky sites

\[
a^2/\ell_d^2 = \left(\frac{F\tau_0}{a}\right) e^{-\varepsilon_0/SkBT},
\]

(6)

which also defines the diffusion length \(\ell_d\), because the fractal dimension of a random walk is two and the adatom can “fully explore” its surroundings on the surface. The average incorporation rate is the inverse of the time needed to hit a sticky site, so \(I_0 = D/\ell_d^2\).

As seen in the context of Eq. (1) deviations from a flat surface change the energy density and the chemical potential near the surface. A natural way to account for this is shifting the energy scale \(\varepsilon_0 \rightarrow \varepsilon_0 - \mu = \varepsilon_0 - \Omega^2\). A positive additional energy density \(\Omega^2\) lowers the depth of potential wells encountered by the adatoms, and changes the incorporation rate by

\[
I - I_0 = -I_0 \log \left(\frac{a}{F\tau_0}\right) - 2I_0 \log \frac{\ell_d}{a} \Omega^2/\varepsilon_0.
\]

(7)

The change is proportional to the relative energy change for adatoms. Flux and temperature enter via \(\ell_d\) and \(I_0\).

Now the surface energetics have to be evaluated in order to obtain \(I_1(k)\) in Eq. (3) via (7). As above in Eq. (4) also here the change in surface free energy enters, so there must be a capillary contribution [23]

\[
\varepsilon_{ca}^\text{lin}(x, t) = -\gamma \nabla^2 h(x, t).
\]

(8)

The other important part of \(\varepsilon^c\) comes from elastic deformations of the growing solid. In the experiments considered here amorphous metallic glasses (i.e. the alloy Zr75.5Al7.5Cu27.5) grow under lateral expansive stress the origin of which is not fully clarified [321427]. It builds
up during growth and reaches a constant level at a film thickness of about 50 nm. The order of magnitude is then 1 GPa, corresponding to a lateral deformation of $\alpha \approx 0.1$ to 1%, given Young's modulus to be roughly $E \approx 10^2$ GPa. Applying the linear relations of stress and strain for small deformations one can calculate the strain and stress tensors in the film with a flat surface, $u_{ij}^0$ and $\sigma_{ij}^0$, as well as the elastic energy density $\mathcal{E}_{el}^0 = \sigma_{ij}^0 u_{ij}^{0}/2$.

Changes in shape are slow compared to mechanical balancing inside the body, so the strain and stress fields follow the surface configuration quasistatically. Surface variations can be seen as perturbing $\sigma_{ij}^0$ by an additional stress field $\tau_{ij}$ with boundary conditions $\tau_{zz} = -\partial_t h E \alpha/(1-\sigma)$ for $i = x, y$ and $\tau_{zz} = 0$ to linear order in $\nabla h$ ($\sigma$ without indices denotes the Poisson number). Green's function corresponding to the geometry of the body yields the perturbative $\tau_{ij}$ and corresponding strain $w_{ij}$ throughout the solid. In view of Eq. (1) only the corrections to the elastic energy density $\mathcal{E}_{el}$ at the surface to linear order in $\tau_{ij}$ and $w_{ij}$ (and therefore $\nabla h$) are needed,

$$\mathcal{E}_{el}^0(x, t) = \frac{\alpha^2}{\pi} \frac{E}{1 - 2\sigma} \int d^2 x' \frac{(x - x') \cdot \nabla h(x', t)}{|x - x'|^3}. \quad (9)$$

Curved parts of the surface also compress or elongate the solid, contributing to the energy density by

$$\mathcal{E}_{el}^0(x, t) = -\sigma \frac{1 - 2\sigma}{1 - \sigma} \alpha \gamma \nabla^2 h(x, t). \quad (10)$$

The derivation of these elastic energy densities will be presented elsewhere in more detail. Here the next step is to gather Eqs. (5), (6), and (10) to the Fourier transform of the energy density variations at the surface,

$$\mathcal{E}_{el}^0(k, t) = B(k) \ h(k, t) \quad (11)$$

$$= \left[ 1 + \sigma \alpha \frac{1 - 2\sigma}{1 - \sigma} \right] \gamma k^2 \frac{E}{\pi} \alpha \frac{1 + \sigma}{1 - \sigma} \ h(k, t),$$

which is local in $k$. With $B(k)$ defined above, the linear surface evolution in Eq. (11) including capillary and elastic effects becomes

$$\partial_t h(k, t) = -2\sigma_0^2 \log \frac{\ell_d}{a} \frac{\Omega B(k)}{\varepsilon_0} k^2 \ h(k, t). \quad (12)$$

In particular, without any elastic effects the kinetic coefficient in Eq. (3) is $\kappa = 2\sigma_0^2 \log(\ell_d/a) F(\Omega\gamma/\varepsilon_0)$.

So far a nonequilibrium dynamic equation for growing surfaces, Eq. (12), has been derived perturbatively close to a horizontal interface. Now it is compared to experimental results. The instability has been carefully observed e.g. for Zr$\text{Al}_2$, for Cu$\text{Zn}_2$, but the lateral stress is documented only for related materials. The best test would be to measure both simultaneously, but already with the given information an order of magnitude estimate for $\lambda_s$ and $1/\tau_s$ is possible.

Here are the experimental parameters: The elastic constants were given above, the surface tension is $\gamma \approx 2$ J/m$^2$, temperature $k_B T \approx 4 \times 10^{-21}$ J, growth velocity $F = 8$ A/s, atomic size $a = 1\Omega^{1/3} \approx 3$ Å. Order of magnitude estimates are used for the time between adatom hop attempts $t_0 \approx 10^{-11}$ s [23], and surface energetics, $\varepsilon_0 \approx 10^{-19}$ J (about 1 eV). This yields a diffusion length $\ell_d \approx 1$ nm, which suits well the observation that atoms move a few diameters before incorporation. Indeed this is smaller than the average distance between mobile adatoms $a \sqrt{\Omega / \rho_0} \approx \ell_d \sqrt{D/\Omega} \approx a \sqrt{\varepsilon_0 / k_B T}$ (D is calculated from the distribution of waiting times in “unsticky” sites [24]), so dimer formation is suppressed. Given these values the theoretical predictions are $\lambda_s \approx 25$ nm and $1/\tau_s \approx 10^{-2}$ s.

![FIG. 1. Comparing 1/\tau_s and \lambda_s (dashed lines) to experiments (diamonds). Left: mean square roughness, growing exponentially after thickness 30 nm. Dotted line shows growth rate 6.5 \times 10^{-3} 1/s. Right: lateral buckle size.](image)

This fits fairly well to experimental observations, as illustrated in Fig. 1. The growing film develops buckles, which after a thickness of about 30 nm take a constant lateral size of $R_c \approx 17$ nm. From 30 to 240 nm film thickness their vertical amplitude increases exponentially with rate $6.5 \times 10^{-3} 1/s$. Surprisingly this quantitative expression of a linear growth instability is not addressed explicitly in the original work, where the authors focus on an observed early time algebraic increase for both quantities. It is caused by kinetic roughening of large k modes at times before $\tau_s$. Besides, in experiments on related materials the lateral homogeneous strain $\alpha$ reaches a constant level only after about 50 nm film thickness. So only then the linear instability as described by Eq. (12) with $B(k)$ constant in time becomes visible.

Some remarks comparing to different interpretations.
of the observed instability [12] are in order. First, the elastic energy density in Eq. (1) is calculated for film and substrate of the same material [22,30]. This does apply to the experimental system, where the Zr alloy film was deposited on a previous 100 nm thick layer of the same material. In particular, effects of perfectly rigid substrates [22] won’t be observed. Second, the partial relaxation of the film close to the modulated surface will not produce a measurable relief of total stress in the layer. Even close to the surface the stress is lowered only by a factor $1 - O(\|\nabla h\|) \approx 1$ and the method of substrate deformation measures only an average stress across the whole film [3]. Third, compression of concave expansion of concave parts by surface tension should not be measurable in the total stress changes, since positive and negative curvature compensate each other. Besides it is only a minor effect (compare Eq. (14) to (8) and (9)). Forth, recently a local continuum equation with linear terms $\partial_t h = (\nu k^2 - \kappa k^4)h$ has been fitted to experimental results [6]. It would be interesting to see whether a destabilizing term $\propto |h|^3$ as in Eq. (5) can give a better description.

In conclusion, in this letter a theoretical framework for a continuum theory of surface growth with diffusion has been constructed. As in the fundamental lattice models [3,4] the basic processes are particle deposition and diffusion until an energetically favourable site is reached. Surface free energy stabilizes the interface by a configuration dependence of substrate deformation. For amorphous solids a mean field type of approach yields Eq. (7), a configuration dependent attachment rate. For amorphous solids diffusion until an energetically favourable site is reached. The instability is enhanced. A challenge is the extension above nonequilibrium framework. Far from equilibrium instability on amorphous films has been shown to be out of (21). Second, an experimentally observed growth variation with an amplitude $\propto k^3$ as in Eq. (5) can give a better description.

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