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Hydrodynamics of a dense adsorbate

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Basic hydrodynamic equations describing the adsorbate dynamics in the presence of adsorbate–host-solid dynamical interactions are derived with use of a combined density-functional and canonical formulation of fluid mechanics. A new dissipative term in the hydrodynamic equations resulting from these interactions is derived. The main emphasis is put on the relation between this term and diffusion in the adsorbate. It is shown that the diffusion coefficient depends in a nontrivial way both on the single-particle interactions between an adparticle and the excitations in the host solid and on the interactions between the adparticles modified by the presence of these excitations. The basic physical assumptions in the model are discussed and suggestions for further developments of the theory, for example, inclusion of desorption, are given. The differences and similarities between our approach and those in the literature are pointed out.

I. INTRODUCTION

One of the key problems in surface physics is the description of the dynamical phenomena in an adsorbate when its density becomes sufficiently large to make the collective effects important. If the dense phase of an adsorbate is formed on the solid surface, the interaction between the adsorbate and the host solid particles determines not only the static-equilibrium properties of the adsorbate but also influences its dynamical properties.[1–3] Since the static parameters of the adsorbate phase, for example its static correlation functions, are affected by the interaction with the solid, so are all the ingredients of the dynamics which depend on the values of the equilibrium state properties. Even more important, however, is that the interaction with the host solid leads to a different type of the adsorbate collective behavior. Those changes in the adsorbate dynamics show up already in the long-wavelength and low-frequency behavior of the adsorbate, i.e., in its hydrodynamics.

The equilibrium properties of the thin layer of a fluid in contact with the solid wall have attracted a lot of attention in view of its relevance to wetting transition phenomena, and considerable progress was achieved in a microscopic theoretical description of the wetting layer statics.[4,5] The analysis of the wetting layer dynamics relies on the hydrodynamic approach[6,7] utilizing the functional density method for nonuniform media.[8]

The important point in these analyses is that the thin—often thought as strictly two-dimensional—layer of a fluid interacts strongly with the underlying medium. This fact is crucial in the dynamical approach because of the well-known *nonexistence* of hydrodynamics of strictly two-dimensional fluids (e.g., divergence of transport coefficients like shear viscosity, etc.).[9] To overcome this difficulty in the hydrodynamical description of an adsorbate, Ramaswamy and Mazenko[10] have suggested supplementing the Navier-Stokes equations by a *single-particle* friction term resulting from interactions between the fluid and the host solid. It was later argued[11] that a similar modification to the hydrodynamic equations should result from allowing for desorption of the adsorbate, and that the latter effect should be the more important of the two for noble-gas adsorbates on solid surfaces. The main theoretical gain here was that such a single-particle-like term removes the infrared divergences in the dynamic density correlation function and results in convergent expressions for $d=2$ transport coefficients.

One of the most important dynamical processes in adsorbed layers is diffusion. Without diffusion, and related atomic migration processes on solid surfaces, the description of the adsorbate layers would be incomplete. Description of the adsorbate diffusion is nowadays attracting much of the attention but full theoretical understanding of these phenomena has not yet been achieved.[2,12] Most of the theoretical and numerical works on these problems use models in which the surface diffusion is fashioned as a random-walk-like phenomenon.[13] It has been shown recently that the $1/q^2$ behavior of the dynamical structure factor, typical of diffusivelike decay of density fluctuations, is modified in more realistic models of hoppinglike diffusion in an adsorbate if desorption is permitted and/or if the host solid surface contains more than one adsorption site per surface unit cell.[14] The master equation based models, like that of Ref. 14, assume a certain form of the transition probabilities for atomic jumps from one allowed site to another and it is generally believed that those jumps are caused by the interaction between adatoms and the host solid. Calculation of those rates requires considerable efforts and involves detailed analysis of the phonon mediated transitions between different adsorption sites. Although similar theory for desorption transition probabilities is well developed the intersite transitions are poorly understood. Banavar, Cohen, and Gomer[15] have analyzed the surface diffusion problem using the Fokker-Planck equation and they were able to relate the diffusion coefficient to the changes in the system free energy due to the presence of a single adsorbate particle. Their model neglects all possible correlations between adatoms and this approximation was also used in the Fokker-Planck equation analysis of diffusion in $d=2$ periodic potentials.[16] Similar in spirit, but a more advanced approach to the analysis of the single-particle adsorbate diffusion was the model proposed by Wahnström,[17] who used the Mori memory-function formalism, and that by Ying, and Ala-Nissila and Ying,[18] who employed a similar technique. In all these approaches, many-body effects in the adsorbate behavior were not taken into account. On the other hand, surface diffusion in an adsorbate was analyzed by Kreuzer and co-workers,[19] who used a generalized lattice-gas model in which many-body effects were taken into account by the introduction of a nonlinear master equation. Attractive as it is, the lattice-gas model and its variants—for example, the Potts-model approach[20]—suffer from an essential difficulty in that they have no intrinsic dynamics and, therefore, the dynamical correlations in them are entirely "static" driven.[21]

The dynamical theory of the adsorbate layer which would take properly into account both intra-adsorbate interactions and correlations as well as realistic models for interaction with the host solid lattice is quite complex; progress is most likely to be obtained by generalizing a memory-function-like approach for a single adsorbate particle as given in Refs. 17 and 18. In this paper we would like to present a simpler analysis of such a system based on a hydrodynamical model for the adsorbate layer. We shall treat the interactions between the adsorbate constituent particles within the simple hydrodynamic extension of the density-functional model[22] and account for the coupling with the host solid, the latter being treated within the harmonic approximation for semi-infinite crystals. In this way, we shall address some dynamical aspects of this system, mostly related to its hydrodynamic (long-wavelength and low-frequency) behavior. We shall develop a formulation which permits us to analyze diffusion processes in dense adsorbates when the mutual interparticle interactions between the adsorbate particles (intra-adsorbate interactions) are as important as the interactions between the adsorbate particles and the host solid. We will also look into the possibilities of incorporating desorption into this description, again trying to understand how it affects the collective behavior of the adsorbate.

The plan of our paper is then as follows. In Sec. II we formulate the model and discuss the underlying essential physical assumptions. In Sec. III, we derive the equations of motion for our dynamical model and show how they generalize previously postulated equations for adsorbate hydrodynamics. In Sec. IV we will discuss our results. Final comments and conclusions will be presented in Sec. V.

II. MODEL

When a freshly cleaved surface of a crystal is exposed to an ambient gas atmosphere, the gas particles begin to interact with it, and, after some initial period of time, a certain amount of gas particle settles down on the solid surface, forming an adsorbate.

If the intra-adsorbate correlations are neglected, the particle dynamics on the surface can be deduced from the laws governing jumps (hopping) between several isolated sites on the solid surface (adsorption sites) and from the laws describing desorption. The desorption phenomena are well understood[23] and hopping diffusion can also be relatively well described by various master equation based models, even if the adsorption sites form a nontrivial lattice.[14] As the adsorbate density increases, one expects the adsorbate to develop many dynamical features similar to those of dense gases and fluids, though modified by its interaction with the host solid. This interaction is responsible for creating the adsorbate density profile in the direction normal to the solid surface. We shall assume that we can describe static properties of the adsorbate using the free-energy-density functional akin to that used in the studies of the interfacial phenomena.[22,8(b)] The dynamics of the adsorbate is then described by supplementing this free-energy functional by the kinetic-energy part and using the canonical fluid dynamics formulation in which this functional plays the role of the Hamiltonian of the fluid.[22,24]

The state of the adsorbate is described in this approach by the adsorbate density $n(\mathbf{r},t)$ and velocity $\mathbf{u}(\mathbf{r},t)$ fields. The vector $\mathbf{r}$ denotes the Eulerian position within the adsorbate. As we shall see in what follows the adsorbate density field changes rapidly in a direction normal to the solid surface and vanishes outside a thin layer distributed evenly on the solid surface. In the hydrodynamic limit we are interested only in long-wavelength and low-frequency variations of $n(\mathbf{r},t)$ and $\mathbf{u}(\mathbf{r},t)$; therefore, the dynamics of the adsorbate layer will be essentially two dimensional. The free-energy functional for the adsorbate consist now of two parts, the kinetic and the potential one, and can be written as

$$F\{n,\mathbf{u}\}=F_{\text{kin}}\{n,\mathbf{u}\}+F_{\text{pot}}\{n\}\ , \tag{2.1}$$

where

$$F_{\text{kin}}\{n,\mathbf{u}\}=\frac{m}{2}\int d\mathbf{r}\, n(\mathbf{r},t)[\mathbf{u}(\mathbf{r},t)]^2\ , \tag{2.2}$$

with m denoting the adsorbate particle mass. The potential-energy part of the free-energy functional, $F_{\text{pot}}\{n\}$, depends on the adsorbate density only and contains both the part responsible for the short-range repulsion between the adsorbate particles and that describing long-range attractive interaction.[8(b)] For example, it can be written as

$$F_{\rm pot}\{n\}=\int d\mathbf{r}\, f_0(n)+\tfrac{1}{2}\int d\mathbf{r}\int d\mathbf{r}'n(\mathbf{r},t)V(\mathbf{r}-\mathbf{r}') \times n(\mathbf{r}',t) \ . \qquad (2.3)$$

In Eq. (2.3), $V(\mathbf{r}-\mathbf{r}')$ denotes the attractive interaction between the adsorbate particles. We shall see that this interaction is further modified by the coupling to the excitations of the host solid.

Consider now the host solid which is thought of as a semi-infinite crystal. We assume that the harmonic approximation is adequate for the description of its dynamics. The fact that the solid is semi-infinite affects its excitation spectrum. In addition to the bulk phonon excitations (modified by the presence of the surface) the medium supports distinct surface (Rayleigh) modes. In several previous analyses of the adsorbate properties, for example desorption, it has been shown that the use of these modes does not lead to qualitatively different results from those based on the simplified model in which the solid is infinite and harmonic.[23] Similar conclusion can also be drawn from the analysis of a single-particle surface diffusion.[25] In view of this, we adopt for the solid a model in which the elementary excitations, phonons, will be labeled by the index **J**. For an infinite solid, **J** denotes both the wave vector **q** and the polarization λ of the phonons propagating in the solid. In a form more appropriate for the surface phenomena description, the index **J** denotes the parallel to the surface wave vector **q** and the remaining "quantum" numbers which are appropriate for the solid with a surface. In a model in which the solid is treated as a semi-infinite elastic medium, these additional indices are $\lambda=(c,\sigma)$, where c is the apparent sound velocity along the surface and σ labels shear horizontal, Rayleigh, and two P-SV modes.[23,25,26] The results of our general analysis presented in this paper do not depend on the particular choice of the solid dynamics we make. Therefore, for the simplicity of the arguments to follow, one can think about the elementary excitations of the solid as being those of the infinite elastic medium. Of course, in particular applications of our theory aiming at the actual calculations of the hydrodynamical quantities of the adsorbate, one must use a proper description of the solid dynamics with the surface. With all that in mind the solid Hamiltonian reads

$$H_s(\{Q_{\mathbf{J}}\},\{\Pi_{\mathbf{J}}\})=\tfrac{1}{2}\sum_{\mathbf{J}}(|\Pi_{\mathbf{J}}|^2+\omega_{\mathbf{J}}^2|Q_{\mathbf{J}}|^2) \ , \qquad (2.4)$$

where $\omega_{\mathbf{J}}$ denotes the frequency of the **J**th mode. The reality of the Hamiltonian requires that

$$\Pi_{\mathbf{J}}^*=\Pi_{-\mathbf{J}},\quad Q_{\mathbf{J}}^*=Q_{-\mathbf{J}},\quad \text{where } -\mathbf{J}=(-\mathbf{q},\lambda) \ .$$

The adsorbate particles do interact with the solid via the central two-body potential $W(\mathbf{r}_a-\mathbf{R}_s)$ where $\mathbf{r}_a$ and $\mathbf{R}_s$ denote, respectively, the position of the ath adsorbate particle and the actual position of the sth particle forming the solid. Writing $\mathbf{R}_s=\mathbf{R}_s^0+\mathbf{u}_s$ where $\mathbf{R}_s^0$ is the equilibrium position of the sth particle, we can expand the adparticle solid interaction in a power series of **u**'s keeping the linear terms only. Expanding then displacements $\mathbf{u}_s$ into the normal variables $Q_{\mathbf{J}}$ we obtain the following form of the interaction between the solid and the adsorbate:

$$\Delta H=H_R+\delta H \ , \qquad (2.5)$$

where H_R denotes the interaction between the rigid solid and the adsorbate

$$H_R\{n\}=\int d\mathbf{r}\, n(\mathbf{r})\sum_s W(\mathbf{r}-\mathbf{R}_s^0)\equiv\int d\mathbf{r}\, n(\mathbf{r})U_s(\mathbf{r}) \ . \qquad (2.6)$$

Note that this is the term which is usually called the static surface potential.[23] It is responsible for maintaining the adsorbate density profile and its range in the direction normal to the surface is of utmost importance in determining the profile properties in wetting theories.[4,5] The second term in Eq. (2.5) is the dynamical part of the interaction which depends on the structure of the solid and that of its surface and has the following form:

$$\delta H\{n,Q\}=-\sum_{\mathbf{J},a}Q_{\mathbf{J}}\Psi_{\mathbf{J}}(\mathbf{r}_a) \equiv-\sum_{\mathbf{J}}\int d\mathbf{r}\, n(\mathbf{r})\Psi_{\mathbf{J}}(\mathbf{r})Q_{\mathbf{J}} \ . \qquad (2.7)$$

The functions $\Psi_{\mathbf{J}}(\mathbf{r})$ carry all the information about the details of the coupling between the solid excitations and the adparticle. They also contain all the geometrical information distinguishing between various modes of the semi-infinite solid. As already mentioned, the detailed form of these functions is not essential for our further analysis. Actually, one can use here their form obtained for an infinite solid. In this case (and for the Bravais solid lattice) they assume a simple form:

$$\Psi_{\mathbf{J}}(\mathbf{r})=\frac{1}{\sqrt{MN_s}}\sum_s \mathbf{e}_{\mathbf{J}}\cdot\nabla W(\mathbf{r}-\mathbf{R}_s^0)\exp(i\mathbf{q}\cdot\mathbf{R}_s^0) \ , \qquad (2.8)$$

where $\mathbf{e}_{\mathbf{J}}$ is a phonon polarization vector, M is the mass of the particles forming the solid, and N_s is the number of these particles.

The full Hamiltonian for our system reads now

$$H=F_{\rm kin}\{n,\mathbf{u}\}+F_{\rm pot}^{\rm eff}\{n\}+H_s(\{Q_{\mathbf{J}}\},\{\Pi_{\mathbf{J}}\}) +\delta H\{n,Q_{\mathbf{J}}\} \ , \qquad (2.9)$$

where $F_{\rm pot}^{\rm eff}\{n\}=F_{\rm pot}\{n\}+H_R\{n\}$ is the potential part of the adsorbate free energy with the surface potential included.

The Hamiltonian H, Eq. (2.9), can now be used within the realm of the canonical description of fluid dynamics and the equations of motion for all the dynamical degrees of freedom: $n,\mathbf{u},Q_{\mathbf{J}},\Pi_{\mathbf{J}}$, can be derived by using the Lie-Poisson brackets for these variables.[24]

III. EQUATIONS OF MOTION

The combined fluid adsorbate-solid Hamiltonian, Eq. (2.9), together with the Lie-Poisson brackets for the fields $n(\mathbf{r},t)$ and $\mathbf{u}(\mathbf{r},t)$,[24] listed in the Appendix, and the usual Poisson brackets for the solid elementary-excitation variables,

$$\{Q_{\mathbf{J}},\Pi_{-\mathbf{J}'}\}=\delta_{\mathbf{J},\mathbf{J}'} \ , \qquad (3.1)$$

leads to the following set of equations of motion:

$$\frac{\partial n(\mathbf{r},t)}{\partial t}=\frac{1}{m}\{n(\mathbf{r},t),H\}_{\mathrm{LPB}}\ , \tag{3.2a}$$

$$\frac{\partial \mathbf{u}(\mathbf{r},t)}{\partial t}=\frac{1}{m}\{\mathbf{u}(\mathbf{r},t),H\}_{\mathrm{LPB}}\ , \tag{3.2b}$$

$$\frac{\partial Q_{\mathbf{J}}}{\partial t}=\{Q_{\mathbf{J}},H\}\ , \tag{3.2c}$$

$$\frac{\partial \Pi_{\mathbf{J}}}{\partial t}=\{\Pi_{\mathbf{J}},H\}\ . \tag{3.2d}$$

Equation (3.2a) is the continuity equation for the adsorbate density, Eq. (3.2b) is the Euler equation for the adsorbate flow in the presence of the adsorbate solid interactions, and Eqs. (3.2c) and (3.2d) are the equations of motion for phonons driven by the same interactions. Explicitly we have

$$\frac{\partial n(\mathbf{r},t)}{\partial t}=-\nabla\cdot[n(\mathbf{r},t)\mathbf{u}(\mathbf{r},t)]\ , \tag{3.3}$$

$$\frac{\partial \mathbf{u}(\mathbf{r},t)}{\partial t}=-\mathbf{u}\cdot\nabla\mathbf{u}-\frac{1}{m}\nabla\frac{\delta F^{\mathrm{eff}}_{\mathrm{pot}}\{n\}}{\delta n(\mathbf{r},t)}+\frac{1}{m}\sum_{\mathbf{J}}Q_{\mathbf{J}}\nabla\Psi_{\mathbf{J}}(\mathbf{r})\ , \tag{3.4}$$

$$\ddot{Q}_{\mathbf{J}}=-\omega_{\mathbf{J}}^2Q_{\mathbf{J}}+\int d\mathbf{r}\,n(\mathbf{r},t)\Psi_{-\mathbf{J}}(\mathbf{r})\ . \tag{3.5}$$

Notice that $\delta F^{\mathrm{eff}}_{\mathrm{pot}}/\delta n$ plays the role of the local chemical potential for the adsorbate in perfect agreement with the meaning of the free-energy functional for the inhomogeneous fluid. All the static interactions between the host solid and the adsorbate are already taken care of by that term. The dynamical coupling between both components of the adsorbate-solid system is contained in the last terms at the right-hand side of Eqs. (3.4) and (3.5).

Now, since we are interested in deriving the effective equation of motion for the adsorbate, we formally solve Eq. (3.5) for the solid excitations. We obtain

$$Q_{\mathbf{J}}(t)=Q_{\mathbf{J}}^{\mathrm{hom}}(t)+\int_0^t dt'\int d\mathbf{r}\,\Psi_{-\mathbf{J}}(\mathbf{r})\frac{1}{\omega_{\mathbf{J}}}\sin[\omega_{\mathbf{J}}(t-t')]\times n(\mathbf{r},t')\ , \tag{3.6}$$

where $Q_{\mathbf{J}}^{\mathrm{hom}}(t)$ is the general solution of the homogeneous harmonic-oscillator equation. The resulting equations of motion for the adsorbate are the continuity equation (3.3) and the integro-differential equations for the velocity field obtained by inserting the solution (3.6) into Eq. (3.4):

$$\frac{\partial \mathbf{u}(\mathbf{r},t)}{\partial t}=-\mathbf{u}\cdot\nabla\mathbf{u}-\frac{1}{m}\nabla\frac{\delta F^{\mathrm{eff}}_{\mathrm{pot}}\{n\}}{\delta n(\mathbf{r},t)}+\frac{1}{m}\sum_{\mathbf{J}}Q_{\mathbf{J}}^{\mathrm{hom}}(t)\nabla\Psi_{\mathbf{J}}(\mathbf{r})$$
$$+\frac{1}{m}\sum_{\mathbf{J}}\int_0^t dt'\int d\mathbf{r}'\Psi_{-\mathbf{J}}(\mathbf{r}')\nabla\Psi_{\mathbf{J}}(\mathbf{r})\frac{1}{\omega_{\mathbf{J}}}\sin[\omega_{\mathbf{J}}(t-t')]n(\mathbf{r}',t')\ . \tag{3.7}$$

The third term at the right-hand side of Eq. (3.7) contains the field $Q_{\mathbf{J}}^{\mathrm{hom}}(t)$ which rapidly oscillates on the hydrodynamical time scale. Thus, it averages out on the time scales larger than the inverse of a typical Debye frequency $\propto 10^{-13}$ sec, and therefore it can be neglected in further analysis.

To proceed further we integrate the last term in Eq. (3.7) by parts in time. We obtain three terms which we shall now discuss successively. The term $\propto \cos(\omega_{\mathbf{J}}t)n(\mathbf{r},t=0)$ oscillates in time on the same time scale as $Q_{\mathbf{J}}^{\mathrm{hom}}(t)$ and can be neglected. The second term is

$$\frac{1}{m}\nabla\sum_{\mathbf{J}}\frac{1}{\omega_{\mathbf{J}}^2}\int d\mathbf{r}'\Psi_{\mathbf{J}}(\mathbf{r})\Psi_{-\mathbf{J}}(\mathbf{r}')n(\mathbf{r}',t)\equiv\frac{1}{m}\nabla\int d\mathbf{r}\,K(\mathbf{r},\mathbf{r}')n(\mathbf{r}',t)\ . \tag{3.8}$$

This term can be incorporated into the term containing the potential part of the free-energy functional $F^{\mathrm{eff}}_{\mathrm{pot}}\{n\}$ resulting in

$$\Phi\{n\}=F^{\mathrm{eff}}_{\mathrm{pot}}\{n\}-\tfrac{1}{2}\int d\mathbf{r}\int d\mathbf{r}'n(\mathbf{r},t)K(\mathbf{r},\mathbf{r}')n(\mathbf{r}',t)$$
$$=\int d\mathbf{r}[f_0(n)+n(\mathbf{r},t)U_s(\mathbf{r})]+\tfrac{1}{2}\int d\mathbf{r}\int d\mathbf{r}'n(\mathbf{r},t)[V(\mathbf{r}-\mathbf{r}')-K(\mathbf{r},\mathbf{r}')]n(\mathbf{r}',t)\ , \tag{3.9}$$

with the surface potential $U_s(\mathbf{r})$ defined in Eq. (2.6). In the remaining term the time derivative of the adsorbate density can be eliminated by using the continuity equation. This permits the integration by parts in a position space. The equation of motion, Eq. (3.7), takes then the following form:

$$\frac{\partial \mathbf{u}(\mathbf{r},t)}{\partial t}=-\mathbf{u}\cdot\nabla\mathbf{u}-\frac{1}{m}\nabla\frac{\delta\Phi\{n\}}{\delta n(\mathbf{r},t)}-\frac{1}{m}\int_0^t dt'\int d\mathbf{r}'n(\mathbf{r}',t')\overleftrightarrow{\zeta}(\mathbf{r},\mathbf{r}';t-t')\cdot\mathbf{u}(\mathbf{r}',t')\ , \tag{3.10}$$

with the nonlocal in space and time memorylike kernel given by

$$\overleftrightarrow{\zeta}(\mathbf{r},\mathbf{r}';t-t')=\sum_{\mathbf{J}}\frac{1}{\omega_{\mathbf{J}}^2}\cos[\omega_{\mathbf{J}}(t-t')]\nabla\Psi_{\mathbf{J}}(\mathbf{r})\otimes\nabla'\Psi_{-\mathbf{J}}(\mathbf{r}')$$
$$=\beta\sum_{\mathbf{J}}\langle Q_{\mathbf{J}}(t)Q_{-\mathbf{J}}(t')\rangle\nabla\Psi_{\mathbf{J}}(\mathbf{r})\otimes\nabla'\Psi_{-\mathbf{J}}(\mathbf{r}') \ . \tag{3.11}$$

The second equality in Eq. (3.11) assumes, valid in the harmonic solid approximation, an expression for the displacement correlation function. One expects that this expression will emerge naturally in a more microscopic analysis.

Equation (3.10) is a new equation of motion for the adsorbate fluid which generalizes those used in Refs. 10 and 11. Note that in addition to the usual terms present in the Euler equations of motion for inviscid fluid, it contains a dissipative term $\propto\overleftrightarrow{\zeta}\cdot\mathbf{u}$. If we would like to generalize our fluid description by equipping the adsorbate with its internal shear and bulk viscosities we should now follow Ref. 24 and replace the Lie-Poisson brackets for fluid degrees of freedom with the full metriplectic brackets.[27] It would result in adding to the right-hand side of Eq. (3.10) the usual Navier-Stokes terms, viz., Eqs. (A4)–(A6). Adding these terms is not essential for our further analysis. In the following section we shall discuss the properties of Eq. (3.10).

IV. RESULTS AND DISCUSSION

In addition to a new dissipative term $\propto\overleftrightarrow{\zeta}$ in Eq. (3.10) the seemingly standard term describing Eulerian pressure deserves some attention. Indeed, the functional $\Phi\{n\}$ is a natural extension of the free-energy functional used in the theory of inhomogeneous liquids.[5,8,22] Note that it contains contributions from the internal adsorbate interactions [short-range repulsion and long-range attraction, viz., Eq. (2.3)], static surface potential, Eq. (2.6), and the phonon induced intra-adsorbate interactions described by the kernel $K(\mathbf{r},\mathbf{r}')$ in Eq. (3.9). The presence of the latter term distinguishes our functional $\Phi\{n\}$ from those used in the theory of wetting[5] where the static attraction between the solid wall and the fluid layer is the only one present. Following standard arguments[8(b)] we can now hypothesize that this functional should have the following form:

$$\Phi\{n\}=\frac{1}{\beta}\int d\mathbf{r}\,n(\mathbf{r})[\ln n(\mathbf{r})-1]$$
$$-\frac{1}{\beta}\int d\mathbf{r}\int d\mathbf{r}'n(\mathbf{r})C(\mathbf{r},\mathbf{r}')n(\mathbf{R}') \ , \tag{4.1}$$

where $C(\mathbf{r},\mathbf{r}')$ is the direct correlation function for the adsorbate with *all* the interactions taken into account.[5,8] It might depend functionally on the density profile.

The stationary solution of the adsorbate equations of motion, Eq. (3.10), which determines the static density profile $\bar{n}(\mathbf{r})$ for the adsorbate,

$$\nabla\frac{\delta\Phi\{n\}}{\delta n(\mathbf{r})}=0 \ , \tag{4.2}$$

has the usual form discussed in Refs. 5 and 8. On physical grounds we expect the solution of Eq. (4.2) to vanish everywhere except in a thin layer forming the adsorbate. Along the surface, the equilibrium density is periodic due to the periodic nature of the surface potential and of the phonon induced modification to the two-body interactions in Φ. Being interested in the variations of the adsorbate density over distances much longer than the typical lattice constant of the solid we will assume that the adsorbate is confined to an infinitely thin layer, i.e., that it is effectively two dimensional and that $\mathbf{r}$ is confined to the (x,y) surface plane. Furthermore, one can show that, in the long-wavelength limit, the phonon induced interaction $K(\mathbf{r},\mathbf{r}')$ is translationally invariant, i.e., it depends only on the difference $\mathbf{r}-\mathbf{r}'$. Any corrections to such a form are necessarily short range in nature. Since our main interest in this work is to present a general framework and to show its simple application already leading to interesting results, we will consequently analyze the adsorbate fluctuations in the long-wavelength limit. This implies that the short-range structure in the density profile $\bar{n}(\mathbf{r})$ is not of primary interest. Therefore we assume it to be constant along the solid surface. Should more detailed analysis be required, for example for surfaces of the type studied in Ref. 14, then the exact solution of Eq. (4.2) should be used leading to convolution-type rather than algebraic equations for the adsorbate density and velocity fluctuations.

It is perhaps less interesting to note that the form Eq. (3.9) of the functional Φ can also be obtained by performing a canonical, polaronlike, transformation of the original degrees of freedom in the Hamiltonian, Eq. (2.9),

$$Q_{\mathbf{J}}\Longrightarrow Q_{\mathbf{J}}'=Q_{\mathbf{J}}-\frac{1}{\omega_{\mathbf{J}}^2}\int d\mathbf{r}\,\Psi_{-\mathbf{J}}(\mathbf{r})n(\mathbf{r},t) \ , \tag{4.3}$$

with the remaining degrees of freedom unchanged. This transformation decouples the adsorbate Hamiltonian from that of the solid [i.e., the term δH disappears from Eq. (2.9)] at the expense of the modification of the original functional $F_{\mathrm{pot}}^{\mathrm{eff}}$ to the form given in Eq. (3.9) and a change in the Lie-Poisson brackets between the solid variables and the hydrodynamical fields. All the dynamics of the system is now "hidden" in the Lie-Poisson brackets. This is a fairly typical situation in generalized Hamiltonian dynamics.[27]

We shall now follow the usual procedure and derive the expression for the time-dependent density correlation function using Eq. (3.10). We restrict ourselves here to the linear analysis. Higher-order corrections can be analyzed following standard procedure.

In the following discussion of the equilibrium density profile for the adsorbate we will assume from now on that Eq. (3.10) holds effectively in two dimensions. Linearizing now Eq. (3.10) and the continuity equation around $\bar{n}(\mathbf{r})=\bar{n}=\text{const}$ we obtain

$$\begin{aligned}\frac{\partial \mathbf{u}(\mathbf{r},t)}{\partial t}&=-\frac{1}{m}\nabla\frac{\delta^2\Phi\{n\}}{\delta\bar{n}^2}\delta n(\mathbf{r},t)-\frac{\bar{n}}{m}\int_0^t dt'\int d\mathbf{r}'\overleftrightarrow{\zeta}(\mathbf{r},\mathbf{r}';t-t')\cdot\mathbf{u}(\mathbf{r}',t')\ ,\\ \frac{\partial\delta n(\mathbf{r},t)}{\partial t}&=-\bar{n}\nabla\cdot\mathbf{u}(\mathbf{r},t)\ .\end{aligned}\tag{4.4}$$

Note that $\delta^2\Phi/\delta\bar{n}^2$ is the differential operator which depends on the details of the free-energy functional, Eq. (4.1). The memory kernel $\overleftrightarrow{\zeta}(\mathbf{r},\mathbf{r}';t)$ depends, in general, on the details of the surface lattice structure via the coupling functions $\Psi_{\mathbf{J}}(\mathbf{r})$, viz., Eq. (2.8) and (3.11). Applying the arguments identical to those used in the discussion of $K(\mathbf{r},\mathbf{r}')$ we can assume that the kernel $\overleftrightarrow{\zeta}(\mathbf{r},\mathbf{r}';t)=\overleftrightarrow{\zeta}(\mathbf{r}-\mathbf{r}';t)$. This approximation is certainly inadequate for models of the surface migration discussed in Ref. 14 in which several inequivalent adsorption sites per surface unit cell were present. In these models, short-range correlations are clearly of importance and they will show up in the present model in the kernels $K(\mathbf{r},\mathbf{r}')$ and $\overleftrightarrow{\zeta}(\mathbf{r},\mathbf{r}';t)$. We can now perform the Laplace (in time) and Fourier (in position space) transform of Eq. (4.4) to get

$$\begin{aligned}&\left[-iz\tilde{\mathbf{u}}(\mathbf{k},z)+\frac{\bar{n}}{m}\overleftrightarrow{\zeta}(\mathbf{k},z)\cdot\tilde{\mathbf{u}}(\mathbf{k},z)\right]=\frac{i}{m}\mathbf{k}R(\mathbf{k})\delta\tilde{n}(\mathbf{k},z)+\mathbf{u}(\mathbf{k},\ t=0),\\ &-iz\ \delta\tilde{n}(\mathbf{k},z)-i\bar{n}\mathbf{k}\cdot\tilde{\mathbf{u}}(\mathbf{k},z)=\delta n(\mathbf{k},t=0)\ ,\end{aligned}\tag{4.5}$$

where the function $R(\mathbf{k})$ is the Fourier transform of $\delta^2\Phi/\delta\bar{n}^2$. We derive the expression for the Laplace transform of the density correlation function $\tilde{C}(k,t)=\langle\delta n(-\mathbf{k},t)\delta n(\mathbf{k},0)\rangle$ by eliminating from Eqs. (4.5) the velocity field. We obtain

$$\tilde{C}(\mathbf{k},z)=\left[-iz+\frac{\bar{n}}{m}R(\mathbf{k})\mathbf{k}\cdot\left[-iz\overleftrightarrow{\mathrm{I}}+\frac{\bar{n}}{m}\overleftrightarrow{\zeta}(\mathbf{k},z)\right]^{-1}\cdot\mathbf{k}\right]^{-1}C(\mathbf{k},t=0)\ .\tag{4.6}$$

For solid surfaces with sufficiently high point symmetry (triangular, hexagonal, or quadratic lattices) the tensor $\overleftrightarrow{\zeta}$ is isotropic, $\overleftrightarrow{\zeta}(\mathbf{k},z)=\zeta(|\mathbf{k}|,z)\overleftrightarrow{\mathrm{I}}$, and Eq. (4.6) simplifies to

$$\tilde{C}(|\mathbf{k}|,z)=\left[-iz+\frac{\frac{\bar{n}}{m}R(|\mathbf{k}|)\mathbf{k}^2}{-iz+\frac{\bar{n}}{m}\zeta(|\mathbf{k}|,z)}\right]^{-1}\times C(|k|,\ t=0)\ .\tag{4.7}$$

In the case of no interaction between the host solid and the adsorbate $\zeta(k,z)=0$ and we recover from Eq. (4.7) the usual expression for the density correlation function for inviscid fluid. The dispersion relation for excitations in the fluid [determined by the pole of the denominator in Eq. (4.7)] is given then by the Bogoliubov-like expression

$$\omega^2(|\mathbf{k}|)=\frac{\bar{n}}{m}R(|\mathbf{k}|)|\mathbf{k}|^2\ ,\tag{4.8}$$

in which $R(|\mathbf{k}|)$ plays the role of the Fourier transform of the interparticle potential. This is in agreement with Eq. (4.1), and the asymptotic behavior of the direct correlation function $[\lim_{|\mathbf{r}|\to\infty}C(|\mathbf{r}|)=-\beta V|\mathbf{r}|)]$. In case of the interacting adsorbate-solid system ζ does not vanish and we expect that the poles of the correlation function, Eq. (4.7) behave as $z\propto|\mathbf{k}|^2$. Thus in the long-wavelength limit, the dispersion relation for the excitations is given by the equation

$$-iz+\frac{R(|\mathbf{k}|)}{\zeta(|\mathbf{k}|,0)}|\mathbf{k}|^2=0\tag{4.9}$$

describing diffusivelike decay of the density fluctuations. By inspection of Eq. (4.9) we can identify

$$\lim_{|\mathbf{k}|\to 0}\left[\frac{R(|\mathbf{k}|)}{\zeta(|\mathbf{k}|,0)}\right]=D\tag{4.10}$$

with the diffusion coefficient in the adsorbate.

Comparing now Eq. (4.10) with the standard definition of the diffusion coefficient in the theory of mixtures, $D=\kappa\partial\mu/\partial c$, where c, μ, and κ are the concentration of a given specie in the mixture, its chemical potential, and the particle mobility, respectively, we find that the inverse of ζ is just a generalization of the particle mobility for our strongly interacting system. Furthermore, notice that the derivative of the chemical potential is replaced in our analysis by the functional derivative of the potential Φ which contains all the information about the intra-adsorbate correlations. If one uses the expression for the free-energy functional Φ in which short-range, hard-core, repulsive interactions of the adsorbate particles are taken into account, then one accounts already for the effects due to the blocking factors, discussed in the lattice-gas approach to surface diffusion.[12,19,20] Note also that the kernels $K(\mathbf{r},\mathbf{r}')$ and $\zeta(\mathbf{r},\mathbf{r}';t)$ for $\mathbf{r}=\mathbf{r}'$ are related to the excess free energy for the solid due to the presence of a single adparticle. For more detailed analysis of this point and its relation to the single adparticle migration consult Ref. 15. In a somewhat unphysical limit of our model corresponding to the adsorbate particles interacting only with the host solid and not among themselves (neither directly nor due to the phonon induced effects) the only term remaining in the free-energy functional Φ is its entropic part in Eq. (4.1). Equation (4.10) gives then a simple relation $D=k_BT/(\bar{n}\zeta)$ which is the analog of the Stokes-Einstein relation.[9] We emphasize again that our expression for the adsorbate diffusion coefficient, Eq. (4.10), indicates a complex interplay between the single-particle effects, embodied in the $\overleftrightarrow{\zeta}$ and the collective effects contained in $R(|\mathbf{k}|)$. Indeed, Eq. (4.10) should be compared and contrasted with the usual parametrization of the diffusion coefficient $D=D_0\exp(-\beta\Delta U)$, where ΔU is conventionally referred to as the activation energy barrier for diffusion and the prefactor D_0 is rather poorly understood at the microscopic level. One can now identify the prefactor $D_0=k_BT/[\bar{n}\zeta(0)]$ and the activation energy $\Delta U=-k_BT\ln[\bar{n}R(0)/k_BT]$, a result compatible with Eq. (4.1).

The generalized inverse mobility $\zeta(|\mathbf{k}|,0)$ should be an analytic function of the wave vector even in dense adsorbates in which a variety of gas-liquid-like phase transformations are expected.[20,28] In such a case we expect $\zeta(|\mathbf{k}|,0)\approx\zeta_0-\zeta_2|k|^2+\cdots$. Inspecting Eq. (4.9) and its straightforward generalization for the case of viscous adsorbate we find that ζ_2 adds to the adsorbate bulk viscosity.

The model presented above permits one to clarify the meaning of the inverse mobility coefficient ζ as introduced in Refs. 10 and 11, and offers a convenient starting point for its further more microscopic analysis. Work along that line is in progress. For example, one can immediately find a close relationship between ζ and the friction coefficient discussed within the memory-function formulation by Wahnström.[17] Indeed, inserting Eq. (2.8) into the definition of the $\overleftrightarrow{\zeta}$, Eq. (3.11), we find

$$\overleftrightarrow{\zeta}(\mathbf{r},\mathbf{r}';t)=\frac{\beta}{MN_s}\sum_{\mathbf{q},\lambda}\sum_{s,s'}\exp[i\mathbf{q}\cdot(\mathbf{R}_s^0-\mathbf{R}_{s'}^0)]\langle Q_{\mathbf{q}\lambda}(t)Q_{-\mathbf{q}\lambda}(0)\rangle(\mathbf{e}_{\mathbf{q}\lambda}\cdot\nabla)\nabla W(\mathbf{r}-\mathbf{R}_s^0)\otimes(\mathbf{e}_{-\mathbf{q}\lambda}\cdot\nabla')\nabla' W(\mathbf{r}'-\mathbf{R}_{s'}^0) \tag{4.11}$$

in agreement with the expression given in Ref. 17. Note that our linearized analysis of the dynamic correlation function $\tilde{C}(\mathbf{k},z)$ can be improved by resorting to the mode-mode-coupling-like analysis. In such a case, the inverse mobility ζ, as well as all other transport coefficients, will become renormalized by the modes interaction and the mobility will no longer contain only the single adsorbate particle–host-solid interactions.

Before closing this section we would like to present a few comments on a possible generalization of our hydrodynamic approach. One of the most intriguing points in the theory of the adsorbate diffusion is its interrelation with other nonequilibrium phenomena on the solid surface, for example desorption. It was shown in Refs. 10 and 11 how this aspect can be included in the hydrodynamic description of the adsorbate. In Ref. 14 a simple master equation model was proposed which permits for a rather detailed analysis of how single-particle, hopping-like, diffusion on simple and complex surface lattices couples to desorption. Here, we would like to show that desorption can be built into our model without essential changes, at least at a simple phenomenological level. Indeed, if desorption occurs at the rate α, then the surface coverage decays in time as $\propto\exp(-\alpha t)$. One can include this fact into our description by adding to the right-hand side of the continuity equation, Eq. (3.3), the sink term

$$\frac{\partial n(\mathbf{r},t)}{\partial t}=-\nabla\cdot n(\mathbf{r},t)\mathbf{u}(\mathbf{r},t)-\alpha[n(\mathbf{r},t)-n_0]\ , \tag{4.12}$$

where αn_0 is proportional to the sticking coefficient.[3,23] Since each of the desorbing particles carries away not only its mass but also the transverse (along the surface) momentum which it had before the act of desorption, we have to supplement the kinematic term in Eq. (3.4) with the damping term equal to $-\alpha\mathbf{u}(\mathbf{r},t)$. Following then the same analysis as that leading to Eq. (3.11), but using the modified continuity equation, Eq. (4.12), we obtain the additional terms in Eq. (3.10) equal to

$$-\alpha\mathbf{u}(\mathbf{r},t)+\frac{\alpha}{m}\int dt'\int d\mathbf{r}'K_d(\mathbf{r},\mathbf{r}';t-t')\nabla' n(\mathbf{r}',t')\ . \tag{4.13}$$

The expression for the kernel $K_d(\mathbf{r},\mathbf{r}';t)$ is similar to that in Eq. (3.11). This additional term in the hydrodynamic equation of motion for the adsorbate describes the coupling desorption and the adsorbate fluctuations. It affects both diffusive and propagating modes in the adsorbate. Making the same approximations as those in Sec. IV concerning space and time scales on which the adsorbate density changes appreciably, one can show that the term given by Eq. (4.13) renormalizes the coefficient $R(|\mathbf{k}|)$, viz., Eq. (4.5). The presence of this term as well as additional function $-\alpha\mathbf{u}$ leads to occurrence of new propagating modes.[10,11,29]

V. FINAL COMMENTS

In this paper we have proposed a hydrodynamic description of dense adsorbate dynamics which takes interactions with the host solid into account on both static and dynamic levels. Using the generalized density-functional approach and the canonical formulation of the many-body dynamics, we have derived the equation of motion for the fluid adsorbate which contains a friction term relating the adsorbate diffusion to the collective properties of the adsorbate. This term automatically accounts also for blocking factors (much discussed in the literature) due to the hard-core adsorbate particles interactions. Our model permits for the incorporation of desorption phenomena and modifies the existing phenomenological models of diffusion of desorbing adsorbates. Although we have restricted ourselves to the simple case of intra-adsorbate Eulerian (nondissipative) motion, there is no difficulty in writing down the full Navier-Stokes model which produces no essential changes in our conclusions. This modification is, of course, necessary when the issue of divergence of the transport processes is analyzed in two dimensions.[10] We have also observed that the coefficient ζ_2 will then renormalize the bulk viscosity of the adsorbate. We have discussed the model assuming the simplest possible situation in which the discrete translational symmetry of the host solid surface is of no consequence. It should be clear from our presentation that no conceptual changes are required to carry out the generalization to real discrete lattices of adsorption sites.[14] Our model, although aimed at particular adsorbate properties, should also be applicable for the description of the dynamical processes in the wetting layer. In the latter case, the usually discussed dynamical processes pertain to the motion normal to the solid surface, necessary for the dynamical description of the wetting transition.[6,7] For thin layers, just before the transition takes place, the transverse motion will be strongly affected by the friction term discussed in this paper.

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APPENDIX

In this appendix we recapitulate basic facts from the canonical fluid dynamics formulation used in Secs. II and III. Following Ref. 24 we write the Lie-Poisson brackets between the velocity and density fields as

$$\{n(x,t),n(y,t)\}_{\mathrm{LPB}}=0\ , \tag{A1}$$

$$\{n(\mathbf{x},t),u^a(\mathbf{y},t)\}_{\mathrm{LPB}}=-\frac{\partial}{\partial x^a}\delta(\mathbf{x}-\mathbf{y})\ , \tag{A2}$$

$$\{u^a(\mathbf{x},t),u^b(\mathbf{y},t)\}_{\mathrm{LPB}} =\frac{1}{n(\mathbf{x},t)}\epsilon^{abc}(\nabla\times\mathbf{u}(\mathbf{x},t))^c\delta(\mathbf{x}-\mathbf{y})\ , \tag{A3}$$

where ϵ^{abc} is the fully antisymmetric, third-rank Levi-Cività tensor. It is sometimes convenient to combine the density and velocity fields into a four-vector $j^\alpha=(n,u^a)$, where $\alpha=0,1,2,3$. The Lie-Poisson brackets (A1)–(A3) define then the antisymmetric four-by-four matrix kernel $L^{\alpha\beta}(\mathbf{x},\mathbf{y})$. The hydrodynamic Euler equations are then derived from the free energy Eq. (2.1) and have the following form:

$$\frac{\partial j^\alpha(\mathbf{x},t)}{\partial t}=\frac{1}{m}\int d\mathbf{y}\,L^{\alpha\beta}(\mathbf{x},\mathbf{y})\frac{\delta F\{n,\mathbf{u}\}}{\delta j^\beta(\mathbf{y})}\ . \tag{A4}$$

The use of the density and velocity fields is customary in hydrodynamics but the density and the particle current fields can be used as well.[24] The equations of motion are then written in the same form as those in Eq. (A4) but with different kernel $L^{\alpha\beta}(\mathbf{x},\mathbf{y})$.

The Navier-Stokes equation describing the dynamics of viscous fluid can also be derived in a similar fashion by replacing the Lie-Poisson kernel $L^{\alpha\beta}$ with the metriplectic one[24,27] $D^{\alpha\beta}(\mathbf{x},\mathbf{y})=L^{\alpha\beta}(\mathbf{x},\mathbf{y})-D'^{\alpha\beta}(\mathbf{x},\mathbf{y})$ where the kernel $D'^{\alpha\beta}$ has the form

$$D'^{\alpha\beta}=\begin{bmatrix}0 & 0\\ 0 & -\nu^{ab}(\mathbf{x},\mathbf{y})\end{bmatrix}\ , \tag{A5}$$

where

$$\nu^{ab}(\mathbf{x},\mathbf{y})=\frac{1}{mn(\mathbf{x})}\left[(\eta_v+\eta/3)\frac{\partial^2}{\partial x^a\partial x^b}+\eta\delta^{ab}\nabla_x^2\right]\times\delta(\mathbf{x}-\mathbf{y})\ , \tag{A6}$$

with η and η_v being shear and bulk viscosities, respectively.

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[1] *Structure and Dynamics of Surfaces I,* edited by W. Schommers and P. von Blanckenhagen, Topics in Current Physics Vol. 41 (Springer-Verlag, Berlin, 1986); *Structure and Dynamics of Surfaces II,* edited by W. Schommers and P. von Blanckenhagen, Topics in Current Physics Vol. 43 (Springer-Verlag, Berlin, 1987).

[2] *Diffusion at Interfaces: Microscopic Concepts,* edited by M. Grunze, H. J. Kreuzer, and J. J. Weimer, Springer Series in Surface Sciences Vol. 12 (Springer-Verlag, Berlin, 1988).

[3] A. Zangwill, *Physics at Surfaces* (Cambridge University Press, Cambridge, 1988).

[4] S. Dietrich, in *Phase Transitions and Critical Phenomena,* edited by C. Domb and J. L. Lebowitz (Academic, London, 1988), Vol. 12, p. 1; M. Schick, in *Liquids at Interfaces,* Les Houches Summer School Lectures, Session XLVIII, edited by J. Charvolin, J. F. Joanny, and J. Zinn-Justin (Elsevier, Amsterdam, 1990).

[5] T. F. Meister and D. M. Kroll, Phys. Rev. A **31**, 4055 (1985); S. Dietrich and M. Napiórkowski, *ibid.* **43**, 1861 (1991).

[6] A. Łusakowski and Ł. A. Turski, Phys. Lett. A **127**, 188 (1988); A. Łusakowski, Ph.D. thesis, Polish Academy of Sciences, Warsaw, 1989.

[7] R. Lipovsky, Phys. Rev. B **32**, 1731 (1985).

[8] (a) R. Evans, Adv. Phys. **28**, 143 (1979); (b) J. K. Percus, J. Stat. Phys. **52**, 1157 (1988).

[9] J. P. Boon and S. Yip, *Molecular Hydrodynamics* (McGraw-Hill, New York, 1980), p. 128.

[10] S. Ramaswamy and G. F. Mazenko, Phys. Rev. A **26**, 1735 (1982).

[11] Ł. A. Turski, Phys. Rev. A **28**, 2548 (1983).

[12] H. J. Kreuzer, Surf. Sci. **231**, 213 (1990); H. J. Kreuzer, J. Chem. Soc. Faraday Trans. **86**, 1299 (1990).

[13] Y. Saito and H. Müller-Krumbhaar, J. Chem. Phys. **70**, 1078 (1979); H. K. McDowell and J. D. Doll, Surf. Sci. **121**, L537 (1982).

[14] Z. W. Gortel and Ł. A. Turski, Phys. Rev. B **43**, 4598 (1991).

[15] J. R. Banavar, M. H. Cohen, and R. Gomer, Surf. Sci. **107**,

113 (1981).

[16] R. Ferrando, R. Spadacini, and G. E. Tommei, Physica A **173**, 141 (1991); R. Ferrando, R. Spadacini, and G. E. Tommei, Surf. Sci. **251/252**, 773 (1991).

[17] G. Wahnström, Surf. Sci. **159**, 311 (1985); J. Chem. Phys. **84**, 5931 (1986); Phys. Rev. B **33**, 1020 (1986); in *Interaction of Atoms and Molecules with Solid Surfaces,* edited by V. Bortolani, N. H. March, and M. P. Tosi (Plenum, New York, 1990).

[18] S. C. Ying, Phys. Rev. B **41**, 7068 (1990); T. Ala-Nissila and S. C. Ying, *ibid.* **42**, 10 264 (1990).

[19] D. J. W. Geldart, H. J. Kreuzer, and F. Rys, Surf. Sci. **176**, 284 (1985); H. J. Kreuzer and Jun Zhang, Appl. Phys. A **51**, 183 (1990).

[20] M. A. Zaluska-Kotur, Ph.D. thesis, Polish Academy of Sciences, Warsaw, 1991.

[21] The situation here is quite analogous to what we know from phase-transformation physics. The Ising model does not have intrinsic dynamics. Thus its time evolution is described by either Glauber or Kawasaki kinetics which is essentially different from that of models possessing intrinsic dynamics, for example the Heisenberg model.

[22] J. S. Langer and Ł. A. Turski, Phys. Rev. A **8**, 3230 (1973); Ł. A. Turski and J. S. Langer, *ibid.* **22**, 2189 (1980).

[23] H. J. Kreuzer and Z. W. Gortel, *Physisorption Kinetics,* Springer Series Surface Sciences Vol. 1 (Springer-Verlag, Berlin, 1986).

[24] C. P. Enz and Ł. A. Turski, Physica **96A**, 369 (1979).

[25] G. Wahnström, Surf. Sci. **164**, 437 (1985).

[26] H. Ezawa, Ann. Phys. (N.Y.) **67**, 438 (1971).

[27] For a discussion of generalized Hamiltonian dynamics as applied to many-body and to statistical physics problems, cf. P. J. Morrison, Physica D **18**, 410 (1986); Ł. A. Turski, in *Continuous Models of Discrete Systems,* edited by G. A. Maugin (Longman, London, 1991).

[28] A. N. Barker, S. Ostlund, and F. A. Puntam, Phys. Rev. B **17**, 3650 (1978); K. Binder and D. L. Landau, Surf Sci **108**, 503 (1983); M. W. Conner and C. Ebner, Phys. Rev. B **36**, 3683 (1987); M. Wortis, in *Fundamental Problems in Statistical Mechanics VI,* edited by E. G. D. Cohen (North-Holland, Amsterdam, 1985).

[29] Z. W. Gortel and Ł. A. Turski, in *Proceedings of RAMIS 91 Conference,* edited by J. Stankowski (Ossolineum, Poznan, in press).