PHYSICAL REVIEW E **67**, 041602 (2003)

Dynamics of atoms in a condensing cluster

A. ten Bosch*
Laboratoire de Physique de la Matière Condensée, CNRS 6622, Parc Valrose, F-06108 Nice Cedex 2, France

(Received 7 October 2002; published 21 April 2003)

The dynamics of single particles in a cluster on condensation from the supersaturated vapor phase is studied by a kinetic approach. An insight into the distinctive flow field in the vicinity of a cluster is obtained for initial and late stage evolution. Inside the core the single atoms diffuse freely and the initial velocity decays rapidly with time. In the interfacial region between the cluster core and the vapor, the surface pressure produces a directed radial motion and a long time radial drift into the cluster core. Far from the cluster, the atoms move in the vapor state of low density and high diffusion constant. The mean square displacement and the velocity correlation lend support to the results and are compared with recent molecular dynamics simulations on a nucleating argon cluster.

DOI: 10.1103/PhysRevE.67.041602 PACS number(s): 64.60.Qb

I. INTRODUCTION

Many problems in materials science are concerned with time dependent phenomena and flow [1]. Nonequilibrium systems are particularly challenging and of great practical interest as the path to fabricate a nanosystem often passes through a phase transition [2]. Single particle dynamics plays a decisive role in the dynamics of a phase transition, and the theoretical framework must be derived from atomic scale behavior and describes the evolution of microstructure on appropriate time and length scales, establishing a connection to the corresponding macroscopic properties. A model independent analytical approach can rapidly explore parameter space and yield results for spatial dynamic averages [3]. It is complementary to a numerical simulation, which produces a detailed picture of atomic processes [4–8]. Each approach involves a series of assumptions that can be tested by a comparative analysis. Much work, theoretical as well as experimental, has been expended in achieving a better comprehension of the dynamics involved [9–14].

The model case studied here is the aggregation of atoms during condensation in the supersaturated vapor. During a first-order phase transition, such as condensation, the metastable vapor develops into the stable liquid phase by nucleation and growth processes. Atoms diffuse and combine into aggregates of different sizes, which can subsequently grow by incorporating other atoms, or shrink as atoms, are lost from the surface. In the vicinity of the cluster surface, atoms arrive from the vapor and penetrate into the liquid core; inside the cluster, atoms diffuse and eventually reach the surface, and are ejected into the vapor.

The (p,T) ensemble has been used to study the single atom dynamics during condensation from the vapor of a Lennard Jones cluster [15]. It was shown by the molecular dynamics simulation that three distinct regions occur for the dynamics of single atoms, which differ inside the cluster, in the interfacial region and in the vapor phase. Far from the cluster, the atoms move in the vapor state of low density and high diffusion constant. Inside the cluster, the density is constant, close to the liquid value at the density and pressure of coexistence. The atomic paths are typical of diffusive motion with a tendency to drift towards the center and remain there. The mean square displacement is linear in time and the diffusion constant is close to the bulk liquid value at the same temperature. The velocity correlation decays rapidly and vanishes after less than one time step. A striking difference in the dynamics is found if the motion is restricted to the interfacial region where the density decays towards the vapor. The motion is no longer diffusive, the atomic paths are smoother, and the circular trajectories can be observed. The single atom dynamics are indicative of directed motion near the cluster surface and cannot be described by simple free diffusion. The mean square displacement is a nonlinear function of time, velocity correlation occurs over a long time scale and can be fit to exponential decay with a long and a short characteristic time.

In order to understand the fundamental basis of the observations and to compare with the results of Ref. [15], the short and long time dynamics of particles are calculated in a nonequilibrium cluster by using the kinetic approach.

II. KINETIC APPROACH

As in molecular dynamics simulations, it is possible to pass from an atomistic picture of a single atom path to a system averaged mesoscopic analysis. In a stochastic system, the single particle motion is not deterministic but can follow many possible paths. An appropriate average over physically possible paths defines the probability $G(\vec{R},\vec{R}_0,\vec{v},\vec{v}_0,t)$ to find a particle that started at $\vec{R}_0$ with velocity $\vec{v}_0$ at position $\vec{R}$ with velocity $\vec{v}$ after a time t. In the case of continuous Markov processes subject to frequent small changes, a kinetic equation for G is obtained [16,17]. Calculation of the solution of the seven-dimensional equation for G has been possible only in a few simple cases. As was discussed in Ref. [16], by the calculation of the moments $\langle \vec{v}\vec{v}\cdots\rangle$ of G for a fixed initial position and velocity, the time and length involved in the atomistic probability are increased to an experimentally more accessible scale. A set of differential equations for the moments of G is found by the multiplication of the kinetic equation by the nth rank tensor $\vec{v}\vec{v}\vec{v}\vec{v}\cdots\vec{v}$ and

---

*Email address: tenbosch@unice.fr

integration in momentum space with the condition that the surface terms in momentum space vanish for $\vec{v}\to\infty$. A set of coupled differential equations, similar to hydrodynamics and physically intuitive, is obtained for probability density $f(\vec{R},t)=\langle 1\rangle$, the average velocity $j(\vec{R},t)=\langle\vec{v}\rangle$, the kinetic tensor $T(\vec{R},t)=\langle\vec{v}\vec{v}\rangle$, and so on. As will be shown, the moments can be calculated and used to characterize the dynamics of the particles of the cluster.

The differential equations become a set of linear equations by the Fourier transformation. The method of solution of Ref. [18] can be applied close to initiation $t\to 0$ and after a long time relative to a characteristic decay time c^{-1}. For $ct\ll 1$ and $ct\gg 1$, the solution is simply of the form $e^{\omega t}$ and the relaxation times ω are found from the condition of vanishing determinant of the linear system. A complete solution is the linear combination of the solutions for each eigenfrequency and is completely determined by the initial conditions. The boundary condition at the cluster surface $R=a$ yields terms of order $\ll 1$ for sufficiently large clusters. In Ref. [15], the diffusive step was much shorter than the radius of the cluster for the times considered and the size effects related to the cluster radius are neglected.

The dynamics of atoms will be studied, which starts with a given velocity at the center of the cluster and moves towards the surface, or which starts on the cluster surface and moves within the interface between the condensed cluster and the supersaturated vapor. The system is expected to rapidly achieve thermal equilibrium and constant temperature T. Close to the cluster surface, a chemical potential gradient must be considered due to the change in density from the condensed phase (n_L) to the vapor (n_0) and decrease in the local interaction energy. The resulting local field $u(\vec{R})$ is the energy of an atom at a given point $\vec{R}$ due to all other atoms of the system.

III. CLASSICAL KINETIC MODEL

The calculations are described in Sec. III A and the results are given inside the cluster core in Sec. III B and in the interfacial region in Sec. III C. The resulting dynamic behavior is also related to the position and velocity correlation functions (Sec. III D).

A. Fokker-Planck equation

The classical description of the phase space dynamics follows the well-known differential equation, usually called the Fokker-Planck (FP) equation:

$$\frac{\partial G}{\partial t}=\frac{\xi}{m}\left[3G+\frac{kT}{m}\frac{\partial}{\partial\vec{v}}\frac{\partial}{\partial\vec{v}}G+\vec{v}\cdot\frac{\partial}{\partial\vec{v}}G\right]-\vec{v}\cdot\left[\frac{\partial}{\partial\vec{R}}G\right]+\frac{1}{m}\frac{\partial u}{\partial\vec{R}}\cdot\frac{\partial}{\partial\vec{v}}G.$$

As discussed in Ref. [16], the truncated linear equations for the first three moments are

$$\frac{\partial f}{\partial t}=-\frac{\partial}{\partial\vec{R}}\cdot\vec{j},\tag{1a}$$

$$\frac{\partial\vec{j}}{\partial t}=-\frac{\xi}{m}\vec{j}-\frac{\partial}{\partial\vec{R}}\hat{T}-\frac{f}{m}\cdot\frac{\partial}{\partial\vec{R}}u,\tag{1b}$$

$$\frac{\partial\hat{T}}{\partial t}=-\frac{2\xi}{m}\hat{T}+\frac{2\xi kT}{m^2}f\hat{E}-\frac{\vec{j}}{m}\frac{d}{d\vec{R}}u.\tag{1c}$$

The friction coefficient ξ also controls the diffusion in position through the Einstein relation. The particle mass is m. Each higher moment decays to the stationary solution with a faster relaxation time than the moment before. The infinite hierarchy is truncated if the viscosity terms contained in the energy flux tensor $\langle\vec{v}\vec{v}\vec{v}\rangle$ are not considered. $\hat{E}$ is the unit tensor. The probability density $f(\vec{R},t)$ is the probability of finding a particle that started at $\vec{R}_0$ at point $\vec{R}$ after a time t. The flux $\vec{j}(\vec{R},t)=f(\vec{R},t)\vec{v}(\vec{R},t)$ measures the average velocity $\vec{v}(\vec{R},t)$ of the particle at that point. The kinetic tensor $\hat{T}(\vec{R},t)$ is a measure of the local pressure tensor. These quantities depend on the initial condition of the particle. On taking the average of Eqs. (1) in all possible initial positions $\vec{R}_0$ and velocities $\vec{v}_0$, the system average density, average velocity, and pressure tensor are obtained. From Eqs. (1), the stationary solution for the average density $n(\vec{R})$ and kinetic tensor T_{eq} is given by setting all time derivatives equal to zero, which leads to

$$\hat{T}_{\mathrm{eq}}(\vec{R})=n(\vec{R})\frac{kT}{m}\hat{E},$$

$$\frac{\partial}{\partial\vec{R}}n(\vec{R})+n(\vec{R})\frac{\partial}{\partial\vec{R}}\frac{u(\vec{R})}{kT}=0.\tag{2}$$

The first relation follows from Eq. (1c) and the second from Eq. (1b). From Eq. (1a) the average flux vanishes in the equilibrium state. An equilibrium cluster size exists if the pressure difference in the liquid vapor interface is balanced by the surface curvature forces [20], producing a stationary aggregate of constant radius. The time independent solution must correspond to a system of constant chemical potential $(\partial/\partial\vec{R})\mu(\vec{R})=0$ and, using the Gibbs-Duhem relation, constant pressure. As discussed in Ref. [19], the limit of thermodynamic equilibrium thus defines the mean field $u(R)$ in Eq. (2) as the change in the internal energy U if a particle is added or removed at R:

$$u(\vec{R})=\frac{\delta U}{\delta n(\vec{R},t)}=\mu(\vec{R})-kT\ln n(\vec{R}),\tag{3}$$

where $\delta F/\delta n(\vec{R},t)=\mu(\vec{R})$ is the local chemical potential of equilibrium density functional theory [10]. For the equilibrium cluster of radius a_c, the capillary pressure of the curved surface balances the external pressure difference, and the linear approximation yields [21]

$$R<a_c: \quad u(R)=u_L,$$

$$R>a_c: \quad u(R)=u_0-Qe^{-R/l_c}/R$$

where $Q=2\sigma/n_0$. The system parameters are σ, the surface energy; l_c, the density correlation length; and $u_0(u_L)$, the mean field in the bulk vapor (condensed core).

The dynamics will be studied in the following for the almost stationary [8,15,22] cluster of radius $a\approx a_c$ close to the equilibrium value.

B. Inside the core

Inside the core, the density is constant [15] and the force field vanishes. The particles move essentially as free particles in a bulk "liquid" phase. The exact solution for the field free FP equation is known [16,17] and the moments can be calculated. In order to test the alternative approach described above, Eqs. (1) are solved directly by the three-dimensional Fourier transformation $y_{\tilde{q}}=\int d\vec{R}e^{2\pi i\vec{q}\vec{R}}y(\vec{R})$, yielding

$$\frac{\partial f_q}{\partial t}=2\pi i\vec{q}\vec{j}_q,$$

$$\frac{\partial \vec{j}_q}{\partial t}=-\frac{\xi}{m}\vec{j}_q+2\pi i\vec{q}\hat{T}_q, \tag{4}$$

$$\frac{\partial \hat{T}_q}{\partial t}=-\frac{2\xi}{m}\hat{T}_q+\frac{2kT\xi}{m^2}f_q\hat{E}.$$

The solution of the equation for the kinetic tensor is given by an adiabatic approximation:

$$\hat{T}_q=\frac{kT}{m}f_q+f_q\left(\vec{v}_0\vec{v}_0-\frac{kT}{m}\right)e^{-2ct}=\hat{F}f_q. \tag{5}$$

This approximation for the dynamics of the kinetic tensor is valid, since the time decay for the flux is more rapid than that of the density. The dynamics of the atoms can be studied relative to the time scale $c^{-1}=m/\xi$. The kinetic tensor is independent of time for $ct\ll 1$ and $ct\gg 1$, the solution is simply of the form $e^{\omega t}$ and the corresponding solutions for each ω are calculated from the system of equations by use of the initial conditions for the probability, the average velocity, and the kinetic tensor at $t=0$. The particle starts from the center of the cluster with a given velocity and $f_q=1$, $\overline{j_q}=\vec{v}_0$, $\hat{T}_q=\vec{v}_0\vec{v}_0$. For $\xi t/m\ll 1$, the probability distribution remains sharply localized around the initial position at the center of the cluster and shows slow broadening through velocity mediated motion:

$$f(\vec{R},t)=\left[\frac{3m^2}{2kT\xi t\pi}\right]^{3/2}$$
$$\times\exp\left[-\frac{3m^2}{2kT\xi t}\left(\frac{\vec{R}}{t}-\vec{v}_0\right)^2\right]\xrightarrow[t\to 0]{}\frac{1}{t^3}\delta\left(\frac{\vec{R}}{t}-\vec{v}_0\right).$$

The flux is determined by the initial velocity flow:

$$\vec{j}_q=f_q\vec{v}_0e^{-(\xi t/m)}.$$

For $\xi t/m\gg 1$, the pressure tensor dominates. The probability is diffusive:

$$f(\vec{R},t)=\left[\frac{1}{4\pi Dt}\right]^{3/2}\exp\left[-\frac{\vec{R}^2}{4Dt}\right],$$

with effective diffusion constant $D=kT/\xi$. A late stage probability flux is found to be

$$\vec{j}(\vec{R},t)=-\frac{kT}{\xi}\frac{d}{d\vec{R}}f(\vec{R},t),$$

which acts as a drift velocity away from the areas of large density.

C. In the interfacial region

In the narrow region close to the cluster surface $R\approx a$ and $1/R\approx 1/a$ and to the lowest order in $1/a$, the internal field gradient is approximated by a constant force within the narrow interfacial zone as given by $skT=du(R)/dR\approx Qe^{-a/l_c}/a^2$. A constant gradient approximation is required for an analytical solution within the core and may overestimate the spatial decay of the probability density and the flux. It can be justified by the effective field term, which, as seen in Eq. (1b), is multiplied by the rapid decay of the probability to find a particle at a point beyond the cluster surface at which it started. Equations (1) for the moments can be solved by the one-dimensional Fourier transformation $y(q)=\int d\,\mathrm{R}e^{2\pi iqR}y(R)$ of the coefficients of the expansion in spherical harmonics:

$$f(\vec{R},t)=\sum_{L,M}b_{LM}(R,t)Y_{LM}(\varphi,\theta),$$

$$\vec{j}(\vec{R},t)=\sum_{L,M}\vec{a}_{LM}(R,t)Y_{LM}(\varphi,\theta),$$

$$\hat{T}(\vec{R},t)=\sum_{L,M}\hat{u}_{LM}(R,t)Y_{LM}(\varphi,\theta).$$

The set of linear equations is

$$\begin{aligned}\frac{\partial b_L(q)}{\partial t}&=2\pi iq\sum_{L'}\vec{z}_{LL'}\vec{a}_{L'}(q),\\ \frac{\partial \vec{a}_L(q)}{\partial t}&=-\frac{\xi}{m}\vec{a}_L(q)\\ &\quad+\sum_{L'}\vec{z}_{LL'}\left(2\pi iq\hat{u}_{L'}(q)-\frac{skT}{m}b_{L'}(q)\right),\end{aligned} \tag{6}$$

$$\frac{\partial \hat{u}_L(q)}{\partial t} = -\frac{2\xi}{m}\hat{u}_L(q) + \frac{2\xi}{m^2}kTb_L(q)\hat{E} - \frac{skT}{m}\sum_{L'} \vec{z}_{LL'}\vec{a}_{L'}(q).$$

The z axis is chosen in the direction of the initial position vector $\vec{R}_0$ and only the $M=0$ components are retained for simplicity. Coupling between coefficients of different angular momentum now occurs due to the local field:

$$\vec{z}_{LL'} = \int d\varphi \sin\theta\, d\theta\, Y_{L0}(\varphi,\theta) Y_{L'0}(\varphi,\theta)\vec{e}_R,$$

where the basis vectors in the local polar coordinate system $\vec{e}_R$, $\vec{e}_\varphi$, and $\vec{e}_\theta$ are introduced. The kinetic tensor is again given by Eq. (5) with more rapid decay of the flux than the density and $\hat{u}_L = \hat{F}b_L$. The remaining equations are solved, using the expansion in two harmonics, $L=0$, 1, to illustrate the main results. In order to study flow along the radial and circular directions define $a_L = \vec{a}_L\cdot\vec{e}_z$, the current along the initial radial direction, and $\vec{a}_L\times\vec{e}_z$, the current in the circular direction around the cluster. The circular flux $\vec{j}\times\vec{q}$ follows a field free equation and decays rapidly:

$$\vec{a}_L\times\vec{e}_z = \vec{v}_0\times\vec{e}_z e^{-\xi t/m}.$$

The remaining set of four equations for a_0, a_1, b_0, b_1 can be solved in the method used inside the cluster in the limits $ct<1$ and $ct>1$ and the four frequencies are found from the condition of vanishing determinant. The initial conditions are a fixed initial position on the cluster surface and a fixed initial velocity:

$$a_0 = \vec{v}_0\cdot\vec{e}_z\frac{e^{2\pi iqa}}{a^2} = a_1, \quad b_0 = \frac{e^{2\pi isa}}{a^2} = b_1.$$

For $\xi t/m \ll 1$, the probability density and the flux are the same as inside the cluster with a tendency to linger at the initial position. For $\xi t/m \gg 1$, the coupling terms cannot be neglected. The result for the probability density is

$$f(\vec{R},t)a^2 = \left[1 - \frac{m}{3\xi}\vec{v}_0\cdot\vec{e}_z\frac{d}{dR}\right]\left[\frac{3}{4\pi Dt}\right]^{1/2} \times\exp\left[-\frac{3\left(R-a+st\frac{D}{3}\right)^2}{4Dt}\right][Y_{00}+Y_{10}(\theta)]$$

and for the flux

$$\vec{j}(\vec{R},t)\cdot\vec{e}_z a^2 = -\frac{D}{3}\left(\frac{\partial}{\partial R}+s\right)\left[\frac{3}{4\pi Dt}\right]^{1/2} \times\exp\left[-\frac{3\left(R-a+st\frac{D}{3}\right)^2}{4Dt}\right][Y_{00}+Y_{10}(\theta)].$$

The probability is diffusive with a shift into the cluster with time and a late stage contribution to the average velocity field from the radial surface pressure field. A tendency to radial symmetry with time is not found.

D. Position and velocity correlation

More information on the dynamics of the atoms follow from the mean square displacement MSD

$$\rho^2_{\mathrm{MSD}} = \int_{\vec{R}_0}^{\vec{R}_f} d\vec{R}\, f(\vec{R},t)(\vec{R}-\vec{R}_0)^2$$

and the velocity correlation

$$\eta^2_{\mathrm{cor}} = \frac{\int_{\vec{R}_0}^{\vec{R}_f} d\vec{R} \int d\vec{v}_0 f(\vec{R},t)\vec{v}_0\vec{v}(\vec{R},t)\exp\left(-\frac{m\vec{v}_0^2}{2kT}\right)}{\int_{\vec{R}_0}^{\vec{R}_f} d\vec{R} \int d\vec{v}_0 f(\vec{R},t=0)\vec{v}_0\vec{v}_0 \exp\left(-\frac{m\vec{v}_0^2}{2kT}\right)} \tag{7}$$

calculated for the initial $\vec{R}_0$ at the center and final $\vec{R}_f$ position at the core surface and for the initial $\vec{R}_0$ at the core surface and final $\vec{R}_f$ position at ∞. Size effects due to the cluster surface at a can be neglected in the range of time studied $(D\tau/a^2 \ll 1)$. Initial behavior and long time behavior are easily calculated. Inside the cluster core after a time m/ξ, FP results in complete loss of velocity correlation and for the MSD a transition from dynamical motion in t^2 to diffusive motion linear in time (also found directly from the FP equation [16]). In the interfacial region, the MSD is nonlinear and, due to the initial velocity, quadratic in time for $ct \ll 1$. The velocity correlation demonstrates a rapid initial exponential decay and a long time exponential with persistence of correlation due to the surface force field.

IV. KINETIC EQUATION WITH CONSTRAINTS

The kinetic equations for a dense fluid are based on an intuitive analysis of the nature of the random processes. The FP equation uses the assumption that the average path follows the classical equation of motion in the force field and, as discussed in Refs. [16,17], may not apply to events happening at times shorter than m/ξ. The present problem provides a unique opportunity to test a fundamental kinetic theory by the confrontation of the results on the dynamics in the cluster.

The proposed model is introduced in Sec. IV A and the results are given inside the cluster core in Sec. IV B and in the interfacial region in Sec. IV C. The resulting dynamic behavior is related to the position and velocity correlation functions (Sec. IV D) and is compared with the FP solution as well as the molecular dynamics simulation.

A. Persistence of velocity

To describe motion in phase space, the model incorporates the idea suggested long ago [23] that single atom paths have a tendency to follow the classical path and show persistence in the direction of velocity [24]. This is often observed in molecular dynamics simulation on liquids and gases. Details of the calculation are given in Ref. [24]. The resulting kinetic equation combines evolution of the probability by diffusion in position as well as in velocity [17,19,25],

$$\frac{\partial G}{\partial t}=\frac{kT}{2c_b}\left[\frac{3m}{kT}G+\frac{\partial}{\partial\vec{v}}\frac{\partial}{\partial\vec{v}}G+\frac{m}{kT}\vec{v}\cdot\frac{\partial}{\partial\vec{v}}G\right]$$
$$-\vec{v}\cdot\left[\left(\frac{\partial}{\partial\vec{R}}\frac{u}{kT}\right)G+\frac{\partial}{\partial\vec{R}}G\right]$$
$$+\frac{kT}{2c_d}\left[\left(\frac{\partial}{\partial\vec{R}}\frac{\partial}{\partial\vec{R}}\frac{u}{kT}\right)G+\frac{\partial}{\partial\vec{R}}\frac{\partial}{\partial\vec{R}}G\right.$$
$$\left.+\left(\frac{\partial}{\partial\vec{R}}\frac{u}{kT}\right)\left(\frac{\partial}{\partial\vec{R}}G\right)\right].$$

As before, the set of differential equations for the moments of G is found. The relevant system of equations for the probability density, the average velocity, and the kinetic tensor are

$$\frac{\partial f}{\partial t}=-\frac{\partial}{\partial\vec{R}}\cdot\vec{j}+\frac{kT}{2c_d}\left[\frac{\partial}{\partial\vec{R}}\cdot\frac{\partial}{\partial\vec{R}}f+\frac{\partial}{\partial\vec{R}}\frac{u}{kT}\cdot\frac{\partial}{\partial\vec{R}}f\right.$$
$$\left.+f\frac{\partial}{\partial\vec{R}}\cdot\frac{\partial}{\partial\vec{R}}\frac{u}{kT}\right],\tag{8a}$$

$$\frac{\partial\vec{j}}{\partial t}=-\frac{m}{2c_b}\vec{j}-\frac{\partial}{\partial\vec{R}}\hat{T}-\hat{T}\cdot\frac{\partial}{\partial\vec{R}}\frac{u}{kT}+\frac{kT}{2c_d}\left[\frac{\partial}{\partial\vec{R}}\cdot\frac{\partial}{\partial\vec{R}}\vec{j}\right.$$
$$\left.+\frac{\partial}{\partial\vec{R}}\frac{u}{kT}\cdot\frac{\partial}{\partial\vec{R}}\vec{j}+\vec{j}\frac{\partial}{\partial\vec{R}}\cdot\frac{\partial}{\partial\vec{R}}\frac{u}{kT}\right],\tag{8b}$$

$$\frac{\partial\hat{T}}{\partial t}=-\frac{m}{c_b}\hat{T}+\frac{kT}{c_b}f\hat{E}.\tag{8c}$$

In Eqs. (8), the square brackets replace the collision terms of an interacting fluid and play an important role in the initial stage of the dynamics. In the effective continuity equation (8a), usually called the Smoluchowski equation in the literature [19] the total variation of the probability is caused by the drift regulated by the entropy gradient $d\ln f/dR$, which tends to disperse the atoms as well as by a field directed term du/dR and includes a possible velocity field of the single particles. The equilibrium solution of Eqs. (8) is again given by Eq. (2), and $u(R)$ must thus be given by Eq. (3).

After an average in all possible initial positions and velocities, the mean velocity field becomes the average particle flux $J(R,t)$ and, using Eq. (3), the dynamic equation for the density is obtained [9]:

$$\frac{\partial n(\vec{R},t)}{\partial t}=-\frac{\partial}{\partial\vec{R}}\cdot\vec{J}(\vec{R},t)+\frac{kT}{2c_d}\left[\frac{\partial}{\partial\vec{R}}\cdot n(\vec{R},t)\frac{\partial}{\partial\vec{R}}\frac{\mu(\vec{R})}{kT}\right].$$

Equation (8c) for the kinetic tensor is as in the FP theory. After averaging initial position and velocity, the tensor rapidly tends to be diagonal and given by the average kinetic energy $kTn(R,t)/m$. The characteristic time is here $1/c=2c_b/m$. Similarly, the probability flux equation (8b) contains the Navier-Stokes terms for the flow field of viscous fluids of constant density. As in Eqs. (1), the viscosity terms that arise from the energy flux tensor will not be considered and the infinite hierarchy is truncated. Using Eq. (3), the dominant terms for the stationary flux in a nonviscous fluid give

$$\frac{m}{2c_b}\vec{J}(\vec{R},t)=-\frac{kT}{m}n(\vec{R},t)\cdot\frac{\partial}{\partial\vec{R}}\frac{\mu}{kT}.$$

On inserting in the equation for the density evolution, the Cahn Hilliard model of nucleation [3] is recovered for times $ct\gg 1$. The same result applies as well to the long time solution of the FP equations (1).

The dynamics near a sufficiently large cluster of radius close to the critical equilibrium value is calculated in the following. The same method and approximations used previously in the FP approach are applied.

B. Dynamics of atoms within the cluster core

Inside the dense core, the density is constant and the mean field is uniform. As in the previous paragraph, the internal field is fully compensated and does not contribute to the motion. This case was calculated previously and revealed different behavior as a function of time relative to a characteristic time [24] $1/c=2c_b/m$. It is reconsidered to test the method. The three-dimensional Fourier transformation of the kinetic equations yields a linear system of first-order differential equations:

$$\frac{\partial f_q}{\partial t}=2\pi i\vec{q}\vec{j}_q+\frac{kT}{2c_d}(2\pi i\vec{q})^2 f_q,$$
$$\frac{\partial\vec{j}_q}{\partial t}=-\frac{m}{2c_b}\vec{j}_q+2\pi i\vec{q}\hat{T}_q+\frac{kT}{2c_d}(2\pi i\vec{q})^2\vec{j}_q,\tag{9}$$
$$\frac{\partial\hat{T}_q}{\partial t}=-\frac{m}{c_b}\hat{T}_q+\frac{kT}{c_b}f_q\hat{E}.$$

In the adiabatic approximation, the solution of the equation for the kinetic tensor is again [as in Eq. (5)]

$$\hat{T}_q=\frac{kT}{m}f_q+f_q\left(\vec{v}_0\vec{v}_0-\frac{kT}{m}\right)e^{-2ct}=\hat{F}f_q.$$

The kinetic tensor is independent of time for $ct\ll 1$ and $ct\gg 1$ and the solution is simply of the form $e^{\omega t}$. The relaxation time ω is found for vanishing determinant of the linear system of equations by use of the initial conditions for the probability, the flux, and the kinetic tensor at $t=0$.

For $ct\ll 1$, $F(t)=\vec{v}_0\vec{v}_0$, the kinetic tensor is dominated by the initial motion and the flux is determined by the initial velocity flow:

$$\vec{j}(\vec{R},t)=f(\vec{R},t)\vec{v}_0 e^{-ct}$$

and the probability density is diffusive:

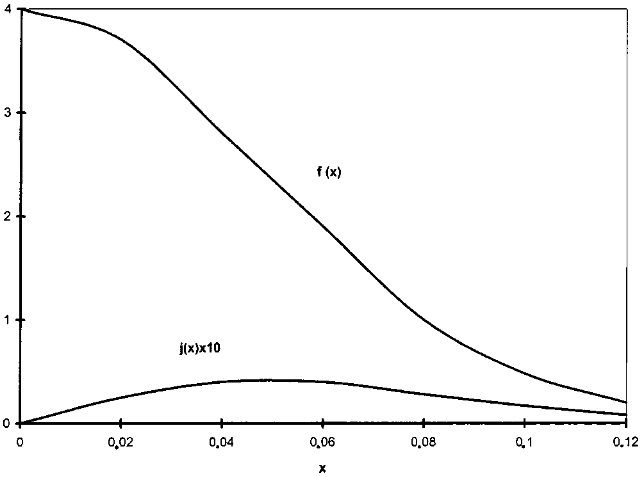

FIG. 1. For the cluster of radius a, the probability distribution f and radial average velocity **j** for the particles that started at the core center and evolved within the cluster core as a function of distance $x=R/a$ to the core at a time $t=4$. The core diffusion coefficient is 8×10^{-3}, the friction decay time $c^{-1}=0.8$, the radius $a=5$. Molecular dynamic units MDU are used ($\tau=4.4\times10^{-13}$ s, $\sigma=3.4\times10^{-8}$ cm: $T=85$ K, kT/m$=3.3\times10^{-2}$, $a=5$, effective surface field as$=12.5$).

$$f(\vec{R},t)=\left[\frac{c_d}{2\pi kTt}\right]^{3/2}\exp\left[-\frac{c_d\vec{R}^2}{2kTt}\right].$$

For $ct\gg1$, the initial motion is lost. The kinetic tensor has spherical symmetry as determined by the equilibrium pressure tensor and the problem can be simplified by studying the flux parallel $\mathbf{j}_\parallel$ and perpendicular to the wave vector $\vec{q}$. Immediately, the perpendicular component is found to follow free motion and

$$\vec{j}\times\vec{q}=\vec{q}\times\vec{v}_0e^{-ct}\exp\left[(2\pi i\vec{q})^2\frac{kTt}{2c_d}\right]\rightarrow0.$$

The remaining vector $\vec{\zeta}=(f,\mathbf{j}_\parallel)$ must fulfill the set of equations $d\vec{\zeta}/dt=\mathcal{M}\vec{\zeta}$ with the tensor

$$\mathcal{M}=\begin{bmatrix} L_q & -2\pi i \\ -2\pi i\vec{q}^2\hat{F} & L_q-c \end{bmatrix}$$

and

$$L_q=\frac{kT}{2c_d}(2\pi i\vec{q})^2.$$

The eigenvalues are easily found from $\det(\mathcal{M}-\omega E)=0$ to be

$$\omega_1=-c+L_q-\frac{(2\pi i)^2}{c}\vec{q}\hat{F}\vec{q},\quad \omega_2=L_q+\frac{(2\pi i)^2}{c}\vec{q}\hat{F}\vec{q}.$$

The results are given in Fig. 1. It is found that the motion proceeds along a radial direction as produced by the radial pressure gradient. The average velocity is caused solely by the need to achieve the equilibrium state of a uniform probability density

$$\vec{j}(\vec{R},t)=-\frac{kT}{mc}\frac{d}{d\vec{R}}f(\vec{R},t).$$

The probability distribution is diffusive as well as flow directed and the long time effective diffusion constant is increased to

$$D=\frac{2kTc_b}{m^2}+\frac{kT}{2c_d}$$

and

$$f(\vec{R},t)=\left(1-\frac{\vec{v}_0}{c}\cdot\frac{d}{d\vec{R}}\right)\left[\frac{1}{4\pi Dt}\right]^{3/2}\exp\left[-\frac{\vec{R}^2}{4Dt}\right].$$

The results of the previous solution of Eqs. (8) are recovered [24]

C. Dynamics of atoms within the interfacial region

Equations (8) for the probability, the flux, and the kinetic tensor can be solved by expansion in the spherical harmonics:

$$f(\vec{R},t)-\sum_{L,M}b_{LM}(R,t)Y_{LM}(\varphi,\theta),$$

$$\vec{j}(\vec{R},t)=\sum_{L,M}\vec{a}_{LM}(R,t)Y_{LM}(\varphi,\theta),$$

$$\hat{T}(\vec{R},t)=\sum_{L,M}\hat{u}_{LM}(R,t)Y_{LM}(\varphi,\theta).$$

The one-dimensional Fourier transformation

$$y(q)=\int d\,\mathrm{R}e^{2\pi iqR}y(R)$$

leads again to a system of first-order differential equations in the coefficients of the expansion:

$$\frac{\partial b_L(q)}{\partial t}=(2\pi iq-s)\sum_{L'}\vec{z}_{LL'}\vec{a}_{L'}(q)+\frac{kT}{2c_d}\left[(2\pi iq)^2-2\pi iq\left(s+\frac{2}{a}\right)-\frac{L(L+1)}{a^2}\right]b_L(q),$$

$$\frac{\partial\vec{a}_L(q)}{\partial t}=-\frac{m}{2c_b}\vec{a}_L(q)+(2\pi iq-s)\sum_{L'}\vec{z}_{LL'}\hat{u}_{L'}(q)+\frac{kT}{2c_d}\left[(2\pi iq)^2-2\pi iq\left(s+\frac{2}{a}\right)-\frac{L(L+1)}{a^2}\right]\vec{a}_L(q),$$

$$\frac{\partial\hat{u}_L(q)}{\partial t}=-\frac{m}{c_b}\hat{u}_L(q)+\frac{kT}{c_b}b_L(q)\hat{E}.\tag{10}$$

The z axis is chosen in the direction of the initial position vector $\vec{R}_0$ and only the $M=0$ components are retained for simplicity. Coupling between coefficients of different angular momentum again occurs due to the local field:

$$\vec{z}_{LL'}=\int d\varphi \sin\theta\, d\theta Y_{L0}(\varphi,\theta)Y_{L'0}(\varphi,\theta)\vec{e}_R .$$

The equation for the kinetic tensor is unchanged and again the linear solution is used, $\hat{u}_L=\hat{F}b_L$, so that

$$\frac{\partial \vec{a}_L(q)}{\partial t}=-\frac{m}{2c_b}\vec{a}_L(q)+(2\pi iq-s)\sum_{L'}\vec{z}_{LL'}\hat{F}b_{L'}(q)+\frac{kT}{2c_d}\left[(2\pi iq)^2-2\pi iq\left(s+\frac{2}{a}\right)-\frac{L(L+1)}{a^2}\right]\vec{a}_L(q). \quad (11)$$

The dynamics is complex, as the coupling between the modes of different L become important but due to the tendency to conserve angular momentum, the modes of $L>0$ decay as

$$\exp\left[-\frac{L(L+1)}{a^2}\right]\frac{kTt}{c_d}$$

and a limited expansion is justified here. To illustrate the case of a two-mode system, $L=0, 1$ is given. With $\vec{a}_L=\vec{a}_L\cdot\vec{e}_z$, the current along the initial radial direction and $\vec{a}_L\times\vec{e}_z$, the current in the circular direction around the cluster, the set of four equations for a_0, a_1, b_0, b_1 can be solved in the method used inside the cluster in the limits $ct<1$ and $ct>1$ and the four frequencies are found from the condition of vanishing determinant. The systems $\{a_0,b_1\}$ and $\{a_1,b_0\}$ are decoupled. The initial conditions are a fixed initial position on the cluster surface and a fixed initial velocity:

$$a_0=\vec{v}_0\cdot\vec{e}_z\frac{e^{2\pi iqa}}{a^2}=a_1 \quad b_0=\frac{e^{2\pi isa}}{a^2}=b_1 .$$

The results are shown in Fig. 2.

For $ct\ll 1$, the result for the probability density is

$$f(\vec{R},t)a^2=\left[\frac{1}{4\pi D_0 t}\right]^{1/2}\exp\left[-\frac{\left[R-a+\left(s+\frac{2}{a}\right)\frac{kTt}{2c_d}\right]^2}{4D_0 t}\right]\times\left[Y_{00}+Y_{10}(\theta)\exp\left(-\frac{kTt}{c_d a^2}\right)\right],$$

with an effective diffusion constant, $D_0=kT/2c_d$. Atoms starting on the surface show a tendency to be drawn into the cluster by the capillary pressure term. The probability shows a slow decay with time towards radial distribution of spherical symmetry.

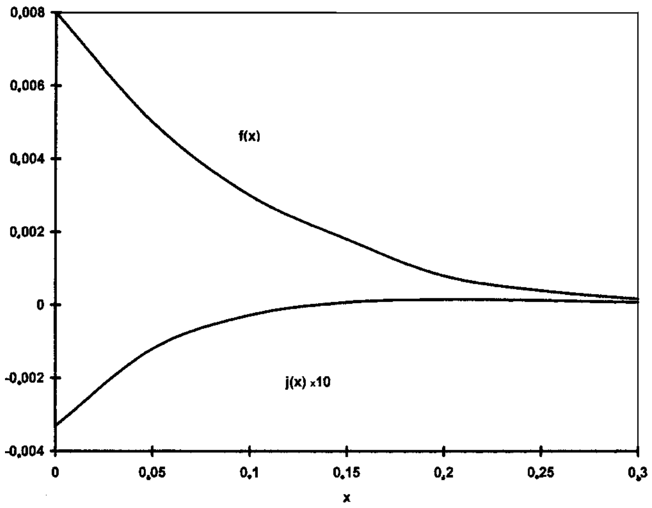

FIG. 2. For the cluster of radius a, probability distribution f and average velocity **j** in the direction of the initial position vector for the particles that started at the core surface and evolved within the cluster interface as a function of distance to the surface $x=R/a-1$ at a time $t=4$. The diffusion coefficient in the interface is 8×10^{-2}, the friction decay time $c^{-1}=1.1$, the effective surface field as$=12.5$, the radius $a=5$ (MDU as in Fig. 1).

The particle flux and the kinetic tensor are dominated by the initial velocity: $\vec{j}(\vec{R},t)=f(\vec{R},t)\vec{v}_0 e^{-ct}$. The loss of the initial velocity follows the usual exponential decay with a characteristic time c^{-1}.

For $ct\gg 1$, the effect of the surface is important. An additional relaxation time can be seen to appear due to the surface force field, which enhances the drift of atoms in the radial direction:

$$f(\vec{R},t)a^2=\left[1-\frac{1}{c}\vec{v}_0\cdot\vec{e}_z\left(\frac{d}{dR}+s\right)\right]\left[\frac{1}{4\pi D_1 t}\right]^{1/2}\times\exp\left[-\frac{\left[R-a+\left(s+\frac{2}{a}\right)t\left(\frac{kT}{2c_d}+\frac{4kTc_b}{3m^2}\right)\right]^2}{4D_1 t}\right]\times\left[Y_{00}+Y_{10}(\theta)\exp\left(-\frac{kTt}{c_d a^2}\right)\right]^2 .$$

The effective diffusion constant is increased:

$$D_1=\frac{2kTc_b}{3m^2}+\frac{kT}{2c_d},$$

the numerical factor of 3 in D_1 being a result of the limited expansion in spherical harmonics.

The effect of the surface is also visible in the average velocity dominated by the response to the total external field:

$$\vec{j}(\vec{R},t)\cdot\vec{e}_z a^2 = -\frac{2kTc_b}{m^2}\left(\frac{\partial}{\partial R}+s\right)\left[\frac{1}{4\pi D_1 t}\right]^{1/2}\exp\left[-\frac{\left[R-a+\left(s+\frac{2}{a}\right)t\left(\frac{kT}{2c_d}+\frac{4kTc_b}{3m^2}\right)\right]^2}{4D_1 t}\right]\left[Y_{00}\exp\left(-\frac{kTt}{c_d a^2}\right)+Y_{10}(\theta)\right].$$

The radial flux persists with a relaxation given by

$$\exp\left[-\frac{t\left(s+\frac{2}{a}\right)^2\left(\frac{kT}{2c_d}+\frac{4kTc_b}{3m^2}\right)^2}{4D_1}\right].$$

The initial circular flow is not coupled to the density and vanishes rapidly due to the friction forces:

$$\vec{j}(\vec{R},t)\times\vec{e}_z a^2=\vec{v}_0\times\vec{e}_z\left[\frac{1}{4\pi D_0 t}\right]^{1/2}$$
$$\times\exp\left[-\frac{\left[R-a+\left(s+\frac{2}{a}\right)\frac{kTt}{2c_d}\right]^2}{4D_0 t}\right]$$
$$\times\left[1+Y_{10}(\theta)\exp\left(-\frac{kTt}{c_d a^2}\right)\right]e^{-ct}\rightarrow 0.$$

D. Correlation functions

Inside the cluster core, the coupling between position and velocity in the persistent diffusion model leads to a linear time dependence for the MSD with an increase in diffusion constant and total loss of velocity correlation after a time c^{-1}. In the interfacial region, the MSD in both kinetics is nonlinear and initially quadratic in time, but the cause is different, arising from velocity effects in the FP rather than due to accelerated motion by the surface pressure gradient in the present model. The velocity correlation in both kinetics demonstrates a rapid initial exponential decay and a long time exponential drop with persistence of correlation due to the surface force field (Figs. 3 and 4).

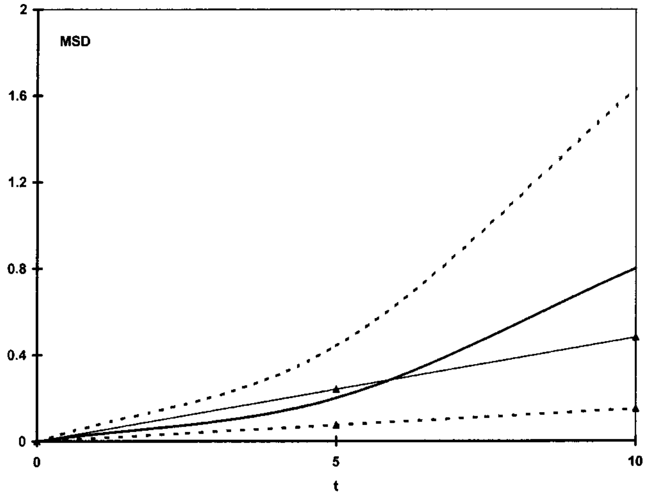

FIG. 3. The mean square displacement (MSD) as a function of time within the core (——▲——) and the interface (—) for the parameters of Figs. 1 and 2. The results of the molecular dynamics simulation in the core (--▲--) and interface (· · · ·) are shown for comparison [15] (MDU as in Fig. 1).

A comparison to molecular dynamics provides a test for the hypothesis on which kinetic equations are based. To compare with the kinetic theory, the simulation results for the MSD and the velocity correlation are also given in Figs. 3 and 4. Qualitative agreement is found. Quantitative agreement is hampered by lack of independent values for the diffusion constant and the friction constant in the interface, although these could be calculated in the method of Ref. [16] or determined from the simulation.

V. CONCLUSIONS

In the proposed kinetic model, the following picture for the average motion of a particle inside a sufficiently large condensing cluster is revealed. For atoms starting at the center of the aggregate with a given velocity, the average velocity initially follows the initial direction but decays rapidly due to onset of diffusive motion, as does the initial kinetic tensor that directs the motion along the initial velocity. With time, entropy dominates as the directing force for the probability flow and the motion is accelerated by the tendency to smooth out the nonuniform probability density. The results for a particle starting on the cluster surface demonstrate a gradual loss of initial flow and directed radial motion of the

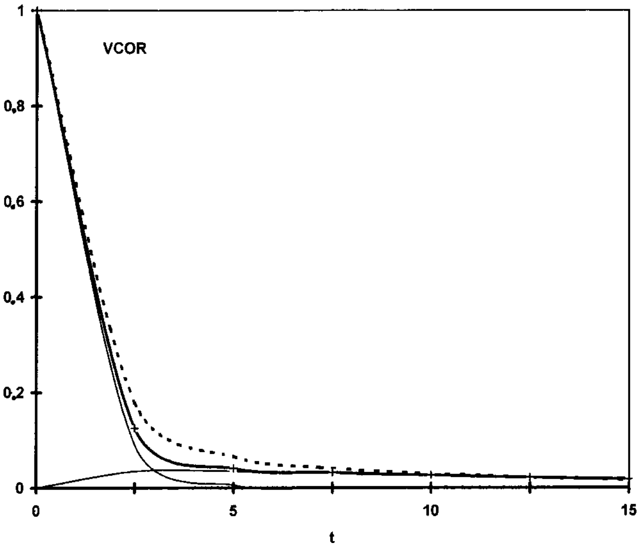

FIG. 4. The velocity correlation V_{COR} as a function of time in the interface (—) for the parameters of Figs. 2 and 3. The short ($ct\ll 1$) and long ($ct\gg 1$) time behavior are plotted separately, the sum is shown as (+++). The results of the molecular dynamics simulation (· · · ·) are shown for comparison [15] (MDU as in Fig. 1). The initial velocity is radial into the core center.

atoms into the cluster due to the favorable chemical potential gradient near the cluster surface. The random thermal motion lessens the directed flow and causes the tendency to spherical symmetry with time. A cluster surface is thus found to be surrounded by a narrow zone of capture where particle motion is affected by the cluster field and the need to enter the new stable phase. Outside this zone, motion is mainly diffusive.

Similar effects occur in the classical Fokker-Planck approach for the properties, parameters, and time scales examined. In both approaches, the long and short time correlation functions are in qualitative agreement with the molecular dynamics simulation on an Argon cluster. A picture of the dynamics of atoms emerges, which is universal and independent of an interaction model. Metal clusters are of importance in applications; it would be interesting to explore the importance of the electronic contribution to the dynamics of a nucleating metal cluster, possibly using the embedded atom potential already applied to wetting [26].

Atomic scale physics explores theoretically or experimentally the underlying atomistic processes of a phase transition: aggregation, diffusion, coalescence, and dissolution, which determine the morphology and characteristics of the system at a given instant of time. The crucial question remains access to nonequilibrium properties. The method presented here folds atomistic understanding into a mesoscopic formulation in terms of average density, flux, and stress tensors and can be compared directly to experiment and molecular dynamics. Collective behavior is captured on this scale and is embedded in a continuum mechanics approach. The mean field approach of density functional theory is extended to nonequilibrium systems to include effects of flow fields and variations in pressure and temperature. Experiments and simulation can benefit from the guidance provided by the analytical modeling, and the analytical theory is useful in applied science, as it is detached from a specific given material. The method is of interest and could be used in other nanosystems. The assumptions of the model are not limited to atomic systems and are pertinent to cluster formation in suspensions [27].

The presence of characteristic flow fields in the vicinity of nucleating clusters was suggested long ago [28] and may be expected to play an important role in the doping of clusters [29], in coalescence [30,31], for deposition near a surface, notably in electrochemical deposition [32].

ACKNOWLEDGMENT

This work was suggested by D. Zhukhovitskii and profited greatly from his expertise.

---

[1] *Proceedings of the International Conference on Computational Nanoscience*, edited by M. Laudon and B. Romanowicz (Computational Publications, Boston, 2001).
[2] M. Ohring, *Materials Science of Thin Films* (Academic Press, San Diego, 1992).
[3] J. D. Gunton, M. San Miguel, and P. Sahni, *Phase Transitions and Critical Phenomena*, edited by C. Domb and J. L. Lebowitz (Academic Press, New York, 1983), Vol. 8, p. 269.
[4] K. Yasuoka and M. Matsumoto, J. Chem. Phys. **109**, 8451 (1998).
[5] V. Shen and P. Debenedetti, J. Chem. Phys. **111**, 3581 (1999).
[6] I. Kusaka, D. Oxtoby, and Z. G. Wang, J. Chem. Phys. **111**, 9958 (1999).
[7] P. ten Wolde, M. Ruiz-Montero, and D. Frenkel, J. Chem. Phys. **110**, 1591 (1999).
[8] D. Zhukhovitskii, J. Chem. Phys. **110**, 7770 (1999).
[9] U. Marconi and P. Tarazona, J. Chem. Phys. **110**, 8032 (1999).
[10] D. W. Oxtoby, *Liquids, Freezing and the Glass Transition*, edited by J. P. Hansen, D. Levesque, and J. Zinn-Justin (Elsevier Science, Amsterdam, 1991).
[11] K. Binder and D. Stauffer, Adv. Phys. **25**, 343 (1976).
[12] J. S. Langer, Ann. Phys. **65**, 53 (1971).
[13] D. Reguera, J. M. Rubi, and A. Perez-Madrid, J. Chem. Phys. **109**, 5987 (1998).
[14] B. Krämer, O. Hübner, H. Vortisch, L. Wöste, T. Leisner, M. Schwell, Z. Ruhl, and H. Baumgärtel, J. Chem. Phys. **111**, 6521 (1999).
[15] A. ten Bosch and D. Zhukhovitskii, in *Proceedings of the International Conference on Computational Nanoscience* (Ref. [1]), p. 41.
[16] S. A. Rice and P. Gray, *The Statistical Mechanics of Simple Liquids* (Interscience, New York, 1965).
[17] S. R. de Groot and P. Mazur, *Nonequilibrium Thermodynamics* (North-Holland, Amsterdam, 1962).
[18] M. San Miguel and J. D. Gunton, Phys. Rev. B **23**, 2317 (1981).
[19] M. Doi and S. F. Edwards, *The Theory of Polymer Dynamics* (Oxford University Press, Oxford, 1986).
[20] R. Bausch and R. Blossey, Phys. Rev. E **48**, 1131 (1993).
[21] A. ten Bosch, J. Chem. Phys. **110**, 12 250 (1999).
[22] H. Vehkamaki and I. J. Ford, J. Chem. Phys. **112**, 4193 (2000).
[23] J. H. Jeans, *The Dynamical Theory of Gases* (Dover, New York, 1954).
[24] A. ten Bosch, Physica A **262**, 396 (1999).
[25] S. Chandrasekhar, Rev. Mod. Phys. **15**, 1 (1943).
[26] E. B. Webb and G. Grest, in *Proceedings of the International Conference on Computational Nanoscience* (Ref. [1]), p. 89; Phys. Rev. Lett. **86**, 2066 (2001).
[27] D. Mozyrsky and V. Privman, J. Chem. Phys. **110**, 9254 (1999).
[28] D. Beysens, A. Steyer, P. Guenon, D. Fritter, and C. M. Knobler, Phase Transitions **31**, 219 (1991).
[29] H. Vach, J. Chem. Phys. **111**, 3536 (1999).
[30] V. Kumaran, J. Chem. Phys. **112**, 10984 (2000).
[31] J. Koplik and J. Banavar, Science **257**, 1664 (1992).
[32] *Nanoscale Probes of the Solid Liquid Interface*, edited by A. Gewirth and H. Siegenthaler (Kluwer Academic, Dordrecht, 1995).