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Transport theory at the nanoscale. II. Interface dynamics for film growth

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Conditions for surface nucleation and growth of a film are determined in a diffuse interface model. A method is given, derived from a Fokker-Planck equation for the nonequilibrium particle distribution, which links atomic and mesoscopic events in a rheological description similar to the classical continuum theory of fluid flow. Film nucleation and growth are modeled by the spatially inhomogeneous continuous evolution of the instantaneous density profile which measures the average number of particles or molecules at given time and position. It is shown how an alteration in the distribution of particles in the vicinity of the boundary between parent and product phases induces transient film growth and damped vibrations at the surface. The method is general but as an illustration, the condensation of a simple classical fluid on cooling is considered in detail.

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I. INTRODUCTION

The dynamic processes of nucleation and growth are important to thin film technology [1]. The structure that develops is strongly influenced by what happens during film formation and process variables have a profound effect on the magnetic, optical, and mechanical properties of the resulting product. To achieve a better understanding and a measure of control, a variety of experimental and theoretical methods are used [2,3].

During macroscopic film growth a transition takes place in the microscopic interfacial region between two phases of the same substance (for example, on condensation of a vapor) or between different distinct substances (for example, in a mixture of phase separating fluids). An effective approach is based on multiscale modeling or mixed atomistic-continuum modeling [4]. A combined first-principles–rheological theory incorporates atomistic parameters as input for the mesoscopic model.

A phase transition can be characterized by one or more order parameters that distinguish parent and product phases. In the diffuse interface description [5] simple film nucleation and growth are modeled by the spatially inhomogeneous continuous evolution of the instantaneous density profile $n(\mathbf{R},t)$ which measures the average number of particles or molecules at time t and position $\mathbf{R}$. The growing film is represented by a propagating interface in a continuum approach with analogy to pattern forming systems [6]. The particle flux $\mathbf{j}(\mathbf{R},t)=n(\mathbf{R},t)\mathbf{v}(\mathbf{R},t)$ measures the average instantaneous velocity $\mathbf{v}(\mathbf{R},t)$ of the particles of the system. The calculation of system averages in kinetic theory requires the probability $P(\mathbf{R},\mathbf{v},t,\mathbf{R}_0,\mathbf{v}_0)$ of particles passing through $\mathbf{R}$ with a velocity $\mathbf{v}$ at a time t starting from initial position $\mathbf{R}_0$ and velocity $\mathbf{v}_0$. In a phase space description the Fokker-Planck (FP) equation, describing the evolution of $P(\mathbf{R},\mathbf{v},t,\mathbf{R}_0,\mathbf{v}_0)$, was derived from considerations on the most probable atomistic paths in an atomistic model for the probability distribution of a particle path $\mathbf{R}(t)$ with velocity $\mathbf{v}(t)$ [7]. The theory introduces two empirical constants: a relaxation time related to frictional collisions and a diffusion coefficient related to the coupling of the velocity and the position. Appropriate averaging results in a rheological description similar to classical continuum theory of fluid flow [8].

The method was applied to investigate nanoscale surface modes at coexistence [9] and is also of interest in the study of the dynamics of phase transitions, for example, film growth. In that case film growth is described by propagation of a density front; on this level, details of the microstructure of the film are lost. On the other hand, the method is not limited to a system with few particles for the short time scale of molecular dynamics simulations. The method is general but as an illustration, the dynamics of a planar interface between two phases of a simple classical fluid at a first-order phase transition, induced in particular by a temperature quench, is considered. Much of the discussion is valid in cases for which one or more of these qualifications are relaxed.

II. NANOSCALE TRANSPORT THEORY

As described in [8], the FP equation is derived and transformed into a set of differential equations for the velocity moments of the distribution function. In a linear adiabatic approximation, local equilibrium is rapidly established for higher moments such as the kinetic tensor and the heat flow. Two equations remain: the equation of continuity for the density $n(\mathbf{R},t)$

$$\frac{\partial n(\mathbf{R},t)}{\partial t} = -\frac{\partial}{\partial R}\mathbf{j}(\mathbf{R},t) \tag{1}$$

and the damped dynamic equation with internal friction coefficient β

$$\frac{\partial \mathbf{j}}{\partial t} = -\beta \mathbf{j} - \frac{1}{m} n(\mathbf{R},t)\frac{\partial}{\partial \mathbf{R}}\mu(\mathbf{R},t). \tag{2}$$

The driving force is the gradient of the local chemical potential $\mu(\mathbf{R},t)$ which dominates over flow by diffusion. In the

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usual effective interaction model valid for small density gradients [10] the chemical potential is

$$\mu(\mathbf{R},t)=\mu(n)-\kappa\Delta n(\mathbf{R},t). \tag{3}$$

The functional $\mu(n)$ is the bulk chemical potential, and the second term measures local deviation from uniform distribution of the density. The constant κ is related to the range of the interaction between particles and to the surface energy.

The two kinetic equations are combined by taking the time derivative of Eq. (1). Inserting Eq. (2) and using Eq. (3), the resulting equation of motion is

$$\frac{\partial^2 n}{\partial t^2}=-\beta\frac{\partial n}{\partial t}+\frac{1}{m}\frac{\partial}{\partial \mathbf{R}}n(\mathbf{R},t)\frac{\partial}{\partial \mathbf{R}}\mu(n)$$

$$-\frac{\kappa}{m}\frac{\partial}{\partial \mathbf{R}}n(\mathbf{R},t)\frac{\partial}{\partial \mathbf{R}}\Delta n(\mathbf{R},t). \tag{4}$$

With Eq. (4) a nonlinear partial differential equation for the density $n(\mathbf{R},t)$ has been derived from a microscopic model. Special cases have been studied in a variety of problems [6,9]. In particular, the phase field equation, ubiquitous in the study of phase transitions and surface physics, is recovered if the dynamics of the system are dominated by friction effects. Equations (1)–(4) form the basis for a general theory of propagation of density fronts which includes inertia effects important for wave excitation as was shown in [9].

Film growth can be described by the time dependence of the surface density profile through the change in the form $n(\mathbf{R},t)$ of the interface with time and the translation of the boundary $L(t)$. To locate the instantaneous position $L(t)$ of the boundary between phases, due to conservation of particle number the velocity of the boundary dL/dt must be equal to the average flux of the particles normal to the interface [11], yielding, for density jump (n_2-n_1):

$$dL/dt=-j_x[L(t),t]/(n_2-n_1). \tag{5}$$

The growth law is found from Eqs. (2) and (5) for a solution $n(\mathbf{R},t)$ of Eq. (4). In general, the propagation of the boundary need not be a linear function of time or the velocity a constant.

III. APPLICATION TO FILM GROWTH

A. The model

Suppose that at $t=0$, a nonequilibrium planar interface between two fluid phases of unequal bulk densities $n_1<n_2$ exists at $x=L_0$ with the x axis chosen perpendicular to the surface. The liquid interface consists of the (high density) parent phase $n(x,t)=n_2$ for $x<L(t)$, and a (low density) product phase $n(x,t)=n_1+\eta(x,t)$ for $x>L(t)$ (Fig. 1). In this solution close to the critical temperature, the final equilibrium state of the system, after decay of the perturbation, is described by the infinitely sharp profile between the two phases. The evolution of the transient $\eta(x,t)$ is calculated by linearization of Eq. (4):

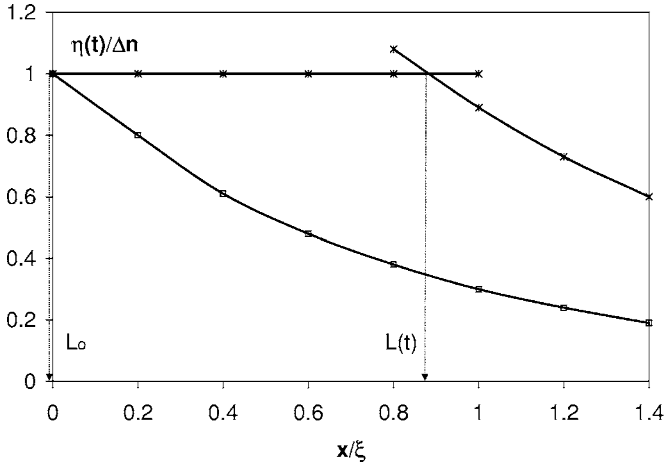

FIG. 1. The transient interfacial profile $\eta(t)/\Delta n$ along the x axis perpendicular to the surface for $\beta t=0$ (□), and $\beta t>0(*)$. The high density film grows from L_0 to $L(t)$, marked by an arrow. The friction constant is β, and Δn the difference in density between coexisting liquid and vapor.

$$\frac{\partial^2 \eta}{\partial t^2}=-\beta\frac{\partial \eta}{\partial t}+c^2\left(\frac{\partial^2}{\partial x^2}\eta(x,t)-\xi^2\frac{\partial^4}{\partial x^4}\eta(x,t)\right) \tag{6}$$

The parameters of the model are the velocity of sound $c^2=(n_1/m)\partial\mu(n_1)/\partial n_1$ and the density correlation length $\xi^{-2}=(1/\kappa)\partial\mu(n_1)/\partial n_1$ in the product phase, and m is the mass of the particles. A propagating interface is the requisite solution of Eq. (6) for film growth. When caused by modification of the average number of particles in the interfacial region the density varies within a range q^{-1} at the boundary with the high density phase. The solution which incorporates the initial and boundary conditions relevant to the phenomena of interest [6] is then an exponential interface of finite width q^{-1} for $x>L(t)$:

$$\eta(x,t)=A\exp[-qx+\ \omega t)]. \tag{7}$$

When Eq. (7) is inserted in Eq. (6) the eigenvalue equation for $\omega(q)$ is obtained,

$$\omega_{\pm}(q)=\frac{1}{2}[-\beta\pm\sqrt{\beta^2+F(q)}],$$

$$F(q)=4q^2c^2(1-\xi^2q^2). \tag{8}$$

As in the classic damped harmonic oscillator, a continuous family of solutions $\omega(q)$ is found for real $q>0$ (Fig. 2). Three dynamic scenarios will be described for different values of the extent q^{-1} of the initial interfacial profile. The dynamics of film growth are found to change at $q=1/\xi$ with $\omega(1/\xi)=0$, and at a critical $q=q_c$ with $\mathrm{Im}\,\omega(q_c)=0$. The critical initial profile width depends on the system parameter $\varepsilon=\beta\xi/c$ and can be calculated from Eq. (8) as $q_c\xi=(1+\varepsilon^2)^{1/2}\cos(1/2\arctan\varepsilon)$. For a simple liquid, $\varepsilon=0.1$ if $\beta=10^{11}\ \mathrm{s}^{-1}$, $\xi=10^{-7}$ cm, $c=10^5\ \mathrm{cm\,s}^{-1}$; in air $\varepsilon=10$ with $\beta=10^{12}\ \mathrm{s}^{-1}$, $\xi=10^{-7}$ cm, $c=10^4\ \mathrm{cm\,s}^{-1}$.

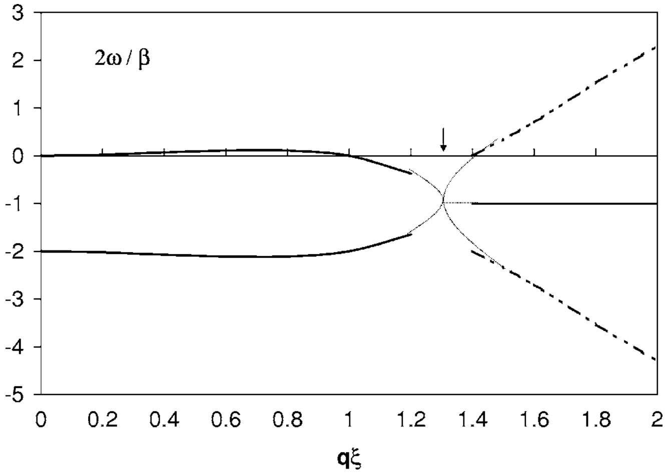

FIG. 2. The eigenvalues $2\omega/\beta$, (—) Re ω and (—··) Im ω, as a function of inverse interfacial width $q\xi$ for the transient profile $\eta(t)=\exp(-qx+\omega t)$. The arrow marks the critical profile width q_c^{-1} between damped front propagation for $q<q_c$ and damped oscillations within the interface for $q>q_c$. The parameter $c/\beta\xi=1$, where c is the velocity of sound in the low density phase.

B. Vibrating film growth

For $q>q_c$, then Re $\omega(q=\beta/2)$ and Im $\omega(q=\Omega_q\neq 0)$. The excess of particles at the surface near the parent phase, in a narrow region relative to the critical length, causes rapid growth of the high density phase accompanied by transient vibrations with contraction and expansion of the entire interface along the direction of front propagation ("breathing"). For initial stationary density ($\partial n/\partial t=0$ at $t=0$), the transient solution is

$$\eta(x,t) = A\exp(-qx-\beta t/2)\left(\cos(\Omega_q t) - \frac{\beta}{2\Omega_q}\sin(\Omega_q t)\right).$$

The particles of the interfacial region all oscillate on an average along x with the dispersion relation $\Omega_q=\frac{1}{2}\sqrt{-\beta^2-F(q)}$. For a very narrow interfacial region $q\gg q_c$, the frequency lies close to the frequency of the elastic bending modes $\Omega_q^2=\kappa q^4/n_1 m$. The vibrations disappear rapidly as $e^{-\beta t/2}$ and, for q close to the critical vector, persist only for a fraction of the oscillation period.

The surface boundary $L(t)$ also oscillates back and forth along the x axis like an elastic membrane with the same frequency Ω_q and the motion decays as β^{-1}. For $\beta t\gg 1$, the transient displacement disappears and the accompanying flow of particles from the interfacial zone into the high density liquid stops. From Eq. (5) the surface boundary rapidly reaches the asymptotic value L_∞:

$$q(L_\infty - L_0) = \ln\left(1 + \frac{Ae^{-qL_0}}{n_2-n_1}\right). \tag{9}$$

The extent of the high density parent phase has then increased by a layer of the order of the width of the initial interface.

C. Smooth film growth

For $1/\xi<q<q_c$, q is smaller than the critical value, the range of the initial interfacial region is smaller but close to the density correlation length. A smoothly propagating interface occurs with no oscillations. Two eigenvalues ω_+ and ω_- are obtained from Eq. (8), both real, Im $\omega(q)=0$, and negative, Re $\omega(q)<0$. The initial condition of the system determines the amplitudes of the two corresponding eigenfunctions. To illustrate with an example of interest, assume the particles arrive at the surface with a constant velocity v_0. In a dynamic interpretation, q^{-1} is a measure of the mean free path of particles in the interfacial region; v_0 is an initial velocity created by the conditions of the experiment or imposed in numerical simulation. The transient is then a combination of two propagating fronts:

$$\eta(x,t) = \frac{A}{\omega_+-\omega_-}\exp(-qx)[(v_0q-\omega_-)\exp(\omega_+t) - (v_0q-\omega_+)\exp(\omega_-t)]. \tag{10}$$

Inserted in Eq. (5), the boundary velocity is found:

$$(n_2-n_1)\frac{dL}{dt} = \frac{-A}{\omega_+-\omega_-}\frac{\exp(-qL)}{q}[(v_0q-\omega_-)\omega_+\exp(\omega_+t) - (v_0q-\omega_+)\omega_-\exp(\omega_-t)]. \tag{11}$$

On integration, the nonlinear evolution of $L(t)$ is obtained, dependent on the initial thickness L_0 (size effect) and on the extent q^{-1} of the interfacial region:

$$q(L(t)-L_0) = \ln\left(1 - \frac{A}{\omega_+-\omega_-}\frac{\exp(-qL_0)}{n_2-n_1}\{(v_0q-\omega_-) \times[\exp(\omega_+t)-1] - (v_0q-\omega_+)[\exp(\omega_-t)-1]\}\right). \tag{12}$$

The extent of the parent phase $L(t)$ increases with time, at first linearly with constant initial growth rate near v_0. After a time $(|\omega_+|)^{-1}$, growth of the liquid phase ceases at the finite asymptotic thickness L_∞ given by Eq. (9). Growth is determined by the smaller eigenvalue $|\omega_+|/\beta<1$ with long equilibration times when smooth film growth is induced by an initial increased density within a range close to the density correlation length of the product phase $\xi>q^{-1}$. On the other hand, if the initial increase occurs close to the critical range q_c^{-1}, growth is rapid and completed within a time β^{-1}.

For $q=1/\xi$, the special case of the stationary profile of coexistence $\omega(q)=0$ occurs; the well-known linear approximation to the profile of coexistence is recovered.

D. Instability

For $q<1/\xi$, the initial interfacial width is larger than the density correlation length, and the eigenvalues are real, Im $\omega(q)=0$. One of the eigenvalues is positive; the corresponding perturbation for Re $\omega_+(q)>0$ is an increasing function of time, invading the low density product phase as particles flow out of the liquid into the interface. The transient cannot be the unstable exponential of Eq. (7); the present simple description of film growth must be modified.

These general results are now adapted to nucleation of the liquid phase by cooling of the vapor. The method is demonstrated for the quench to a low temperature from initial coexistence between parent and product phases. The calculations are easily extended to other initial and final states.

IV. FILM GROWTH BY COOLING

The system is initially in stationary coexistence between vapor and liquid at temperature T_0. The boundary with the high density liquid phase is located at $x=L_0$ for $t=0$; the width of the planar interfacial zone between the two phases is $\xi(T_0)=\xi_0$ (Fig. 1). The temperature is then lowered to $T<T_0$. The density profile is to be calculated for $t>0$. At $t=0$, for $x>L_0$, the interface is $\eta(x,t=0)=(n_2-n_1)\exp[-(x-L_0)/\xi_0]$. The density correlation length of the vapor phase is greater at lower temperature. Once the transient state has disappeared the final state is the equilibrium interface $n_{\mathrm{eq}}(x)$ of width $\xi(T)=\xi>\xi_0$. The density n_2 (n_1) of the liquid (vapor) is greater (smaller) at T, but the relative change in $\Delta n=n_2-n_1$ is small and, for $T_0-T<T_0$, not significant. The solution is then found from Eq. (6) as

$$n(t)=\begin{cases} n_2(T), & x<L(t),\\ n_1(T)+\eta(x,t), & x>L(t),\end{cases}$$

$$\eta(x,t)=(1-e^{-\beta t})n_{\mathrm{eq}}(x)+\Delta n\exp\left(-\frac{x-L_0}{\xi_0}\right)\times\left[\frac{(\omega_+e^{\omega_-t}-\omega_-e^{\omega_+t})}{\omega_+-\omega_-}\right]. \tag{13}$$

For small values of cooling T_0-T, the eigenvalues $\omega_\pm$ corresponding to $q=\xi_0^{-1}$ are real (see Fig. 2). The system evolves in two distinct stages. Rapid appearance of the new equilibrium profile coincides with the slow disappearance of the initial profile of smaller interfacial width until the form of the profile remains stationary. The parent phase grows; the nonlinear time dependence of the boundary $L(t)$ is given in Fig. 3. For $\beta t<1$, early film growth occurs with a constant velocity $v=\xi\beta$. For $\beta t\geqslant 1$ the boundary $L(t)$ can be approximated by

$$\frac{L(t)-L_0}{\xi}=\ln\left[1/2(1+e^{-\beta t})\left(1+\frac{\xi_0}{\xi}\right)-\left(\frac{\xi_0}{\xi}\right)\times\left(\frac{\omega_+e^{\omega_-t}-\omega_-e^{\omega_+t}}{\omega_+-\omega_-}\right)\right].$$

After a characteristic time $\tau=(|\omega_+|)^{-1}$, the new surface will be located at L_∞:

$$\frac{(L_\infty-L_0)}{\xi}=\ln\left[1/2\left(1+\frac{\xi}{\xi}\right)\right].$$

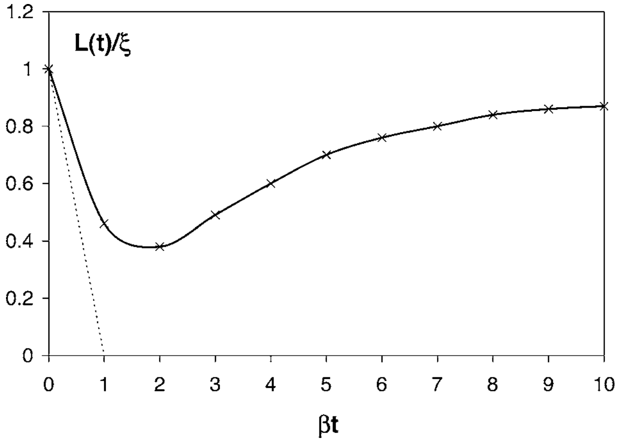

FIG. 3. The thickness (×) of the high density phase $L(t)/\xi$ as a function of time βt on cooling. Initial growth occurs with constant growth rate $v=\beta\xi$ (···) for $\beta t<0.2$.

The time to reach the new equilibrium state is a function of the cooling temperature essentially through ξ. As shown in Fig. 4 for a linear expansion in the cooling temperature, $\xi^2/\xi_0^2=1+2(T_0-T)/T_0$, the initial velocity increases and the time for completion of the growth process decreases with increasing cooling.

For deep quenches, it may be possible that the initial profile width becomes smaller than the critical width at T and $\xi(T_0)=\xi_0<q_c^{-1}$. Then the initial thin liquid layer of coexistence, which must grow once the temperature is lowered, is accompanied by periodic contraction and expansion in the interfacial region as described previously in Sec. III. The particles in the interface need to rearrange continuously, forming transient layers, empty sites, even clusters in a kind of nonequilibrium roughening with frequency Ω_{1/ξ_0}. The oscillations are overdamped and are localized close to the interface between phases.

These results can be extended also to the spherical geometry of a condensing liquid cluster [12]. A calculation of the radial density $\mathbf{R}n(\mathbf{R},t)$ follows the planar case from the linear equation (6) in spherical coordinates with the transient $\eta(\mathbf{R},t)=(A/\mathbf{R})\exp(-q\mathbf{R}-\omega t)$ present near the surface of the cluster at $\mathbf{R}\geqslant a(t)$. The dynamics of the cluster radius $a(t)$ are derived as in Eq. (5) for stationary particle number and are determined from the radial flux j_R through the cluster

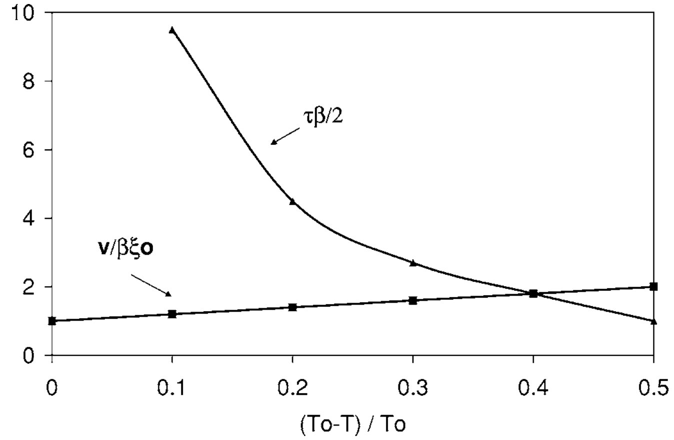

FIG. 4. The early stage growth rate $v/\beta\xi_0$ (■) and the time to completion $\tau\beta/2$ (▲) on cooling from T_0 to T as in Fig. 1.

surface. A variety of growth laws is possible which depend on the local environment near the cluster surface.

V. CONCLUSIONS

It was shown that nucleation and growth can be induced by the density distribution in the vicinity of the surface between two phases or materials. Nonlinear growth of the parent phase is found and, depending on the initial conditions of the growth procedure, a constant growth rate in the early stages of the growth process. Strongly damped collective oscillations, often observed in molecular dynamics, may accompany or even nucleate [13] film growth. What is new in the present model is the inertia term in the dynamic equation, which cannot be neglected for events on a short time scale, smaller than the time for loss of memory by internal friction, and which are essential to describe nanoscale oscillations or waves [9].

A continuum method was developed to link atomic and mesoscopic events through a kinetic theory for the nonequilibrium probability distribution $P(\mathbf{R},\mathbf{v},t,\mathbf{R}_0,\mathbf{v}_0)$. In the same method it is possible to follow probable trajectories of a single particle during growth [14]. After averaging in the distribution of initial and final velocities of particles, the system is described by a local density and flux and the interactions by a local chemical potential. Information on the single-particle dynamics is lost as well as on the microstructure. A given profile may correspond to a set of clusters as well as to a uniform film. Crystallization is especially complex; films can be polycrystalline, amorphous, with defects and voids, or aggregates [1]. In a more detailed model supplementary order parameters can be introduced [15], for example, to describe the crystalline structure [16,17]; in the simplest case, the evolution of crystalline order is enslaved by the local density. In thin films, an active substrate results in strong repulsive or attractive external fields in the local chemical potential which especially affect early stage growth [18].

The theory is general and can be adapted to many different experimental situations as was illustrated for film growth by cooling from an equilibrium state. Many of the phenomena described have been observed: nonlinear growth laws [19,20], slow dynamics [21], surface modes and dynamic roughening [22], and strong temperature dependence [23]. But the intent here was to introduce a generic method rather than to explain a specific experiment. The ideas presented may prove useful in the interpretation of experimental and simulation results and help to fix efficient initial and boundary conditions to initiate growth in real and numerical studies.

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