Dynamic density functional theory of fluids

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We present a new time-dependent density functional approach to study the relaxational dynamics of an assembly of interacting particles subject to thermal noise. Starting from the Langevin stochastic equations of motion for the velocities of the particles we are able by means of an approximated closure to derive a self-consistent deterministic equation for the temporal evolution of the average particle density. The closure is equivalent to assuming that the equal-time two-point correlation function out of equilibrium has the same properties as its equilibrium version. The changes in time of the density depend on the functional derivatives of the grand canonical free energy functional $F[\rho]$ of the system. In particular the static solutions of the equation for the density correspond to the exact equilibrium profiles provided one is able to determine the exact form of $F[\rho]$. In order to assess the validity of our approach we performed a comparison between the Langevin dynamics and the dynamic density functional method for a one-dimensional hard-rod system in three relevant cases and found remarkable agreement, with some interesting exceptions, which are discussed and explained. In addition, we consider the case where one is forced to use an approximate form of $F[\rho]$. Finally we compare the present method with the stochastic equation for the density proposed by other authors [Kawasaki, Kirkpatrick etc.] and discuss the role of the thermal fluctuations.
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I. INTRODUCTION

In recent years the off-equilibrium properties of extended systems have represented a very active field of research. In fact, while the present understanding of systems in thermodynamic equilibrium is rather satisfactory and is based on well established theoretical methods, the comprehension of their dynamical aspects is far from complete, in spite of massive experimental and theoretical investigations.[1,2]

In the present article we shall focus attention on the density functional method, which represents a powerful and widely used tool to investigate the static properties of many particles systems[3] and consider the possibility of extending this approach to off-equilibrium situations. Some authors have already employed similar approaches on a purely phenomenological basis by analogy with the popular Ginzburg–Landau time dependent equation and the Cahn–Hilliard equation, but these methods are not applicable to the highly structured density profiles that one observes at the onset of crystallization.

The density functional (DF) formalism, with advanced models for the nonlocal functional dependence of the Helmholtz free energy on the density distribution, has provided a good framework to study the solid–liquid transition and other highly structured systems. There have been previous attempts to derive a dynamic density functional (DDF) theory from the microscopic equations of motions,[4–8] so that the density functional approximations developed for systems at equilibrium might be extended to the dynamics of these systems. However, none of these proposals is fully satisfactory as we shall demonstrate, while the derivation that we consider makes direct contact with the equilibrium DF formulation and is therefore consistent with thermodynamic requirements.

The theoretical foundations of the density functional methods are based on the concept that the intrinsic Helmholtz free energy of a fluid that exhibits a spatially varying equilibrium density $\rho(r)$, is a unique functional $F[\rho]$ and is independent of the applied external fields for a given intermolecular potential. An exact knowledge of $F[\rho]$ allows obtaining in a self-consistent fashion the profile $\rho(r)$ and all the n-point correlations via functional differentiation. When dealing with nonequilibrium situations, caused by some changes of the external constraints, such as the temperature, the pressure, or electric field, it would be extremely useful to have similar methods at our disposal. Mode coupling theories[9] provide a kinetic approach to the dynamic of supercooled fluids and structural glass transitions, but fail to predict the crystallization process. In other cases the phase ordering dynamics of liquids has been based on schematic model Hamiltonians of the Ginzburg–Landau type, which neglect the microscopic structure or on heuristic approximations for the free energy.[10]

In principle the density is not the only relevant variable in a dynamical description. The velocity distribution and cor-

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relation are crucial in the understanding of hydrodynamic modes, while they do not appear in the equilibrium DF for classical fluids. However, one could argue following Cohen and de Schepper[11] that when the density is large, the momentum and the energy flow quickly through the system via collisions, while the density variable decays slowly. The hydrodynamic modes should become irrelevant for the dynamics of dense and strongly structured systems; the only relevant variable should be the density distribution, as in the equilibrium case, and the use of the equilibrium $F[\rho]$ is a promising starting point to include the effects of the density correlations.

In the present study we restrict ourselves to systems with such ''relaxational dynamics,'' in which the velocity distribution plays no relevant role. Instead of starting directly with the Newtonian dynamics of the particles, we force the irrelevance of the velocity distribution at microscopic level and begin from the stochastic Brownian equations of motion of a system of N particles interacting via two-body forces. In the equilibrium limit, as a very long time average of the dynamic evolution, the Newtonian and the Brownian equations of motion should give the same results and be equal to those of the equilibrium statistical ensemble. The relaxational dynamics of dense systems has also to be similar for the two types of microscopic dynamics: the rapid flow of momentum and energy due to particle-particle collisions in the Newtonian dynamics, is given (most efficiently) by the bath in the Brownian dynamics. Of course, there are cases (including some of the examples analyzed in this work) for which the Newtonian and the Brownian dynamics have very different results. In those cases our proposed DF approach to the dynamics would still be useful for systems following the Brownian equation of motion, like colloidal particles in a bath, but it would not be appropriate for systems in which the microscopic dynamics is Newtonian and the velocity distribution becomes relevant.

The article is organized as follows: in Sec. II we derive the dynamic density functional theory starting from the stochastic equations of motion of the particles and discuss the main features of the resulting DDF approach. In Sec. III we apply the method to few systems of hard molecules in one dimension, for which the exact equilibrium free energy density functional is known; the comparison between the DDF and the averages over the Langevin simulations gives a clear view of the validity of our proposal. In Sec. IV we explore the same systems but using now approximate forms for $F[\rho]$, of the same type as those developed for realistic systems in three dimensions; in this way we analyze the effects of the approximations used for $F[\rho]$, which would be unavoidable in the practical use of the DDF formalism. In Sec. V we draw the conclusions, discuss previous approaches, and present the future perspectives.

II. TRANSFORMATION FROM BROWNIAN TRAJECTORIES TO THE EQUATION FOR THE DENSITY VARIABLE

One considers an assembly of N Brownian particles of coordinates $\mathbf{r_i}$ interacting via an arbitrary pair potential $V(\mathbf{r_i}-\mathbf{r_j})$ and experiencing an external field $V_{\text{ext}}(\mathbf{r_i})$. Neglecting the inertial term and the hydrodynamic interaction their motion can be described by the following set of coupled stochastic equations:

$$\frac{d\mathbf{r}_i(t)}{dt}=-\Gamma\nabla_{\mathbf{i}}\left[\sum_j V(\mathbf{r_i}-\mathbf{r_j})+V_{\text{ext}}(\mathbf{r_i})\right]+\boldsymbol{\eta}_i(t), \tag{1}$$

where the term $\boldsymbol{\eta}_i(t)=[\eta_i^x(t),\eta_i^y(t),\eta_i^z(t)]$ represents the influence of the thermal bath and has the properties:

$$\langle\eta_i^\alpha(t)\rangle=0 \tag{2}$$

and

$$\langle\eta_i^\alpha(t)\,\eta_j^\beta(t')\rangle=2D\,\delta_{ij}\delta^{\alpha\beta}\delta(t-t'), \tag{3}$$

where the average is over the Gaussian noise distribution and α,β run over x,y,z. The constants Γ and D give the mobility and the diffusion coefficient of the particles, respectively. The Einstein relation gives $\Gamma/D=\beta\equiv 1/T$, and from here on we take $\Gamma=1$ to fix the unit of time and have $D=T=\beta^{-1}$. The evolution law drives the system towards the equilibrium situation which is described by the canonical Gibbs probability measure. Instead of considering all the trajectories generated from Eq. (1) we shall consider the evolution of the density of particles.

In order to render the paper self-contained we rederive briefly the transformation,[4] using the rules of the Ito stochastic calculus. In order to do so, we recall that if f is an arbitrary function of $x(t)$ given by the process:

$$\frac{dx}{dt}=a(x,t)+b(x,t)\xi(t) \tag{4}$$

with $\langle\xi(t)\xi(t')\rangle=2\,\delta(t-t')$ its evolution is given by the following Ito prescription for the change of variables (see Ref. 12):

$$\frac{df(x,t)}{dt}=a(x,t)\frac{df(x,t)}{dx}+b(x,t)\frac{df(x,t)}{dx}\xi(t)+\frac{1}{2}[b(x,t)]^2\frac{d^2f(x,t)}{dx^2}. \tag{5}$$

Thus employing Eqs. (5) and (1) we obtain

$$\frac{df[\mathbf{r}_i(t)]}{dt}=-\nabla_{\mathbf{i}}\left[\sum_j V(\mathbf{r_i}-\mathbf{r_j})+V_{\text{ext}}(\mathbf{r_i})\right]\nabla_i f(\mathbf{r_i})+\nabla_i^2 f(\mathbf{r_i})+\nabla_{\mathbf{i}}f(\mathbf{r_i})\,\eta_{\mathbf{i}}(\mathbf{t}). \tag{6}$$

After inserting the identity $f(\mathbf{r_i})=\int\delta(\mathbf{r_i}-\mathbf{r})f(\mathbf{r})d\mathbf{r}$ and using the arbitrariness of f, we obtain the equation for the partial density operator, $\hat{\rho}_i(\mathbf{r},t)\equiv\delta(\mathbf{r_i}-\mathbf{r})$:

$$\frac{\partial\hat{\rho}_i(\mathbf{r},t)}{\partial t}=T\boldsymbol{\nabla}^2\hat{\rho}_i(\mathbf{r},t)+\boldsymbol{\nabla}\left[\hat{\rho}_i(\mathbf{r},t)\left(\int d\mathbf{r}'[\hat{\rho}(\mathbf{r}',t)\boldsymbol{\nabla}V(\mathbf{r}-\mathbf{r}')+\boldsymbol{\nabla}V_{\text{ext}}(\mathbf{r})]\right)\right]+\eta_i(+)\boldsymbol{\nabla}\hat{\rho}_i(\mathbf{r},t), \tag{7}$$

where, after some manipulation, the instantaneous global density operator, $\hat{\rho}(\mathbf{r},t)=\Sigma_{i=1,N}\delta[\mathbf{r_i(t)}-\mathbf{r}]$, can be shown to obey the following multiplicative noise equation:

$$\frac{\partial\hat{\rho}(\mathbf{r},t)}{\partial t}=\nabla\Big[T\nabla\hat{\rho}(\mathbf{r},t)+\hat{\rho}(\mathbf{r},t)\nabla V_{\text{ext}}(\mathbf{r})+\hat{\rho}(\mathbf{r},t)\int d\mathbf{r}'\hat{\rho}(\mathbf{r}',t)\nabla V(\mathbf{r}-\mathbf{r}')+\eta(\mathbf{r},t)\sqrt{\hat{\rho}(\mathbf{r},t)}\Big]. \tag{8}$$

Equation (7) contains the same information as Eq. (1) but in a more useful form. Both are stochastic equations for the movement of N Brownian particles, represented directly by their positions in Eq. (1) and by the N delta-function spikes of $\hat{\rho}(r,t)$ in Eq. (7). This latter form, as derived by Dean,[4] opens the connection with the density functional formalism which was already suggested by the same author in the following terms: the Helmholtz free energy functional,

$$F[\rho]=T\int d\mathbf{r}\rho(\mathbf{r})\{\log[\rho(\mathbf{r})]-1\}+\int dr\rho(\mathbf{r})V_{\text{ext}}(\mathbf{r})+\Delta F[\rho], \tag{9}$$

contains the exact ideal gas entropy and the external potential contribution in the first two terms, while the third one includes the effects of interactions and correlations between the particles and its exact form is known only for very few systems. The first two terms in the bracket of Eq. (8) correspond precisely to the contributions of the ideal gas and the external potential to $\rho\nabla\delta F/\delta\rho$, and within an implicit mean field approximation it was observed that the third term in the bracket of Eq. (8) can also be cast in terms of the functional derivative of $\Delta F[\rho]$. In a slightly different language the analysis by Kawasaki[5,6] led to the same type of proposal: a dynamic density functional equation for $\hat{\rho}(\mathbf{r},t)$ in terms of the functional derivative of $F[\rho]$ and a remaining stochastic contribution, from the noise term in Eq. (8). However, the use of the equilibrium functional $F[\rho]$ only makes sense with an ensemble averaged density distribution. The delta-function peaks in $\hat{\rho}(\mathbf{r},t)$ would give infinite contributions to the first term in Eq. (9), because they correspond to a single microscopic state and not any statistical ensemble average. To make the connection between Eq. (8) and a density functional description one has to implement some kind of averaging over the instantaneous distribution of particles.

Within the microscopic Brownian dynamics the obvious way to proceed is to average over the realizations of the random noise $\eta(\mathbf{r},t)$. We denote by brackets, $\langle\ldots\rangle$, the results of this averaging and in particular we define the noise-averaged density $\rho(\mathbf{r},t)\equiv\langle\hat{\rho}(\mathbf{r},t)\rangle$. In the equilibrium limit, when the system has been allowed to relax for long enough time under the Brownian dynamics, this average would correspond precisely to the Gibbsian equilibrium average. In the study of the dynamics, out of equilibrium, the density $\rho(\mathbf{r},t)$ has to be interpreted as an ensemble average, as in a collection of colloidal systems with the colloidal particles at the same initial conditions but with different (thermalized) microscopic states for the bath. We may hope, without demonstration, that this Brownian ensemble may also give an accurate description of dense systems with Newtonian dynamics near the crystallization, for which the ensemble should be interpreted as a collection of systems with the same initial positions but different (thermalized) velocities for the particles.

When we proceed to take the noise average over the Brownian evolution Eq. (8) the first effect is to cancel out the noise contribution in the last term. The stochastic equation for time evolution of $\hat{\rho}(\mathbf{r},t)$ becomes a deterministic equation for $\rho(\mathbf{r},t)$,

$$\frac{\partial\rho(\mathbf{r},t)}{\partial t}=\nabla\Big[\int T\nabla\rho(\mathbf{r},t)+\rho(\mathbf{r},t)\nabla V_{\text{ext}}(\mathbf{r})+\int d\mathbf{r}'\langle\hat{\rho}(\mathbf{r},t)\hat{\rho}(\mathbf{r}',t)\rangle\nabla V(\mathbf{r}-\mathbf{r}')\Big], \tag{10}$$

in contrast with previous authors,[4,6,7] who maintain the stochastic character of the dynamic DF evolution keeping a random noise term.[13]

Systems of noninteracting ideal particles, $V(\mathbf{r}-\mathbf{r}')=0$, provide an exact test of this point. In that case the free energy density functional $F_{\text{id}}[\rho]$ reduces to the first two contributions in Eq. (9), since $\Delta F[\rho]=0$, and Eq. (10) may be written as a closed deterministic equation for the density distribution,

$$\frac{\partial\rho(\mathbf{r},t)}{\partial t}=T\nabla^2\rho(\mathbf{r},t)+\nabla[\rho(\mathbf{r},t)\nabla V_{\text{ext}}(\mathbf{r})]=\nabla\cdot\Big[\rho(\mathbf{r},t)\nabla\frac{\delta F_{\text{id}}[\rho(\mathbf{r},t)]}{\delta\rho(\mathbf{r},t)}\Big], \tag{11}$$

which is the exact Fokker–Planck equation for the diffusion and drift of an ideal Brownian gas. In the proposals of Dean[4] and Kawasaki[6] this equation would include a stochastic noise term, leading to an overcounting of the fluctuations. In particular the Boltzmann equilibrium state predicted by Eq. (11) in the static limit would be spoiled by the presence of the random noise, which would be equivalent to an overestimation of the temperature.

In the case of interacting particles Eq. (10) is not a closed relation, since in order to obtain $\rho(\mathbf{r},t)$ one needs the equal-time two-point correlation $\rho^{(2)}(\mathbf{r},\mathbf{r}',t)\equiv\langle\hat{\rho}(\mathbf{r},t)\hat{\rho}(\mathbf{r}',t)\rangle$. The simplest mean field approximation assumes $\rho^{(2)}(\mathbf{r},\mathbf{r}',t)\approx\rho(\mathbf{r},t)\rho(\mathbf{r}',t)$ and gives a closed equation for $\rho(\mathbf{r},t)$, but it would give quite pathological results for the molecular core repulsions. Following the same procedure used for $\rho(\mathbf{r},t)$ we may obtain an equation for the time evolution of $\rho^{(2)}(\mathbf{r},\mathbf{r}',t)$ which in turn depends on the three-point correlation. In fact eq. (10) is only the first member of an infinite hierarchy of relations known as Born–Bogolubov–Green–Kirkwood–Yvon (BBGKY) integro-differential equations connecting n-point functions to $(n+1)$-point functions.[14] As in the equilibrium case one can get approximated results breaking the chain at any level. The so called Kirkwood superposition approximation, replaces the three-point correlation by a product of two-point correlations

as the next step after the mean field approximation and may already give reasonable results for hard core interactions.

Here we propose a different strategy, a density functional approach in which the two-point correlation function may be approximated with the help of equilibrium free energy density functionals. The excess free energy density functional $\Delta F[\rho]$ in principle contains all the equilibrium correlation structures in the system and, although the exact functional form is known only for very few systems, there are workable and very accurate approximations for most systems of interest. We may use the information contained in $\Delta F[\rho]$, about the correlation structure at equilibrium, to approximate $\langle \hat{\rho}(\mathbf{r},t)\hat{\rho}(\mathbf{r}',t)\rangle$ in a system out of equilibrium. In this way we get a generic, closed, dynamic density functional relation for $\rho(\mathbf{r},t)$ equivalent to Eq. (11) with a clear interpretation of the approximations involved.

Let us consider an equilibrium state of the system characterized by an arbitrary profile $\rho_0(\mathbf{r})$ (the subscript 0 indicates the equilibrium average), which we shall eventually take equal to the profile $\rho(\mathbf{r},t)$ at a given instant t. Such an equilibrium state certainly exists and represents a minimum of the grand potential functional provided we add an appropriate equilibrating external potential. One can prove, in fact, that for fixed temperature, chemical potential, and pair interactions there always exists a unique external potential $u(\mathbf{r})$ which induces the given $\rho_0(\mathbf{r})$. In other words, upon adding the external potential $u(\mathbf{r})$, we would pin the system to be at equilibrium in a configuration corresponding to the instantaneous average density $\rho(\mathbf{r},t)$; the potential $u(\mathbf{r})$ is a functional of $\rho_0(\mathbf{r})$ and changes with t as $\rho(\mathbf{r},t)$ varies.[3]

From the general properties of the equilibrium functionals we have that the following two exact equilibrium relations must be satisfied by $\rho_0(\mathbf{r})$ and $u(\mathbf{r})$. First, the local balance of momentum at any point implies the BBGKY relation,

$$\frac{1}{\rho_0(\mathbf{r})}\nabla\rho_0(\mathbf{r})+\beta\nabla[V_{\text{ext}}(\mathbf{r})+u(\mathbf{r})] = -\beta\frac{1}{\rho_0(\mathbf{r})}\int dr'\,\rho_0^{(2)}(\mathbf{r},\mathbf{r}')\nabla V(\mathbf{r}-\mathbf{r}'). \tag{12}$$

Second, the thermodynamic equilibrium implies that the functional derivative of $F[\rho]$ at any point is equal to a uniform chemical potential μ. Taking the gradient gives the equation, first obtained by Lovett *et al.*,[3,15]

$$\frac{1}{\rho_0(\mathbf{r})}\nabla\rho_0(\mathbf{r})+\beta\nabla[V_{\text{ext}}(\mathbf{r})+u(\mathbf{r})] = -\nabla\frac{\delta}{\delta\rho_0(\mathbf{r})}[\beta\Delta F[\rho_0]] = \int d\mathbf{r}'c^{(2)}(\mathbf{r},\mathbf{r}')\nabla\rho_0(\mathbf{r}'), \tag{13}$$

where

$$c^{(2)}(\mathbf{r},\mathbf{r}')=-\beta\frac{\delta^2\Delta F[\rho_0]}{\delta\rho_0(\mathbf{r})\,\delta\rho_0(\mathbf{r}')}$$

is the direct correlation function, related to the functional inverse of the equilibrium two point density-density correlation $\rho_0^{(2)}(\mathbf{r},\mathbf{r}')$. The functional $\Delta F[\rho_0]$ serves to generate the sequence of inverse linear response or direct correlation functions[16] upon functional differentiation with respect to ρ. Let us emphasize that Eqs. (12) and (13) are exact for the instantaneous potential $u(\mathbf{r})$. Comparing these two equations and assuming that the equal time correlation $\rho^{(2)}(\mathbf{r},\mathbf{r}',t)$, averaged over the Brownian noise, may be approximated by that of the equilibrium system with the same density distribution, we get the last term in Eq. (10) as:

$$\int d\mathbf{r}'\langle\hat{\rho}(\mathbf{r},t)\hat{\rho}(\mathbf{r}',t)\rangle\nabla V(\mathbf{r}-\mathbf{r}')=\rho(\mathbf{r},t)\nabla\frac{\delta\Delta F[\rho(\mathbf{r},t)]}{\delta\rho(\mathbf{r},t)}. \tag{14}$$

In summary, we have used the fact that at any instant we can find a fictitious external potential $u(\mathbf{r})$ which equilibrates the system, i.e., constrains its grand potential to be minimal. This minimum is characterized by the imposed density profile $\rho_0(\mathbf{r})=\rho(\mathbf{r},t)$ and by equilibrium correlations $\rho_0^{(2)}(\mathbf{r},\mathbf{r}')$ consistent with it. The present approximation replaces the true off-equilibrium pair distribution function $\langle\hat{\rho}(\mathbf{r},t)\hat{\rho}(\mathbf{r}',t)\rangle$ by the equilibrium $\rho_0^{(2)}(\mathbf{r},\mathbf{r}')$, and then uses the equilibrium density functional $\Delta F[\rho]$ to obtain the relevant information on this function.

The assumption that the two routes, Eqs. (12) and (13), are equivalent implies that the fluctuation dissipation theorem holds, while in general, out of equilibrium, it is violated.[17] In fact the relation connecting $\rho_0^{(2)}(\mathbf{r},\mathbf{r}')$ to $c^{(2)}(\mathbf{r},\mathbf{r}')$ (the O.Z equation) is an exact equilibrium property and is based on the idea that the correlation function is the matrix inverse of the second derivative of the functional F with respect to $\rho_0(\mathbf{r})$.

With Eqs. (9) and (14) we may recast Eq. (10) into the main result of the dynamic density functional approach, based on the use of the equilibrium functional $F[\rho]$:

$$\frac{\partial\rho(\mathbf{r},t)}{\partial t}=\nabla\left[\rho(\mathbf{r},t)\nabla\frac{\delta F[\rho(\mathbf{r},t)]}{\delta\rho(\mathbf{r},t)}\right], \tag{15}$$

which has the form of a continuity equation, $\partial\rho/\partial t+\nabla\cdot\mathbf{j}=0$, with the current of particles given by:

$$\mathbf{j}(r,t)=-\rho(r,t)\nabla\frac{\delta F[\rho]}{\delta\rho(r)}\bigg|_{\rho(\mathbf{r},t)}. \tag{16}$$

The main features of this approach are the following:

(a) $F[\rho]$ is a functional solely of the density field and thus Eq. (15) is a closed non linear equation for $\rho(\mathbf{r},t)$.

(b) The equation is deterministic, but the variable $\rho(\mathbf{r},t)$ has to be interpreted as the instantaneous density operator averaged over the realizations of the random noise $\eta_i(t)$. The contribution from the ideal gas entropy generates the diffusion term in Eq. (11) and reflects the presence of the thermal noise.

(c) The only assumptions leading to Eq. (15) are that the systems follows a relaxative dynamics, which may be described by the Brownian motion of the particles in a thermalized bath, and that the instantaneous two-particle correlations are approximated by those in an

equilibrium system with the same density distribution, as given by the (exact or approximated) density functional $F[\rho]$.

Before concluding this section we note an interesting feature of the dynamics: using the equation of evolution for $\rho(\mathbf{r},t)$ it is straightforward to show that for any system with closed or periodic boundary conditions, the dynamics always tends to decrease the free energy functional, i.e.,

$$\frac{dF[\rho]}{dt}=-\int d\mathbf{r}\rho(\mathbf{r},t)\left[\nabla\frac{\delta F}{\delta\rho}\right]^2\leqslant 0. \tag{17}$$

In the long time limit, the evolution of the system leads to its equilibrium density distribution, which corresponds to a uniform value of $\mu=\delta F/\delta\rho(\mathbf{r})$, i.e., the usual Euler-Lagrange equation in the equilibrium DF formalism. However, the trajectories that lead to the minima of F are not necessarily along the directions corresponding to the maximum slope. The continuity equation, implies that the local conservation of particles is built in and imposes important constrains on the local changes of $\rho(\mathbf{r},t)$.

For any system with a finite number of particles there is a unique canonical equilibrium density distribution, $\rho_0(\mathbf{r})$, which corresponds to the unique local (and global) minimum of the exact free energy density functional $F[\rho]$. However, the use of approximations for $F[\rho]$ may lead to the existence of several local minima in which the dynamics of Eqs. (15) and (17) may get trapped; this deserves further comment. Notice first that these local minima of the free energy density functional, and the barriers between them, cannot be directly associated to the local minima, and to the barriers, of the potential energy in the Langevin description. Consider the dynamics of an ideal Brownian gas in an external potential with two local minima, separated by a barrier V_b; the Langevin representation requires the Gaussian noise $\eta_i(t)$ to allow the particles to go over the barrier. The probability of such a jump is proportional to $\exp(-V_b/T)$ and, for large barriers, it sets the scale of time for the equilibration of the system. The same time scale appears in the exact Fokker–Planck representation of Eq. (11) through a different mechanism: the free energy landscape has a single minimum, at the equilibrium density $\rho_0(\mathbf{r})\sim\exp[-V_{\mathrm{ext}}(\mathbf{r})/T]$, there are no free-energy barriers, and the deterministic time evolution is set by the particle current Eq. (16) along the functional path to equilibrium. When the equilibration requires moving particles across a large potential barrier, the relaxation time is imposed by the density there, $\rho(\mathbf{r},t)\sim\exp(-V_b/T)$, which may produce a very weak current even if the gradient of the local chemical potential is large.

The presence of different local minima in approximate free energy density functionals is often found in the use of the density functional formalism for equilibrium properties. The usual interpretation is that the global minimum gives the true equilibrium state, while other local minima are associated with metastable states, and phase transitions are described as the crossover of different minima.[18] This is a (generalized) mean-field level of description, in which the phase transition is described in terms of an order parameter related to the one-particle distribution functions. The exact description should always give convex thermodynamic potentials and it requires the description of the phase transitions in terms of the N-particle correlations, rather than in terms of a one-particle order parameter.

In the present context, the use of approximate free energy density functionals with more than one local minima poses a problem of interpretation. When the deterministic time evolution Eq. (15) gets trapped at a ''metastable state'' it can never reach the true equilibrium state. In previous attempts to use $F[\rho]$ for dynamics, both Dean[4] and Kawasaki[6] have kept an extra random noise term in Eq. (15), as a remnant of the original random noise in the Langevin dynamics. This random noise, allows the system to jump over any ''metastability barrier'' in a finite time but it leaves the problem of identifying its origin and intensity. From our analysis it is clear that the use of the free energy density functional makes sense only for the density $\rho(\mathbf{r},t)=\langle\hat{\rho}(\mathbf{r},t)\rangle$, averaged over the realizations of $\eta_i(t)$ in the Langevin dynamics, and this averaging gives the deterministic Eq. (15). We proceed here to explore the results of the deterministic DDF formalism and come back to this point in the conclusion section.

The practical use of Eq. (15) to study problems like the growth of a liquid drop from an oversaturated vapor seems to be limited. The classical Lifshitz–Slyozov–Wagner theory[19] for the late stages of growth, beyond the critical droplet size, is given directly from Eq. (15), even if we use the simplest local density approximation for $F[\rho]$. However, any available approximations for $F[\rho]$, will be unable to describe the early stages of nucleation, as they do not include the effects of long-range critical-like correlations. However, we now have density functional approximations with a good description of the short range correlation structure in highly packed systems. The DF description of the freezing of a liquid[20,21] or the study of fluids confined to narrow pores[22] are the most remarkable achievements of the nonlocal density functionals developed in the last decades. We believe that the DDF formalism may be used to study the dynamics of densely packed fluids taking full advantage of the description of the correlation structure at short range, given by suitable approximations for the equilibrium $F[\rho]$. The most interesting (and difficult) problem would be the study of a closely packed system, which has not crystallized. The Langevin description in Eq. (1) may give extremely slow dynamics since either the random noise has to take the system over large energy barriers (like in the ideal gas described above), or it has to produce rearrangements which are only possible through unlikely correlations of many particles. Within the deterministic dynamic density functional approach in Eq. (15) this situation may be seen in two possible ways:

(1) The free energy landscape becomes rough and displays many local minima, whose number grows exponentially with the size of the system,[23] and within our description the system would remain indefinitely trapped in any of these minima, unless it is annealed at a higher temperature. The idea is that when a uniform liquid is forced to have a density larger than the one corresponding to a liquid at coexistence with the solid, the system starts

developing inhomogeneous patterns, which are associated with local minima of the free energy.[24,25] One conjecture relates the origin of the glassy behavior in liquids to the existence of these minima, as an extension of the well founded theory of mean-field spin glasses.[7,23]

(2) Alternatively, the free energy landscape $F[\rho]$ may be smooth, with a single minimum, because the correlations required to relax the system are described well enough by the free energy functional. In this case, the system will never get really frozen, until it reaches the true equilibrium state, but the dynamics may become so slow that it may appear to be frozen in any practical computation. The slow dynamics of Eq. (15) may be a result of having very low density along current path (again, as in the ideal gas above) or of requiring very unlikely (but not impossible) correlations of many particles. This case would correspond to the conjecture that the glassy behavior in liquids is due to a divergence in the viscosity, and in the relaxation times, rather than to the existence of a metastable freezing.

Within the dynamical density functional approach having one or the other way would be a result of using a worse or a better approximation for $F[\rho]$. The configurations with a very large escape time, when described by a good density functional, may appear like permanent stable states when the dynamics is described with a poorer approximation for $F[\rho]$. In the next section, we present explicit results for a simple model in one dimension which displays these features and illustrates how the structure of the nearly frozen states may be given by simple DF approximations, while the actual calculation of the escape time may require a density functional giving good account of the many-particle correlations.

III. APPLICATIONS TO 1D PROBLEMS EMPLOYING THE EXACT FUNCTIONAL

Since neither the correctness nor the feasibility of the approach presented have been tested so far, we shall begin comparing the two levels of description: the Brownian dynamics and DF dynamics and in order not to introduce unnecessary sources of discrepancies we consider a one dimensional hard-rod system, whose exact equilibrium DF is known[26,27] and which includes strong correlation effects due to the infinite repulsion between the particles.

Long ago, Percus[26] was able to determine the exact form of the free energy density functional for an assembly of hard rods of length σ. The excess functional due to the interactions reads

$$\Delta F[\rho(x)]=\int_{-\infty}^{\infty} dx\,\phi[\eta(x)]\frac{\rho(x+\sigma/2)+\rho(x-\sigma/2)}{2}, \tag{18}$$

where

$$\phi(\eta)=-T\log[1-\eta(x)], \tag{19}$$

and the local packing fraction η is defined as

$$\eta(x)=\int_{x-\sigma/2}^{x+\sigma/2} dx'\rho(x'). \tag{20}$$

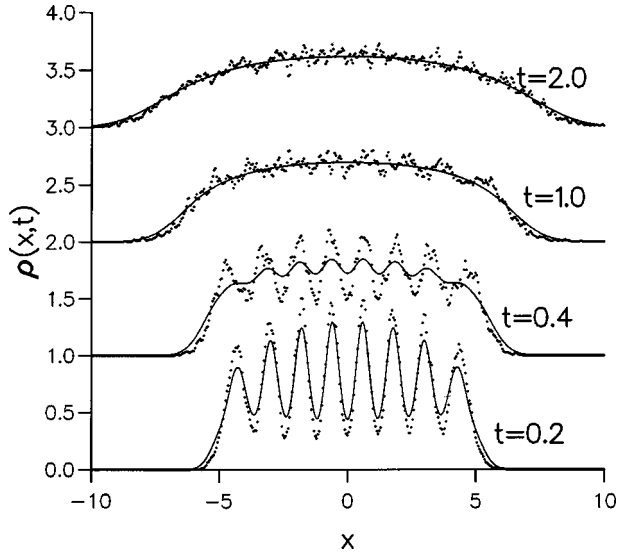

FIG. 1. Density profiles for a system of $N=8$ hard rods of unit length in free expansion, at different times. The full lines are the results of the DDF equation and the dots are the average over 2000 Langevin simulations. The results have been shifted in the vertical direction to allow a clear view.

There are other equivalent ways to calculate F (like taking the weighting graining only towards the right, or towards the left) which yield the same value of F for any density distribution. Using Eq. (15) we obtain the following equation for the time evolution of the density:

$$\frac{\partial\rho(x,t)}{\partial t}=\frac{\partial^2\rho(x,t)}{\partial x^2}+\frac{\partial}{\partial x}\left[\rho(x,t)\left(\frac{\rho(x+\sigma,t)}{1-\eta(x+\sigma/2,t)}-\frac{\rho(x-\sigma,t)}{1-\eta(x-\sigma/2,t)}\right)\right]+\frac{\partial}{\partial x}\left[\rho(x,t)\frac{dV_{\text{ext}}(x)}{dx}\right], \tag{21}$$

where we have chosen the energy units such that $T=1$.

The first term in Eq. (21) represents the diffusion equation for ideal gas case, the second term is the correction due to the hard-rod interaction. It is worthwhile to point out that $\rho(x)\rho(x+\sigma)/[1-\eta(x+\sigma/2)]$ is just the two-point equilibrium correlation function $\rho_0^{(2)}(x,x')$ evaluated at contact, i.e., when $x'=x+\sigma$, so that this term takes into account the collisions of the rod at x with the remaining particles on the right hand side. Similarly the other term describes the interactions with the left sector.

When the density profile varies very smoothly (compared with the hard-rod length) the second term may be written in terms of the local chemical potential and the compressibility and one obtains a diffusion equation with a renormalized constant.

A. Free expansion from a dense state

Our first check has been to compare the results of Langevin simulations in Eq. (1) with the results obtained by means of the DDF Eqs. (15) and (21), using the exact $F[\rho]$, for the free expansion of N hard rods in absence of external potential. In Fig. 1 we present the density profiles for a system of $N=8$ hard rods of unit length, $\sigma=1$. The temperature is

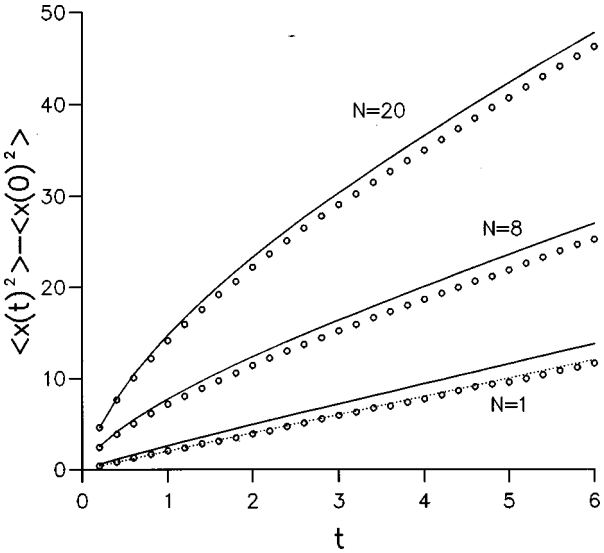

FIG. 2. Mean squared displacements for systems of N hard rods of unit length, in free expansion from highly dense initial state. The full lines are the results of the DDF equation and the open circles are the average over 2000 Langevin simulations, for the respective values of $N=1$, 8, and 20. The dotted line is the result for any number of ideal, noninteracting, particles.

fixed to $T=1$ and in the initial configuration, at $t=0$, the rods are set at fixed positions separated by a distance 1.05 between their centers. In the first stages of the time evolution each rod develops a Gaussian density distribution, and the superposition of all the rods gives a total density distribution with strong oscillations, typical of tightly packed hard molecules. With increasing time the packet expands, the oscillations become weaker and then disappear. For very large t (not shown in the figure) the packet becomes very wide, with $\rho(x,t)\ll 1$ everywhere, so that the collision term in Eq. (21) is nearly irrelevant. In that limit the system evolves like an ideal gas with a gaussian distribution of width proportional to $\sqrt{2t}$.

The dots in Fig. 1 are the average over 2000 Langevin simulations for the same system. The qualitative trend is similar to the DDF results, but the damping of the oscillations is clearly slower in the simulation. In Fig. 2 we present the time evolution of $\langle x(t)^2-x(0)^2\rangle$ for packets with $N=1$, 8, and 20, to give a measure of the rate of expansion. The dotted line is the exact result for the ideal gas, $\langle x(t)^2-x(0)^2\rangle=2t$, which is independent of N. For hard rods there is a clear enhancement of the effective expansion rate, because the rods at the two ends of the packet have a strong bias towards moving away from the the packet. The result of this effect increases with N because it acts until the whole packet has expanded. For $t\gg 1$ and any value of N the slope of $\langle x(t)^2-x(0)^2\rangle=2t$ goes to the ideal value, but the enhanced expansion at small t produces a shift of the values with respect to the ideal gas. The comparison between the DDF and the average over 2000 Langevin simulations again shows the same overall trend and also the same dependence with N, but the DDF always gives a slightly larger expansion rate. The case with $N=1$ offers a clear explanation for this discrepancy: with a single rod in the system there should be no collisions and the results should be those of the ideal gas, but the second term in the DDF in Eq. (21), obtained with the exact $F[\rho]$, still gives a contribution, unless $\rho(x,t)\rho(x+\sigma,t)=0$ for any x. The reason is that in the exact $F[\rho]$ Eq. (18), as for any density functional used in the DDF, the density distribution has to be interpreted in the grand-canonical ensemble. It corresponds to a system in contact with a particle reservoir, in which the chemical potential is set to give the average value of N; however, the configurations contributing to the density distribution may have any number of particles. In the system with $\langle N\rangle=1$, there would be contributions from the density distributions with $N=2$, 3,... (compensated with the contribution with $N=0$), and these contributions include the effects of the collisions.

In general, the fluctuation in the number of particles opens a relaxation path which is not present in the Langevin simulations, carried with fixed N. This extra relaxation path produces the faster damping of the oscillations in the density profiles and the larger diffusion rate of the DDF. The effect is important only in the intermediate stage of the expansion because for $t\ll 1$ the compressibility of the system is too low to have important fluctuations in N and for $t\gg 1$ the system is so diluted that the total effect of collisions is negligible.

B. Collapse to a dense equilibrium state

In Fig. 3 we display the density profiles for a system of four hard rods falling to the bottom of a parabolic potential well, $\beta V_{\text{ext}}(x)=ax^2$, with $a=10$. At $t=0$ the rods are located at $x=\pm 3$ and $x=\pm 6$, well separated from each other. During the first stages of the time evolution each rod follows a steady drift due to the external force and, at the same time, they develop Gaussian peaks of increasing width, due to the random diffusion. The collisions between the two rods at each side of the potential well become important for $t\approx 0.05$; later the two packets collide and relax to the equilibrium density distribution, which is reached for $t=0.1$, within our numerical precision. The results of the DDF and the average over 2000 Langevin simulations are in good agreement, although small discrepancies may be observed both in the early drifting peaks and in the final (equilibrium) profiles. The origin of these discrepancies is again the difference between the Langevin simulation with fixed N and the grand-canonical DDF. The final equilibrium density distribution with the Langevin simulation corresponds to the canonical ensemble and for systems with small number of particles it is known to be different from the grand-canonical distribution.[28] In our case, the difference depends on the value of the parameter a, in the external potential: for $a\gg 1$ the rods are very tightly packed, the compressibility is very low and the fluctuations in the number N are very small; for $a\ll$ the final equilibrium profile is very broad, without oscillations, and the effect of the collision is too weak to produce observable differences; but for intermediate values $a\approx 1$ the difference between the canonical and the grand-canonical ensemble may be quite important and it is reflected in the different time evolution predicted by the DDF and by the Langevin simulations. The use of a canonical $F[\rho]$ in the DDF in Eq. (15) would, in all probability, give a better agreement between the two methods, but unfortunately we

are not aware of any explicit canonical density functional for interacting particles. Nevertheless, the use of the equilibrium $F[\rho]$ to include the role of the molecular correlations is always an approximation, so that even without considering the difference in the thermodynamic ensemble, it was not obvious that the agreement between the DDF and the Langevin simulation would be as good as observed in the preceding figures.

C. Relaxation through highly correlated states

The third check of the theory, being considered, is the relaxation in a system which requires strongly correlated motions of all the particles. We place the hard rods in a periodic external potential $V_{\text{ext}}(x) = -V_o \cos(2\pi x)$, with minima at any integer values of x. The hard-rods length is taken as $\sigma = 1.6$, so that two rods cannot be at the bottom of nearest-neighbor wells. We take periodic boundary conditions with total length $L = 8$ and set $N = 4$ rods, which at the initial time are at the bottom of every second well of $V_{\text{ext}}(x)$. The equilibrium density distribution, which may be obtained directly by the minimization of the exact free energy density functional, has the full symmetry of the external potential, so that the relaxation process has to shift (on average) half a particle from the initially occupied wells to those wells which are initially empty. However, the jump of a rod over the barrier, to the next potential well, is not compatible with keeping the next rod at the bottom of its potential well. The system has to pay the extra energy of keeping the two consecutive rods away from the minima or it has to relay on a correlated motion of the N rods, to shift from one subset of minima to the other one.

In Fig. (4) we present the time evolution of the density profiles with $\beta V_o = 2$ showing different times, for both the DDF Eqs. (15) and (21) and the average of the Langevin simulations over 2000 realizations of the noise. In both cases the relaxation is slow (compared with the previous examples) and it becomes much slower for increasing values of βV_o or σ. In agreement with our general prediction Eq. (17), the system flows to the unique equilibrium state, density peaks grow at the positions of the potential wells which were initially empty until the exact equilibrium density profile is obtained. The comparison of the result clearly shows that the DDF equation, with the exact Percus free energy, approaches the equilibrium state faster than the average of the Langevin simulation. This difference is related again to the use of different statistical ensembles: the canonical Langevin equation keeps constant N while the grand-canonical $F[\rho]$ allows for fluctuations in the number of particles, keeping only the average. The changes in N in the DDF open a new relaxation path and gives a faster relaxation, even is the final equilibrium density profiles in the canonical and the grand-canonical ensembles are very similar.

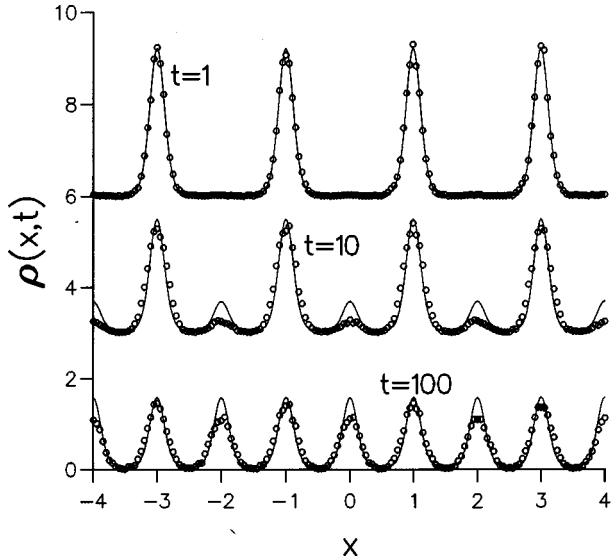

FIG. 4. Density profiles of four hard rods of length $\sigma = 1.6$ in a periodic external potential with eight minima separated by the unit length. In the initial state the rods are in alternate minima, located at the odd integer values of x, and the system relaxes towards the equilibrium state in which all the potential wells are equally populated. The full lines are the results of the DDF equation and the circles are the average over 2000 Langevin simulations. The results have been shifted in the vertical direction.

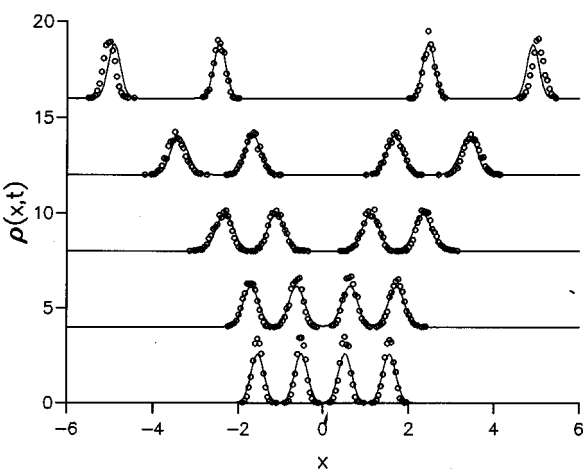

FIG. 3. Density profiles of four hard rods of unit length, collapsing to the equilibrium state, in a parabolic potential. The full lines are the results of the DDF equation and the circles are the average over 2000 Langevin simulations. The results have been shifted in the vertical direction and they correspond, from top to bottom from $t = 0.01$ to $t = 0.09$, at 0.02 intervals. The equilibrium state is very close to the later time results.

To get a quantitative description of the relaxation times we define an order parameter which gives, at any time, the relative difference between the occupation of the odd and the even potential wells, $\xi = (N_{\text{odd}} - N_{\text{even}})/N$. The initial condition sets $\xi = 1$ and the final equilibrium state corresponds to $\xi = 0$. Both in the case of the DDF and of the Langevin dynamics we observe a pure exponential decay, $\xi(t) = \exp(-t/\tau)$ so that whole process may be described by the relaxation time τ. The importance of the particle correlations in the slowing of the relaxation dynamics is shown in Fig. (5) through the dependence of the relaxation time with on the size of the hard cores, $\tau(\sigma)$, keeping the same external potential. Both the Langevin dynamics and the DDF show a fast decrease of τ, by nearly two orders of magnitude, when the rod size decreases from $\sigma = 1.6$ to $\sigma = 1$, which makes the occupancy of neighbor potential wells easier.

The increase of the external potential amplitude, for

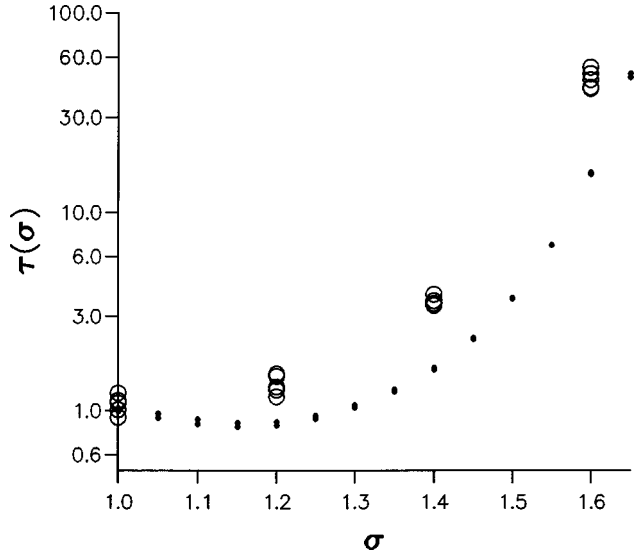

FIG. 5. Relaxation time τ for the system in Fig. 4 as a function of the rod length σ, for fixed amplitude of the external potential $\beta V_o = 2$, calculated from the results of the DDF equation (dots) and the average over 2000 Langevin simulations (circles), the dispersion of the data reflects the results of $\tau = -t/\log[\xi(t)]$ at different times.

fixed $\sigma = 1.6$, produces similar results, as presented in Fig. 6. The relaxation time grows faster than exponentially with βV_o, and the results of the DDF follow from below the general trend of the Langevin dynamics, over several order of magnitude for τ. For comparison we present in the same figure the relaxation times for the ideal gas in the same external potential.

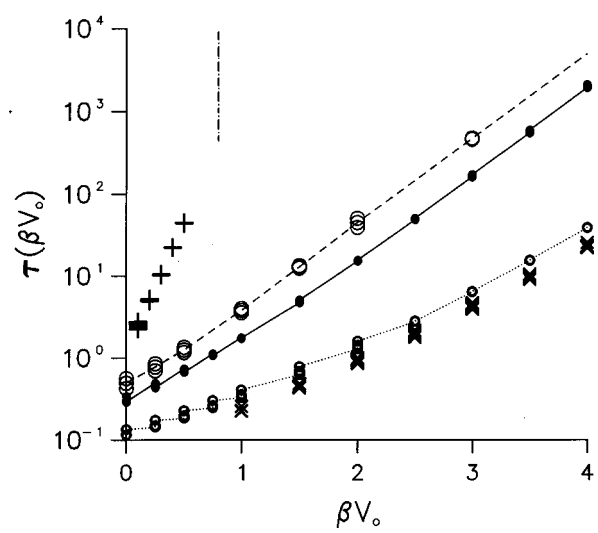

FIG. 6. Relaxation time τ for the system in Fig. 4 as a function of the external potential amplitude βV_o, for fixed rod length $\sigma = 1.6$, from the results of the DDF equation with the exact $F[\rho]$ (dots and full line) and the average over 2000 Langevin simulations (large circles and dashed line). For comparison we include the ideal gas results (small circles and dotted line). In all the cases the lines are a guide to the eye. We also include the results of the DDF equation with approximate $F[\rho]$: WDA (+) and RY (×). The vertical dash-dotted line is the approximated location of the divergence of the WDA relaxation times, for larger values of βV_o the results of this approximation do not decay to $\xi = 0$.

The conclusion is that the DDF formalism, with the exact equilibrium free energy density functional, is able to reproduce qualitatively the low relaxational dynamics of a system produced by the packing constraints of molecular hard cores. In our example the final equilibrium state, with equal occupancy of all the potential wells, represents a superposition of highly correlated states, in which all the particles are in alternate wells, either in the odd or the even positions. The relaxation from the asymmetric initial state requires strong correlations, with all the particles moving together or in cascade, and the unlikeliness of these correlations gives the long relaxation time. This process may be regarded as a (very simplified) simile of the relaxation from a very dense, noncrystalline initial state: the approach to equilibrium may require the correlated rearrangement of many molecules, the unlikeliness of these correlations produces relaxation times which are so long that the system may appear as frozen in an ill crystallized state.

IV. RESULTS WITH APPROXIMATE DENSITY FUNCTIONALS

The one-dimensional hard-rod system provides an interesting test to the DDF, because we may use the exact equilibrium density functional. Unfortunately, given the Hamiltonian describing a set of N interacting particles in a d-dimensional space, the exact free energy functional is in general unknown, since the exactness would be equivalent to calculating the exact partition function of the model in any external potential. Consequently one must rely on suitable approximation schemes and, in the case of repulsive hard-core interactions, there exist several approximate methods which yield accurate results.[3] The requirements imposed are first, one must recover the thermodynamic properties of the homogeneous fluid; second, one must reproduce the structure of highly inhomogeneous systems; finally, the approximation must satisfy a number of exact relations.

Among the most successful density functionals approximations for the free energy of hard spheres we have those known under the generic name of weighted density approximations (WDA). The main assumption is that for each particle, at some point $\mathbf{r}$, there is a contribution to the excess free energy, $\phi[\overline{\rho}(\mathbf{r})]$, which is a local function of a weighted density $\overline{\rho}(\mathbf{r})$, obtained by averaging the true density profile $\rho(\mathbf{r})$ over a small region centered at $\mathbf{r}$:

$$\overline{\rho}(\mathbf{r}) = \int d\mathbf{r}' w(|\mathbf{r}-\mathbf{r}'|, \overline{\rho}(\mathbf{r}))\rho(\mathbf{r}'). \tag{22}$$

The excess free energy per particle, $\phi(\rho)$, is obtained from the bulk equation of state and the weight function is set to get a good (approximate) description of the bulk correlation structure. Different recipes have been used and in general they require a density dependent weight function.[20,21] However, even the simplest version in which $w(r)$ is taken to be density independent and equal to the normalized Mayer function, $f = 1 - \exp[-\beta V(r-r')]$, is enough to give a qualitative description of the hard-sphere freezing.[20]

In this section we explore the consequences of using the DDF formalism, Eq. (15) with approximate forms for $F[\rho]$,

so that the molecular correlations are represented by an approximation to the true equilibrium correlations. To carry out this analysis we study the same systems described in the previous section but instead of taking the exact Percus density functional, Eq. (18), we use an approximate description of the hard rods similar to those developed for hard spheres. In particular, the WDA for hard rods with the exact bulk equation of state and the zeroth-order constant weight function takes

$$\Delta F_{\mathrm{WDA}}[\rho(x)]=\int_{-\infty}^{\infty} dx\,\phi[\overline{\rho}(x)]\rho(x), \tag{23}$$

with the exact $\phi(\rho)$ given by Eq. (19) and

$$\overline{\rho}(x)=\int_{-\infty}^{\infty} dx'\rho(x')w(|x-x'|)=\frac{1}{2\sigma}\int_{x-\sigma}^{x+\sigma} dx'\rho(x'). \tag{24}$$

The time evolution equation from the DDF in Eq. (15) with this density functional approximation is similar to Eq. (21) but with the bracket in the second term given by

$$\frac{\delta\Delta F_{\mathrm{WDA}}[\rho]}{\delta\rho(x)}=\frac{1}{2}\left(\frac{\rho(x+\sigma,t)}{1-\overline{\rho}(x+\sigma,t)}+\frac{\rho(x+\sigma,t)}{1-\overline{\rho}(x,t)}-\frac{\rho(x-\sigma,t)}{1-\overline{\rho}(x-\sigma,t)}-\frac{\rho(x-\sigma,t)}{1-\overline{\rho}(x,t)}\right). \tag{25}$$

Notice that the weighted density $\overline{\rho}(x)$ averages the density profile from $x-\sigma$ to $x+\sigma$, while the variable $\eta(x)$, in the exact DF, takes the average only over half that distance. There is also a different combination of the functions evaluated in Eqs. (21) and (25), but it is easy to check that in the low density limit, truncating at second order in the density, both equations become identical. This reflects that the WDA includes the exact leading term of the molecular correlations in a density expansion, while the higher-order terms are approximated. For the equilibrium properties it is known that this type of zeroth-order WDA overestimates the effects of the hard-core packing and it becomes more accurate when the weight function is allowed to depend on the weighted density.

The results obtained with this approximate free energy for the problems A and B in the previous section are qualitatively similar to those with the exact $F[\rho]$. In the free expansion of a dense state the WDA keeps the oscillations in $\rho(x,t)$ for a longer time than the results with Eq. (21), reflecting the overestimation of the hard core packing, but the mean square displacements are very similar to those in Fig. (2). The equivalent trends are observed in the problem B; although there is some difference between the exact and the WDA equilibrium states, the dynamics is rather similar. We have also checked, in some cases, that the use of a better WDA approximation, with the density dependence of the weight function expanded up to second order, gives results closer to those with the exact $F[\rho]$. In this way we have checked that the practical use of the DDF formalism does not depend on having the exact equilibrium $F[\rho]$. The use of WDA or other density functional approximations opens a wide road for the study of the dynamical properties of many systems, with a level of approximation comparable to the accuracy of the results for the equilibrium properties.

The system studied in the last subsection provided the most severe test for the DDF, since it was the case in which the molecular correlations played the most important role, and this system is the one in which the the use of an approximated $F[\rho]$ may lead to qualitative differences. We have solved Eq. (15) with Eq. (25) for the same system of $N=4$ hard rods in a periodic external potential as before and look for the relaxation from the asymmetric density distribution. For the system presented in Fig. (4), with $\sigma=1.6$ and $\beta V_o=2.$, there is a qualitative difference with the results of using the exact $F[\rho]$. With the WDA free energy the time evolution of $\rho(x,t)$ goes to a stable very asymmetric profile, with an order parameter $\xi=0.99216$, indicating that the particles remain mainly in the potential wells where they are initially located. The freezing of the initial asymmetry is only possible because the WDA equilibrium free energy for this system has two different minima, with positive and negative values of ξ, instead of the single minimum with $\xi=0$ given by the exact $F[\rho]$. The approximate inclusion of the hard-core correlations in the WDA is not good enough to average over the two types of configurations which appear as separated equilibrium states and, for the same reason, the DDF equation cannot include the dynamic path between the two types of configurations.

For lower values of the external potential (or higher temperature) we find that the final order parameter predicted by the WDA decreases, as in a phase transition. Indeed, the splitting of the equilibrium state is nothing but a spurious phase transition predicted by an approximate $F[\rho]$. Below a critical value of $\beta V_o\approx 0.7$ the WDA recovers a single symmetric equilibrium state with $\xi=0$. The relaxation time diverges as we approach the phase transition and it is presented in Fig. 6 together with the results of the exact $F[\rho]$. This divergence is obviously a spurious result of the approximation used for $F[\rho]$. The only reasonable interpretation is that whenever an approximate free energy density functional has different local minima, in which the DDF equation may get trapped, the exact dynamics of the system would require rather long times to relax the density along the functional path related to the ''order parameter'' of the spurious phase transition. The DDF with the WDA is good enough to identify the slow density path, along the parameter ξ, and it is good enough to describe the relaxation dynamics along other functional directions, but it cannot be used to describe the relaxation of ξ.

We have checked that on improving the WDA, by including the density dependence of the weight function, the spurious phase transition is shifted towards larger values of βV_o. Again a better approximation for the equilibrium free energy functional also gives a better account of the molecular correlations in the DDF equation, since it is able to find relaxation paths which ''were not seen'' by simpler DF approximations. However, when βV_o goes beyond a new threshold value (i.e., when the exact relaxation time becomes too large for the approximate $F[\rho]$) the spurious phase transition reappears.

We have also tested the predictions of the DDF with an

even simpler approximation for the equilibrium density functional. This is the Ramakrishnan–Youssouf (RY) functional,[25,7] sometimes referred as the HNC density functional approximation, which considers a functional Taylor expansion of the free energy about a global mean density ρ_b. Truncating the series at the second order (higher order coefficients are in general not known) one gets:

$$\Delta F_{\mathrm{RY}}[\rho] = -\frac{1}{2}\int d\mathbf{r} \times \int d\mathbf{r}'[\rho(\mathbf{r})-\rho_b]c_b(\mathbf{r}-\mathbf{r}')[\rho(\mathbf{r}')-\rho_b], \tag{26}$$

where $c_b(\mathbf{r}-\mathbf{r}')$ is the direct correlation function of a uniform fluid with density ρ_b. The merit of the RY functional is that it is perhaps the simplest recipe and is easy to implement numerically. However it requires that the system have a well-defined mean density, ρ_b, and it may become unreliable when the density varies rapidly over a length scale of the order of molecular size. Notice that in our case using the RY approximation is equivalent to saying that during its evolution the system has the same two point correlations that it would have at constant density ρ_b.

In our one-dimensional hard-rod system we may use the exact direct correlation function of the bulk hard-rods system, and the DDF equation is again similar to Eq. (21) but with the second term bracket given by

$$\frac{\delta \Delta F_{\mathrm{RY}}[\rho]}{\delta \rho(x)} = \left(\frac{\rho(x+\sigma,t)-\rho(x-\sigma,t)}{1-\eta_b} + \rho_b \frac{\eta(x+\sigma/2,t)-\eta(x-\sigma/2,t)}{1-\eta_b^2} \right). \tag{27}$$

The application to examples A and B is uncertain because they do not have a clearly defined mean density. In the third example we have used Eqs. (15) and (27) with the obvious choice $\rho_b = N/L = 0.5$ to get the relaxation of the density distribution in the periodic external potential. The results, in Fig. 6, show a surprisingly fast relaxation towards the symmetric density profile. This density functional approximation never has spurious minima, so that the dynamics is never trapped in asymmetric distributions, but the relaxation is even faster than in the ideal gas case, in clear contradiction with the Langevin simulation. This shows an example opposite to the WDA result, the effect of the approximation for the free energy may be to underestimate the packing effects. In this case there is no risk that the system gets trapped out of the true equilibrium, but the approximation fails to describe the long relaxation times imposed by these packing constraints.

V. CONCLUSIONS

We have presented a dynamic density functional approach for the relaxation of a classical system in terms of its equilibrium free energy density functional $F[\rho]$. The approach is valid only when the velocity correlations (not included in $F[\rho]$) are irrelevant, which excludes hydrodynamic modes and temperature gradients but may include problems like the Brownian motion of colloidal particles and the molecular rearrangements of highly packed systems, when the collision time is much shorter than the relaxation time. In the derivation of the approach we start with the stochastic equations for the Langevin dynamics of Brownian particles and get a deterministic DDF equation for the time dependence of the density distribution, $\rho(\mathbf{r},t)$, which has to be interpreted as the ensemble average over the realizations of the random noise in the Langevin dynamics. The equilibrium DF formalism is used to go from a formal BBGKY hierarchy, for the coupled dynamics of the n-particle distribution functions, to a closed DDF equation for $\rho(\mathbf{r},t)$. The assumption leading to this result is that the correlation structure in the system out of equilibrium is replaced by that in the equilibrium system with the same density distribution. Moreover, we do not need to calculate the correlation structure explicitly because its effects on the dynamics are given directly in terms of the functional derivative of $F[\rho]$.

The main advantage of the approach, for practical purposes, is being able to use the good approximations developed for the free energy functional of hard-core molecules to include the packing constraints in the dynamics of dense systems. We have presented several examples of one-dimensional hard rods to compare the DDF with the average of Langevin simulations. The results, with the exact $F[\rho]$, are always in qualitatively good agreement, even in those cases in which the dynamics becomes extremely slow, when the relaxation requires very unlikely correlations between the particles. The main source of discrepancy is probably due to the fact that the free energy density functional developed for equilibrium always refers to the grand-canonical ensemble, so that the DDF includes the relaxation through changes in the number of particles, while the Langevin dynamics keeps N fixed. With the use of approximate density functionals, of the same type as developed for realistic models in three dimensions, we get an approximate description of the relaxation dynamics of a quality comparable to that for the equilibrium properties arising from the same $F[\rho]$. In some cases, when the role of the correlations is not too important and the relaxation times are not too long, the approximate $F[\rho]$ is fairly accurate for the dynamic properties. In the third case, in which strong effects of the hard core packing lead to very long relaxation times, the difference between the results of the exact and the approximate $F[\rho]$ are qualitative both for the equilibrium and for the dynamic properties. The presence of different local minima in the equilibrium free energy density functional produces, in the approximate DDF equation, the permanent freezing of system in any of these states, in contrast with the results of the exact free energy functional.

In an interesting series of papers Kawasaki[6] derived a dynamic equation, in terms of a density functional hamiltonian $H[\rho]$, by a method different from ours, but his resulting Fokker–Planck equation for the probability distribution of the density:

$$\frac{\partial P[\rho(\mathbf{r}),t]}{\partial t} = -\int d\mathbf{r} \frac{\delta}{\delta\rho(\mathbf{r})} \nabla\cdot\rho(\mathbf{r})\nabla\left[T\frac{\delta}{\delta\rho(\mathbf{r})} + \frac{\delta H[\rho]}{\delta\rho(\mathbf{r})}\right]P[\rho(\mathbf{r}),t] \tag{28}$$

is equivalent to our Eq. (15), apart from the presence of a term due to the stochastic noise. If ρ in Kawasaki Eq. (28) is interpreted as a density operator, $\hat{\rho}(\mathbf{r},t)$, his approach is equivalent to Dean's Eq. (10); leading to a stochastic equation for this density operator. The main qualitative difference of this approach with our deterministic Eq. (15) is that, when the approximate density functional for the equilibrium free energy has different local minima, the random noise in the DDF equation would always give a chance for changing from one minimum to another. The long time average of the density would always be a superposition of the density in the different local minima and the long relaxation times would appear as the result of high barriers between the local minima. All these features may appear to be physically correct and to represent a qualitative improvement over the deterministic DDF developed here. However, the use of the equilibrium free energy density functional requires always a density defined as a thermal ensemble average, while Eq. (10) refers to the instantaneous density operator. The Hamiltonian H in Eq. (28) should also be a functional of the density operator, $\hat{\rho}(\mathbf{r},t)$, and it is a completely different mathematical object that the excess free energy $\Delta F[\rho]$, as a functional of the equilibrium density $\rho_o(\mathbf{r})$. Thus, Eqs. (10) and (28) are correct, for the density operator $\hat{\rho}(\mathbf{r},t)$ but impossible to translate in terms of the equilibrium free energy density functional. On the other hand, if these equations are interpreted as equations for the ensemble averaged density, $\rho(\mathbf{r},t)$, the random noise term would lead to a double counting of thermal fluctuations in the equation for $\rho(\mathbf{r},t)$. In particular, it would lead to a wrong equilibrium distribution, as can be verified in the simple case of non interacting particles for which the FPE in Eq. (28) converges to a probability distribution:

$$P_{\mathrm{eq}}[\rho(r)] \sim \exp(-F[\rho]/k_B T) = \exp\left[-\int dr\,\rho(\mathbf{r})([\ln\rho(\mathbf{r})-1]+\beta V_{\mathrm{ext}}(\mathbf{r}))\right], \tag{29}$$

where the first term in the exponential is clearly due to the overcounting of thermal fluctuations.

Moreover, we have shown that if we use the exact functional $F[\rho]$ the DDF equation does not require random noise to give the correct results: the system always flows towards the true and unique equilibrium state. The DDF relaxation time may become very long when the system has to go through highly correlated states, but this effect corresponds to systems in which the true relaxation time (in the Langevin description) is also very long. When we use an approximate $F[\rho]$ these long relaxation times may become infinite, with the system trapped at a local minima of $F[\rho]$. An attempt to avoid this effect would require the intensity of random noise not to be proportional to the temperature, but to the error made by the approximation to $F[\rho]$, an error which is obviously unknown until we make a better approximation. Otherwise, the relaxation time given by the stochastic DDF in these cases would just be a direct result of the uncontrolled level of noise kept in the functional equation.

Within our deterministic DDF, the existence of frozen states in the local minima of the approximate $F[\rho]$ should be interpreted as the signature of very long relaxation times, but the only way to calculate how long these times are is to improve the approximation for the equilibrium free energy. Nevertheless, knowing the existence and the approximate structure of these states, as given by workable approximations for $F[\rho]$, is already an interesting use of the DDF, together with its use to study the relaxation process in those cases in which there are no problems with different local minima.

Finally, as a plan for future work, we can consider a systematic way to improve the use of the equilibrium $F[\rho]$ to estimate the correlation structure in the following terms: We tag particle number 1 and follow its position $\mathbf{r}_1(t)$ separately, while all the other particles $(i=2,\ldots,N)$ are included in a density description, with $\rho[\mathbf{r}_1(t),\mathbf{r},t]$ as the noise-averaged conditional probability of finding a particle at position $\mathbf{r}$, and time t, if the tagged particle is at position $\mathbf{r}_1$. Now, we may consider that the $N-1$ particles are moving in an effective external potential, $V_{\mathrm{ext}}(\mathbf{r})+V(\mathbf{r}-\mathbf{r}_1)$, which also contains the interaction with the tagged particle. The equivalent to the DDF Eq. (15) may be applied to the conditional density $\rho(\mathbf{r}_1,\mathbf{r},t)$, which is now coupled to the stochastic equation for $\mathbf{r}_1(t)$. The advantage is that the correlation structure becomes partially described at the level of an effective one-particle density in an effective external potential, which is in principle much easier to describe with approximate free energy density functionals. This type of description would be similar to the ''reaction path'' description of chemical reactions, in which one, or a few, variables are used to describe the relevant functional directions for the changes in the molecular conformations. However, the formal and the practical use of density functional approximations along this line is still an open problem.

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