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Transport theory at the nanoscale. I. Surface waves

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Small scale particle motion is the cause of dynamic roughening and plays a role during film growth. To study surface waves on the molecular level, a continuum approach is used that links atomic and macroscopic dynamics though a Fokker-Planck equation for the distribution of particle trajectories. The dynamic equation for the density interfacial profile includes inertia terms indispensable for high frequency fluctuations. For wave vectors below the critical value, an initial periodic deformation of the surface on the order of the density correlation length simply decays with time. Above the critical wave vector, collective periodic motion is induced in the interface. A picture of short lived, localized high frequency wavelets emerges with contributions from acoustic, capillary, and elastic surface modes.

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I. INTRODUCTION

Materials are known to be influenced by events occurring at the interface between phases during processing and the properties of the surface have a long history of study with numerous applications [1]. The interfacial region between different forms of matter, whether between two phases of the same substance or between different materials, provides a contact zone that can easily be deformed and modified. Vibrations affect the shape and the sharpness of the interface [2]. In fluids, the importance of capillary waves is well known in the stationary regime of coexistence.

Whereas the surface is macroscopic, the interfacial region is microscopic with modifications on a scale of the order of the density correlation length. Particle motion is ultimately the cause of displacement of the surface during film growth and of excitation of collective modes. Although descriptions designed for macroscopic considerations may continue to hold as the scale is depressed to molecular level, the reverse may not be true [3]. When the characteristic mean free path or the collision time is comparable to molecular scales, results may be qualitatively correct but quantitative conclusions should be regarded with caution. Motions of the surface have been commonly discussed in terms of a continuous elastic membrane and surface modes which cover an extended region of the surface [4,5]. Over long periods, hydrodynamic modes appear to displace the location of the surface. The short time profile, seen in experiments for observation times of the order of a number of collision times, points to the presence of surface excitations which do not extend in space for more than a fraction of the wave length and do not persist for more than a fraction of the vibration period. Also found in numerical molecular dynamics simulation [6,7], overdamped high frequency local modes, intermediary between molecular vibrations and large scale collective modes, cause a greater roughness of the surface and may play a role in the dynamics of phase transitions [8–11].

A multiscale approach has been developed to bridge the gap from the molecular level to long range phenomena [12]. The characteristics of an interface are described by a continuous profile of the average local particle density, the interactions between distant particles by a mean field corrected when necessary by the potential between near neighbors. It is then possible to study surface waves as in the leading edge dynamics of pattern formation [13]. In contrast to the classical calculation on a sharp boundary, excitation within a finite surface layer can be investigated. The main idea of the method is that the motion of the front is governed by the asymptotic exponential leading edge far from the boundary. In this region, the dynamics are simplified and can be calculated by linearization of the evolution equation of the interfacial profile.

II. NANOSCALE TRANSPORT THEORY

The calculation is based on a model of the nonequilibrium probability distribution of particle paths to derive the Fokker-Planck equation [12].

Consider a system in a nonequilibrium state at time t. If some (initial) constraints are removed, it will be observed that processes are initiated that work to establish a state of equilibrium. The processes depend on the initial local deviation from equilibrium and involve transport of mass, momentum and energy. Often the processes take place predominantly at a dividing surface between different phases or materials; in the case of interest, mass transport occurs under conditions where large density gradients at the surface create a local driving force. The dynamical response of a system of particles to a driving force may be analyzed in terms of a sliding friction and an adiabatic potential. The friction coefficient relates the driving force to the induced drift velocity. The adiabatic potential is an equilibrium temperature dependent field which describes model or semi empirical interparticle interactions.

The Fokker-Planck kinetic equation is a phenomenological approach which allows for a choice of model of adiabatic potential and friction parameter. It can be derived rigorously from a microscopic Hamiltonian in various ways, by separating variables into slow degrees of freedom to be treated explicitly and fast degrees of freedom to be integrated out. It

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is also possible to propose a simple statistical model of the randomizing mechanism underlying the otherwise deterministic behavior. In the path integral approach, the probability for a single particle trajectory is determined by a positive definite functional. The acceleration on the path obeys a Gaussian distribution with a self correlation function related to the friction constant. The formalism provides a method to derive and solve the Fokker Planck equation.

In a useful mesoscopic method, the equation is then transformed into a set of differential equations for velocity moments. A solution is found in a linear adiabatic approximation whereby two equations remain: the equation of continuity which couples the density $n(\boldsymbol{R},t)$ and the average velocity of the particles $\boldsymbol{v}(\boldsymbol{R},t)$

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

and the damped dynamic equation for the flux $\boldsymbol{j}(\boldsymbol{R},t) = n(\boldsymbol{R},t)\mathbf{v}(\boldsymbol{R},t)$

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

The first term on the right hand side introduces the coefficient β and defines the relaxation time due to random collisions of internal friction. The driving force is the gradient of the local chemical potential $\mu(\boldsymbol{R},t)$ which dominates flow by diffusion. In the effective interaction model for small density gradients [14], the chemical potential is

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

The function $\mu(n)$ 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 effective interaction between particles which also determines 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

$$\frac{\partial^2 n}{\partial t^2} = -\beta\frac{\partial n}{\partial t} + \frac{1}{m}\frac{\partial}{\partial \boldsymbol{R}} n(\boldsymbol{R},t)\frac{\partial}{\partial \boldsymbol{R}}\mu(n) - \frac{\kappa}{m}\frac{\partial}{\partial \boldsymbol{R}} n(\boldsymbol{R},t)\frac{\partial}{\partial \boldsymbol{R}}\Delta n(\boldsymbol{R},t). \tag{4}$$

Equation (4) is a generic nonlinear partial differential equation for the density profile. It can be applied to a variety of problems [4]; in particular, the dynamics of a system to reestablish equilibrium from an initial nonequilibrium state. Being derived from a microscopic model, application to molecular scale phenomena is justified.

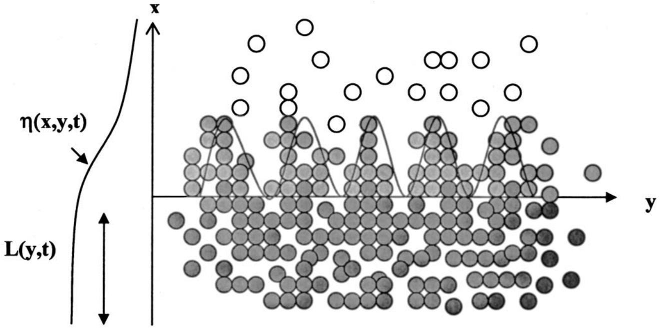

FIG. 1. Sketch of the instantaneous density surface mode in the x-y plane, the profile $\eta(x,y,t)$, and the surface boundary $L(y,t)$ for a fixed position y. The high density fluid fills the space for $x < L(y,t)$; far from the surface, $x \to \infty$, the low density phase is found.

III. APPLICATION TO SURFACE MODES

The method is used to study surface waves in the interface between two coexisting phases of density $n_1 < n_2$ (Fig. 1). In the leading edge approach, the proposed solution for surface modes in the interfacial region between phases is

$$n(x,t) = \begin{cases} n_2, & x < L(t), \\ n_1 + e^{-u}, & x > L(t). \end{cases}$$

The boundary between the two phases $L(t)$ describes the dynamics of the film surface. The function $\eta = e^{-u}$, given as $u = qx - \omega t + \eta_s(x,y,z,t)$, describes the dynamics of the small perturbation η_s within the propagating front. The exponential tail of the front into the low density phase is determined by q. The dynamics of the propagating front are exponential and ω can be calculated from Eq. (4) for $\eta_s = 0$. Film growth, for which $\omega \neq 0$, is described in detail in [15].

For a given q and ω, the perturbation η_s obeys the linear equation obtained from Eq. (4):

$$\frac{\partial^2\eta_s}{\partial t^2} + (\beta+2\omega)\frac{\partial\eta_s}{\partial t} = c^2\Bigg\{ -2q\frac{\partial}{\partial x}\eta_s + \Delta\eta_s - \xi^2\Bigg[2q^2\Bigg(2\frac{\partial^2\eta_s}{\partial x^2} + \Delta\eta_s\Bigg) - 4q\frac{\partial}{\partial x}\Delta\eta_s + \Delta\Delta\eta_s - 4q^3\frac{\partial\eta_s}{\partial x}\Bigg]\Bigg\}. \tag{5}$$

The parameters in the product phase are the velocity of sound $c^2 = (n_1/m)\partial\mu(n_1)/\partial n_1$ and the density correlation length $\xi^{-2} = (1/\kappa)\partial\mu(n_1)/\partial n_1$; m is the mass of the particles.

In the following the dynamics are derived for a localized surface mode in the yz plane $\eta_s(x,y,z,t) = \eta_0 e^{\nu t - kx}\cos(ky)e^{-kz}$ for $z > 0$. Here k is real and measures the extent and the periodicity along the y axis of the periodic deformation localized within the interface between phases (Fig. 1). When inserted in Eq. (5), the eigenvalue $\nu(k)$ is found:

$$\nu^2 + (\beta+2\omega)\nu = c^2\{(q+k)^2 - q^2 - \xi^2[(k+q)^4 - q^4]\}. \tag{6}$$

The interface of stationary coexistence, $\omega = 0$, $q = 1/\xi$, between vapor and liquid phases is a special case which will be examined here in detail. Similar results are also found in a moving interface.

The eigenvalue equation (6) is written as $\nu^2 + \beta\nu + \nu_0^2 = 0$. The eigenvalues in the absence of internal friction are $\nu_0^2 = c^2(2k/\xi + 5k^2 + \xi^2 k^4 + 4k^3\xi)$. The solutions for $\nu(k)$ are

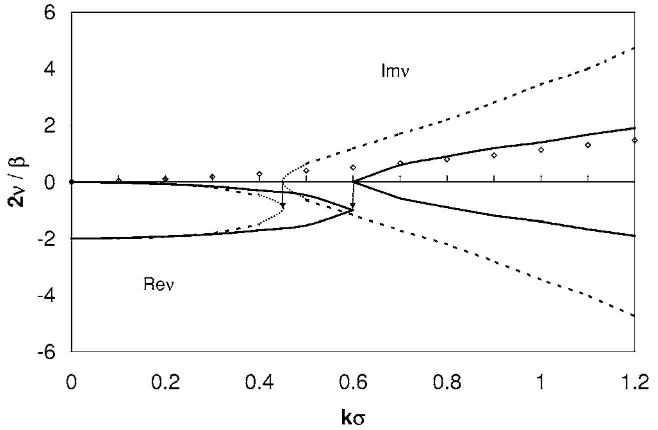

FIG. 2. The eigenvalue $2\nu/\beta$ of the surface mode as a function of the wavelength $k\sigma$ of the deformation for $\xi/\sigma=1$ (—) and 5 (⋯). The critical wave length k_c is marked with an arrow; the data above k_c correspond to Im ν and wave propagation; below, to Re ν and attenuated front propagation. The system parameter $c/\beta\sigma=0.25$, c is the velocity of sound in the low density phase, ξ is the density correlation length, and β is the friction constant. The hard core radius is σ. The classical macroscopic capillary wave frequency $\Omega^2=n_1\kappa k^3/\xi m$ is also shown (◇) for $\xi/\sigma=5$.

shown in Fig. 2. A critical size is found at the value $k=k_c$ for which Im $\nu(k_c)=0$. Two types of behavior are found for stationary initial density distribution (Fig. 3).

For $k>k_c$, the transient $\eta_s(x,z,t)=\eta_0 e^{-kx}e^{-kz}\cos(ky)\cos v_k t e^{-\beta t/2}$ is an attenuated standing wave of short wavelength and wave frequency $v_k^2=\nu_0^2-\beta^2/4$. A superposition of three types of waves is found [16]: surface acoustic waves of frequency $\sqrt{5}\,ck$ caused by density fluctuations inside the interface; localized capillary waves with frequency $2k^{3/2}(n_1\kappa/\xi m)^{1/2}$ driven by the surface pressure; bend elastic surface modes with a frequency $k^2(\kappa n_1/m)^{1/2}$. For wave vectors close to k_c, in the range of frequency $0<v_k<\beta/2$ characteristic of overdamping, the surface modes do not persist for more than a fraction of the vibrational period. A lower limit wave vector is found; these surface waves cannot be excited for wave vectors below k_c.

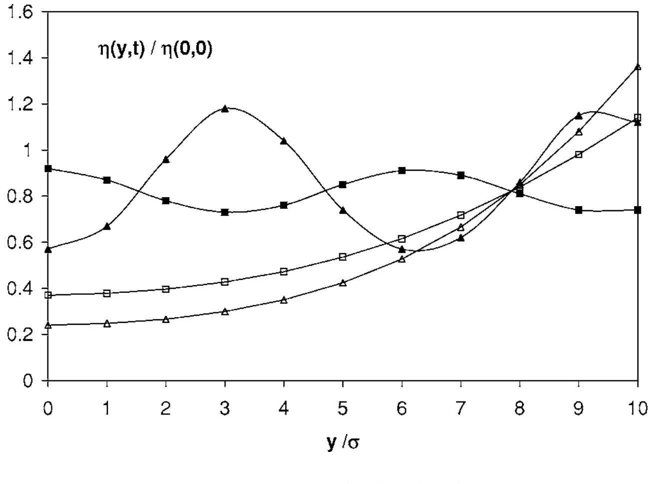

FIG. 3. The interfacial profile $\eta(y,t)/\eta(0,0)$ along the surface y axis at $x=\sigma$, $z=0$ for a periodic deformation with amplitude $\eta_0=1$, wave vector $k\sigma=0.2$ (△, $\beta t=0$; □, $\beta t=2$, $\eta_0=1.5$) and $k\sigma=1$ (▲, $\beta t=0$; ■, $\beta t=2$). The density correlation length $\xi/\sigma=5$, and the dispersion relation is given in Fig. 2. Induced wave motion is seen for $k\sigma=1$, simple decay for $k\sigma=0.2$.

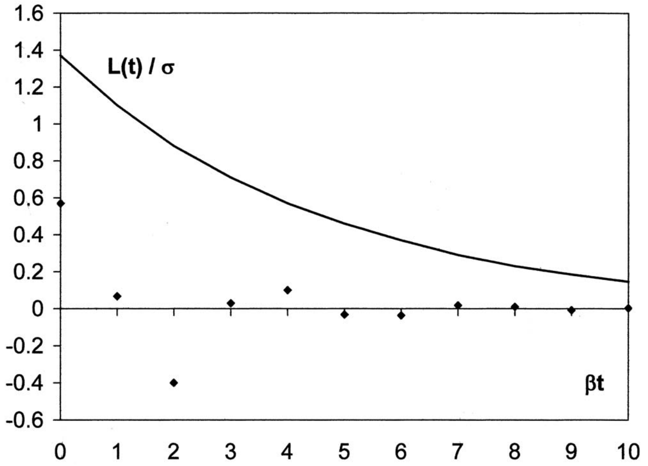

FIG. 4. The time dependence of the boundary $L(t)$ for simple decay of the periodic deformation of the surface, amplitude $\eta_0=1$, with wave vector $k\sigma=0.4$ (—). For excitation of surface waves with $k\sigma=1$ (◆), transient roughness of the surface is evident. The corresponding dispersion relation is given in Fig. 2 for $\xi/\sigma=5$. The motion is followed at $\cos ky=1$, $z=0$.

For $k<k_c$, the dispersion relation $\nu(k)$ is real and negative. No wave propagation occurs, the initial periodic deformation simply decays with time in exp $\nu(k)t$ as displaced interfacial particles return to the high density phase. For large wavelengths $k\ll k_c$, the transient $\eta_s(x,z,t)=\eta_0 e^{-k(x+ut)}e^{iky-kz}$ disappears into the liquid phase with a propagation velocity $u=2c^2/\xi\beta$.

To locate the film surface L the boundary condition for the conservation of particle number is applied [4]. At the interface in the y-z plane between the two fluid phases, the velocity dL/dt of the boundary must be equal to the average flux j_x of the particles, yielding $dL/dt=-j_x(L,t)/(n_2-n_1)$. The flux is calculated to linear order in η_s. For $k<k_c$, the periodic deformation of the surface defined by $L(y,z,t)$ decays in a time determined by the largest eigenvalue $\nu^+(k)$. For $k>k_c$, high frequency damped waves of small wavelength are excited with small scale kinetic "roughening" of the surface (Fig. 4).

The critical wave vector k_c is a decreasing function of the parameter $\varepsilon=\xi\beta/c$, of the order of the inverse density correlation length. The larger the density correlation length, the greater the range of possible wave propagation. ε is a strong function of temperature mainly through ξ. In simple fluids for $\xi=10^{-7}$ cm, $\beta=10^{11}$ s^{-1}, and $c=10^5$ cm s^{-1} then $\varepsilon=0.1$.

IV. DISCUSSION

Autoexcitation of nanoscale surface waves is possible by thermal fluctuations, motion of a localized heterogeneity (defects, impurities), or coupling to molecular vibrations. A picture emerges for surface waves on the scale of the correlation length as an excitation of a band of localized short lived high frequency wavelets. The method is general [17] and can be applied to other surface modes besides the specific example discussed, as well as to fluctuations on a crystal [18].

Classical low frequency capillary waves are a special solution of Eqs. (1) and (2) for sharp profiles ($\xi \rightarrow \infty$) between phases of stationary uniform density. Motion is then limited to the surface boundary determined by $\eta_s(x = L, y, t) = L(y,t)/\xi$. The average velocity of particles at the surface is the phase velocity of the waves. At low frequency, the average motion of the particles is slow and the decay time of collective oscillations is significantly larger. The details of the nearest neighbor interactions are possibly no longer described by the local mean field of density functional theory and local acceleration can offset the loss of motion by random friction [19].

The effect of fluctuations on front propagation is well known in spatiotemporal pattern formation [20]. What is different in the proposed model is the effect of the self-consistent surface field driving the front propagation and the inertia term in the dynamic equation, essential for events on a time scale short relative to the relaxation time β^{-1} or for high frequency fluctuations $\omega > \beta$. Of interest would be an exact solution of the derived nonlinear kinetic equation with, as in the Kuramoto-Sivashinsky equation, a promising richness of dynamic effects including complex patterns, temporal chaos, and even turbulence [21,22].

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