Phase-space approach to dynamical density functional theory

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We consider a system of interacting particles subjected to Langevin inertial dynamics and derive the governing time-dependent equation for the one-body density. We show that, after suitable truncations of the Bogoliubov-Born-Green-Kirkwood-Yvon hierarchy, and a multiple time scale analysis, we obtain a self-consistent equation involving only the one-body density. This study extends to arbitrary dimensions previous work on a one-dimensional fluid and highlights the subtleties of kinetic theory in the derivation of dynamical density functional theory.

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I. INTRODUCTION

Equilibrium density functional theory (DFT) provides a very powerful tool to investigate the structure of inhomogeneous fluids\cite{1,23}. For systems at thermodynamic equilibrium, all the statistical properties can be expressed in terms of the average density field, $\rho(x)$. In turn, $\rho(x)$ can be obtained by minimizing the grand potential functional, $\Omega[\rho(x)]$, which for a given interaction potential and external one-body potential, is unique. Although $\Omega[\rho(x)]$ is known exactly only in few particular cases, fairly good approximations can be devised, so that the method is versatile and generally applicable with success.

In out of equilibrium situations, there is no rigorous analogue of the free energy, so that the description must be necessarily more complex. In many instances, the density field is not sufficient to represent the state of a system, and one has to identify the minimal set of relevant fields which provide a satisfactory description of its evolution. In the past, phenomenological equations have been devised to deal with a large class of non equilibrium processes, such as Navier-Stokes, reaction-diffusion, Ginzburg-Landau equations, etc\cite{4,5,6}. Standard hydrodynamics, for instance, identifies $d+2$ relevant fields, number, momentum and energy density, where $d$ is the spatial dimensionality of the embedding space, each of these fields satisfying a conservation law, and thus relaxing slowly toward equilibrium. On the other hand, kinetic theory provides a truly microscopic derivation of the Navier-Stokes equations and requires some assumptions about the evolution of the phase space distribution\cite{7}.

When the dynamics of the particles is dissipative and overdamped, as in the case of colloids strongly coupled to the solvent, one may assume that the evolution of the density field is sufficient to capture the relevant physics of the system. This occurs because the momentum and energy fluxes are not conserved any more and thus become rapidly enslaved by the density field. If the friction coefficient, $\gamma$, is large, the particles velocities rapidly relax in a time of order $\gamma^{-1}$, so that the evolution on longer timescales is only determined by the dynamics of the configurational contribution to the distribution. This is the point of view of the Smoluchowski description\cite{8,9,10}, which takes into account only the configurational degrees of freedom. Based on these considerations, in recent years a dynamical density functional theory (DDFT) has been put forward by several authors\cite{11,12}. In DDFT the evolution of the noise-averaged, time-dependent, one-particle density is completely deterministic and is driven solely by the gradient of the equilibrium free energy functional.

In more general terms, inertial effects can play a role in a number of different physical systems, as in the case of colloidal particles weakly coupled to the solvent. Inertial effect must be accounted for by means of the Kramers description in full phase space\cite{20,21}. In the present paper, we derive a deterministic evolution equation for the density field starting from the Kramers equation. A second goal of the present derivation is to show that the kinetic approach leads quite naturally to an evolution equation which contains DDFT as a limiting case.

There are a few reasons for working in the framework of the Kramers equation. The first is that Kramers is a more general description since it contains as limiting cases the Liouville equation and the fully overdamped dynamics. In addition, the Kramers equation allows to deal quite naturally with systems under temperature gradients\cite{22}. Finally, from a fundamental point of view, it seems to us rewarding to reconcile the density functional approach, whose major success has been in explaining equilibrium phenomena, with the kinetic approach which is usually applied to non equilibrium situations. Whereas the current treatments show that it is quite natural to obtain the DDFT equations for overdamped dynamics, it is not straightforward to derive the DDFT from the Liouville equation, such as in the case of a dense liquid, where the hydrodynamic currents carried by particles are not strongly damped by the viscosity.
of the surrounding fluid. A previous work by Marconi and Tarazona has shown that in the case of one dimensional hard-rods the full inertial dynamics gives rise to DDFT in a perturbative analysis truncated at lower order. However, the extension to d-dimensional of this procedure is not trivial, because the number of independent tensorial components of the moments of the distribution increases with the order, $n$, as $d^n$.

We briefly recall the several approaches appeared in recent literature to build the equation of evolution of the one-body density profile in a classical fluid. One class of approaches starts from the fundamental Hamiltonian description of the fluid and aims to derive an equivalent evolution equation for the density. By using the Kawasaki-Gunton projection operator formalism, Yoshimori has recently derived an equation of motion for the density which differs from standard DDFT and is stochastic on account of the coupling with fast degrees of freedom not explicitly retained. Another class of equations for the density is obtained starting from the Langevin microscopic dynamics of the particles. Within this class, some authors have kept the stochastic character of the evolution of the instantaneous density, whereas others have focused attention on an ensemble averaged density and obtained a purely deterministic equation. Both methods do not require spatio-temporal coarse graining.

The different approaches underline the need for a theoretical framework which is capable of deriving equations similar to the DDFT in systems described by second order thermostatted inertial dynamics, instead of the Langevin overdamped dynamics. To this purpose one must consider a phase space rather than a configurational space description. The natural framework turns out to be the kinetic theory which has predated the modern liquid state approaches. Unfortunately, a Boltzmann equation suitably modified to include the coupling to the heat bath only applies to a dilute gas regime. However, several authors have extended the kinetic approach to the dense regime, where the harsh repulsion between particles is taken into account via a revised version of the Enskog theory (RET). Ernst and van Beijeren have obtained the RET equation for the distribution function from the full phase space representation of the N-particle dynamics. In addition, Ernst and van Noije have considered the evolution of thermostatted systems. We assume this theory as the starting point to derive the time evolution equation for the one body density for hard-sphere systems.

The present paper is organized as follows: in section II we describe the microscopic model and write the evolution equation for the N-particle distribution function. Subsequently, we contract the description to the one-particle distribution function, using the BBGKY hierarchy, and separate the velocity from the spatial dependence of the distribution obtaining an open hierarchy for the moments. In section III we close the hierarchy of the distribution functions in the case of two explicit models for the intermolecular forces. In the case of soft potentials we apply a Random Phase Approximation, whereas in the case of hard-core potentials we consider the Revised Enskog Approximation. In section IV we apply the multi-scale method to close the open hierarchy of the moments and to obtain an equation for the density of the system.

II. MODEL

Let us consider an assembly of $N$ heavy particles suspended in a solution of light particles and moving in a d-dimensional region with positions $r_n$ and velocities $u_n$ with $n = 1, N$. Due to their small mass, the solvent particles perform rapid motions so that their influence on the heavy particles can be described according to Langevin’s idea by means of an effective stochastic force. As a result of such elimination of microscopic degrees of freedom the heavy particles experience a viscous drag force proportional to their velocity plus a random stochastic acceleration. In addition the $N$ heavy particles of identical mass $m$ may move under the action of an external force $f_e(x)$ and interact through a pair potential $U(|r - r'|)$, which for simplicity we take as a continuous function. The equations of motions are:

\begin{equation}
\frac{d r_n}{d t} = u_n dt
\end{equation}

\begin{equation}
md\dot{u}_n = \left[ f_e(r_n) - \sum_{m(\neq n)} \nabla r_n U(|r_n - r_m|) - m\gamma u_n \right] dt + dW_n(t)
\end{equation}

where $dW_n(t) = \xi_n(t)dt$ is the increment of the Wiener process and $\xi_n(t)$ is a Gaussian white noise with properties

\begin{equation}
\langle \xi_n^i(t) \rangle = 0 \quad \langle \xi_n^i(t) \xi_n^j(s) \rangle = 2\gamma m k_B T \delta_{mn} \delta^{ij} \delta(t - s)
\end{equation}

where $T$ is the “heat-bath temperature” and $\langle \cdot \rangle$ indicates the average over a statistical ensemble of noise realizations. We include the friction exerted by the solvent via the coefficient $\gamma$.

We now derive an equation for the singly conditioned probability distribution $p(x, t|x_0, v_0)$ defined as the
probability that the random variables \( \{r(t), u(t)\} \) will lie between \( \{x, v\} \) and \( \{x+dx, v+dv\} \) given that \( \{r(0), u(0)\} = (x_0, v_0) \).

Let us consider the infinitesimal time evolution of an arbitrary function \( G(\{r(t), u(t)\}) \) of the trajectory of the system.

\[
dG(\{r(t), u(t)\}) = \sum_n \left\{ u_n \cdot \nabla r_n + \left( \frac{f(r_n)}{m} - \frac{1}{m} \sum_{m(\neq n)} \nabla r_n U(|r_n - r_m|) - \gamma u_n \right) \cdot \nabla u_n \right. \\
+ \left. \frac{\gamma k_B T}{m} \nabla u_n \cdot \nabla u_n \right\} dt + \frac{1}{m} dW_n(t) \cdot \nabla u_n \right\} \frac{\partial}{\partial u_n} G(\{r(t), u(t)\}) \\
\frac{d}{dt} \langle G(\{r(t), u(t)\}) \rangle =
\langle \left\{ \left[ \sum_n \left\{ u_n \cdot \nabla r_n + \left( \frac{f(r_n)}{m} - \frac{1}{m} \sum_{m(\neq n)} \nabla r_n U(|r_n - r_m|) - \gamma u_n \right) \cdot \nabla u_n \right. \\
+ \left. \frac{\gamma k_B T}{m} \nabla u_n \cdot \nabla u_n \right\} \right\} \rangle \frac{\partial}{\partial u_n} G(\{r(t), u(t)\}) \rangle
\]

The average over the realizations of such a function reads

\[
\frac{d}{dt} \langle G(\{r(t), u(t)\}) \rangle =
\sum_n \left\{ u_n \cdot \nabla r_n + \left( \frac{f(r_n)}{m} - \frac{1}{m} \sum_{m(\neq n)} \nabla r_n U(|r_n - r_m|) - \gamma u_n \right) \cdot \nabla u_n \right. \\
+ \left. \frac{\gamma k_B T}{m} \nabla u_n \cdot \nabla u_n \right\} G(\{r(t), u(t)\})
\]

Since the random variables \( \{r, u\} \) have the conditional probability density \( p(\{x, v\}, t|\{x_0, v_0\}, 0) \), we can equally write

\[
\langle G(\{r(t), u(t)\}) \rangle = \int d^N x d^N v G(\{x, v\}) p(\{x, v\}, t|\{x_0, v_0\}, 0)
\]

and

\[
\frac{d}{dt} \langle G(\{r(t), u(t)\}) \rangle = \int d^N x d^N v G(\{x, v\}) \frac{\partial}{\partial t} p(\{x, v\}, t|\{x_0, v_0\}, 0)
\]

Similarly, the r.h.s. of equation (4) can be expressed as

\[
\int d^N x d^N v \sum_n \left\{ v_n \cdot \nabla x_n + \left( \frac{f(x_n)}{m} - \frac{1}{m} \sum_{m(\neq n)} \nabla x_n U(|x_n - x_m|) - \gamma v_n \right) \cdot \nabla v_n \right. \\
+ \left. \frac{\gamma k_B T}{m} \nabla v_n \cdot \nabla v_n \right\} G(\{x, v\}) p(\{x, v\}, t|\{x_0, v_0\}, 0)
\]

We next integrate by parts and discard surface terms in equation (8) and use the arbitrariness of the function \( G \). The result is

\[
\left( \frac{\partial}{\partial t} + \sum_n [L_0^{(n)} - L_{FP}^{(n)}] \right) p(\{x, v\}, t|\{x_0, v_0\}, 0) =
\frac{1}{m} \sum_n \sum_{m(\neq n)} \nabla x_n U(|x_n - x_m|) \cdot \nabla v_n p(\{x, v\}, t|\{x_0, v_0\}, 0)
\]

where we have introduced the notation

\[
L_0^{(n)} = v_n \cdot \nabla x_n + \frac{f(x_n)}{m} \cdot \nabla v_n
\]

\[
L_{FP}^{(n)} = \gamma \left[ \nabla v_n \cdot v_n + \frac{k_B T}{m} \nabla v_n \cdot \nabla v_n \right]
\]

To make contact with the standard statistical mechanical approach, we introduce the \( \Gamma \) phase-space distribution, \( f^{(N)}(\{x, v\}, t) \) as the probability density of finding the many body system between \( \{x, v\} \) and \( \{x + dx, v + dv\} \) at time \( t \). Knowing the value of \( f^{(N)} \) at time \( t = 0 \) we obtain its value at time \( t \) via the relation

\[
f^{(N)}(\{x, v\}, t) = \int dx_0 dv_0 p(\{x, v\}, t|\{x_0, v_0\}, 0) f^{(N)}(\{x_0, v_0\}, 0)
\]
One concludes that the evolution equation for \( f^{(N)}(\{x, v\}, t) \) has the same form as equation (9) relative to \( p(\{x, v\}, t; \{x_0, v_0\}, 0) \), i.e.:

\[
\frac{\partial}{\partial t} + \sum_{n} \left[ L^{(n)}_0 - L^{(n)}_{FP} \right] f^{(N)}(\{x, v\}, t) = \frac{1}{m} \sum_{n} \sum_{m(\neq n)} \nabla_{x_n} U(|x_n - x_m|) \cdot \nabla_{v_n} f^{(N)}(\{x, v\}, t) \tag{13}
\]

If one sets \( \gamma = 0 \), the term \( L^{(n)}_{FP} \) drops and the dynamics turns out to be conservative and the evolution of \( f^{(N)} \) is described by Liouville equation.

The description contained in \( f^{(N)} \) is for any practical purpose unnecessarily detailed, so that we are lead to consider the reduced s-particle distribution functions obtained by integrating over 2\(d(N - s)\) degrees of freedom:

\[
f^{(s)}(x_1, \ldots, x_s, v_1, \ldots, v_s, t) = \frac{N!}{(N-s)!} \int \prod_{n=s+1}^{N} dx_n dv_n \times f^{(N)}(x_1, \ldots, x_s, x_{s+1}, \ldots, x_N, v_1, \ldots, v_s, v_{s+1}, \ldots, v_N, t). \tag{14}
\]

Thus integrating equation (13) over (N-1) particle’s coordinates and velocities we obtain the exact evolution equation for the one particle distribution

\[
\frac{\partial}{\partial t} f^{(1)}(x, v, t) + L_0 f^{(1)}(x, v, t) = L_{FP} f^{(1)}(x, v, t) + k(x, v, t) \tag{15}
\]

where, the left hand side of equation (15) contains the free streaming of the particles, while the right hand side describes the interactions with the heat bath and those among the particles. The interaction term \( k(x, v, t) \), in the case of continuous potentials, reads

\[
k(x, v, t) = \frac{1}{m} \nabla_v \int dx' \int dv' f^{(2)}(x, v, x', v', t) \nabla_x U(|x - x'|) \tag{16}
\]

For particles with hard core interactions the term \( \nabla_x U(|x - x'|) \) is undefined and we have to modify the treatment as briefly explained in section III We remark that \( f^{(1)} \) is the p.d.f. in the 2d dimensional \( \mu \)-space and equation (15), supplemented by equation (16), represents the first equation of the Bogoliubov-Born-Green-Kirkwood-Yvon (BBGKY) hierarchy, which connects the evolution of the \( n \)-particle distribution function, to the distribution function for \((n+1)\) particles. Since \( f^{(1)}(x, v, t) \) depends on the two-particle distribution \( f^{(2)}(x, v, x', v', t) \), some approximate closure is required to obtain a workable scheme.

Before closing this section three remarks are in order: i) the stationary solution \( f^{(N)} \) of equation (13) reduces to the equilibrium Gibbs (N,V,T) phase-space distribution. ii) if we take the limit \( \gamma = 0 \), i.e. decouple the system from the heat bath, the dynamics becomes micro-canonical, i.e. at constant energy, and the evolution of \( f^{(N)} \) is completely reversible. iii) The number density \( \rho(x, t) \) can be obtained from the ensemble average of the microscopic operator \( \sum_n \delta(x - r_n(t)) \), so that \( \rho(x, t) = \int dv f^{(1)}(x, v, t) \), the average particle current is \( j(x, t) = \int dv f^{(1)}(x, v, t) v \) and so on.

In the following we shall employ the non dimensional set of variables which are obtained by measuring the velocities in units of the thermal velocity \( v_T = \sqrt{\frac{k_B T}{m}} \) and lengths in unit of \( \sigma \), i.e. \( V \equiv \frac{v}{v_T} \) and \( X \equiv \frac{x}{\sigma} \). The remaining variables can be non-dimensionalized according to the transformations \( \tau \equiv t v_T^d, \Gamma \equiv \frac{v_T}{v_{\tau}} \), \( \bar{F}(X) \equiv \frac{\sigma}{mv_T} F(x) \). Finally, the distribution function and the collision term are rescaled according to the transformations: \( P(X, \bar{V}, \tau) \equiv \sigma^d v_T^d f^{(1)}(x, v, t) \) and \( K(X, \bar{V}, \tau) \equiv \sigma^{d+1} v_T^{d+1} k(x, v, t) \), where \( d \) is the dimensionality of the embedding space.

By rewriting equation (15) as

\[
\frac{1}{\Gamma} \frac{\partial P(X, \bar{V}, \tau)}{\partial \tau} = L_{FP} P(X, \bar{V}, \tau) - \frac{1}{\Gamma} \bar{V} \cdot \nabla_X P(X, \bar{V}, \tau) - \frac{1}{\Gamma} \bar{F}(X, \tau) \cdot \nabla_{\bar{V}} P(X, \bar{V}, \tau) + \frac{1}{\Gamma} K(X, \bar{V}, \tau) \tag{17}
\]
one sees that, when the non dimensional damping constant $\Gamma$ is large, the Fokker-Planck term

$$L_{FP} P(X, V, \tau) \equiv \nabla_V \cdot \left[ \nabla_V + \dot{V} \right] P(X, V, \tau)$$

(18)

is dominant. This operator has non positive eigenvalues $\nu = 0, -1, -2, \ldots$ and corresponding eigenfunctions $H^{(\nu)}(V)$ defined as

$$H^{(\nu)}(V) = h^{(\nu)}(V) \omega(V)$$

(19)

where

$$\omega(V) = \frac{1}{(2\pi)^{d/2}} e^{-V^2/2}$$

(20)

and the subscript $\alpha$ represents an array of $\nu$ integer elements each ranging from 1 to $d$. The properties and the explicit representation of some of these polynomials are given in appendix A.

To separate the spatial dependence from the velocity dependence we expand the distribution function as:

$$P(x, v, \tau) = \Phi^{(0)}(x, \tau) H^{(0)}(v) + \Phi^{(1)}(x, \tau) H^{(1)}(v)$$

$$+ \frac{1}{2!} \Phi^{(2)}(x, \tau) H^{(2)}(v) + \frac{1}{3!} \Phi^{(3)}(x, \tau) H^{(3)}(v) + \ldots$$

(21)

where the Einstein convention on repeated indices is used. Similarly, we expand the interaction term and obtain

$$K(x, v, \tau) = C^{(0)}(x, \tau) H^{(0)}(v) + \frac{1}{2!} C^{(2)}(x, \tau) H^{(2)}(v) + \frac{1}{3!} C^{(3)}(x, \tau) H^{(3)}(v) + \ldots$$

(22)

The first term $C^{(0)} = 0$ since the number of particles is conserved, while the remaining are obtained from the formula:

$$C^{(l)}(x, \tau) \equiv \int d^dV h^{(l)}(V) K(x, v, \tau).$$

(23)

Using the orthogonality of the tensorial Hermite polynomials one derives a set of differential equations for their coefficients $\Phi^{(l)}(X, \tau)$. This is achieved by multiplying both sides of equation (17) by $h^{(l)}(V)$ and integrating with respect to $V$. One finds the following set of equations, which reduce to the standard hydrodynamic ones for $\Gamma = 0$:

$$\frac{\partial}{\partial \tau} \Phi^{(0)}(X, \tau) = -\partial_X \Phi^{(1)}(X, \tau)$$

(24)

$$\frac{\partial}{\partial \tau} \Phi^{(1)}(X, \tau) = -\Gamma \Phi^{(1)}(X, \tau) - D_i \Phi^{(0)}(X, \tau)$$

$$- \frac{1}{2} \partial_X \left( \Phi^{(2)}_{ij}(X, \tau) + \Phi^{(2)}_{ji}(X, \tau) \right) + C^{(1)}(X, \tau)$$

(25)

$$\frac{\partial}{\partial \tau} \Phi^{(2)}_{ij}(X, \tau) = -2\Gamma \Phi^{(2)}_{ij}(X, \tau) - \left[ D_i \Phi^{(1)}(X, \tau) + D_j \Phi^{(1)}(X, \tau) \right]$$

$$- \partial_X \Phi^{(3)}_{ijk}(X, \tau) + C^{(2)}_{ij}(X, \tau)$$

(26)

having introduced the short hand notation:

$$D_i \equiv \partial_X - F_i$$

### III. EXPLICIT MODELS

In order to proceed further we need to provide an explicit representation of the collision operator $K(X, V, \tau)$. We shall do that in two cases which may serve to illustrate different aspects of the dynamics.
A. Mean-field model

Given a continuous and differentiable pair potential \( U(|\mathbf{X} - \mathbf{X}'|) \), we can write the collision kernel as

\[
K(\mathbf{X}, \mathbf{V}, \tau) = \nabla \mathbf{V} \cdot \int d\mathbf{V}' \int d\mathbf{X}' P^{(2)}(\mathbf{X}, \mathbf{X}', \mathbf{V}, \mathbf{V}', \tau) \nabla \mathbf{X} U(|\mathbf{X} - \mathbf{X}'|) \tag{27}
\]

which contains the two particle distribution function \( P^{(2)}(\mathbf{X}, \mathbf{X}', \mathbf{V}, \mathbf{V}', \tau) \). We assume, as Enskog did, that the doublet distribution function \( P^{(2)}(\mathbf{X}, \mathbf{X}', \mathbf{V}, \mathbf{V}', \tau) \) factors into the product: \( P^{(2)}(\mathbf{X}, \mathbf{X}', \mathbf{V}, \mathbf{V}', \tau) = P(\mathbf{X}, \mathbf{V}, \tau)P(\mathbf{X}', \mathbf{V}', \tau)g_2(\mathbf{X}, \mathbf{X}'|\rho) \) in which the pair correlation \( g_2 \) is not a function of the velocities, but only of the particle positions. It is assumed that \( g_2 \) is a nonlocal equilibrium function of the profile \( \rho(\mathbf{X}, t) \) and depends on time only through the density profile, and to have the same form as in a nonuniform equilibrium state whose density is \( \rho(\mathbf{X}, t) \). Given the above, \( g_2 \) can be determined exactly from the second functional derivative of the free-energy functional for a inhomogeneous system.

With this approximation we find:

\[
K(\mathbf{X}, \mathbf{V}, \tau) = -\mathbf{F}^{mol}(\mathbf{X}, \tau) \cdot \nabla \mathbf{V} P(\mathbf{X}, \mathbf{V}, \tau) \tag{28}
\]

where, using \( \rho(\mathbf{X}, \tau)\sigma^d = \int d\mathbf{V}' P(\mathbf{X}', \mathbf{V}', \tau) \), we have introduced the molecular field

\[
\mathbf{F}^{mol}(\mathbf{X}, \tau) = -\int d\mathbf{X}' \rho(\mathbf{X}', \tau) g_2(\mathbf{X}, \mathbf{X}'|\rho) \nabla \mathbf{X} U(|\mathbf{X} - \mathbf{X}'|) \tag{29}
\]

In order to obtain the coefficients \( C^{(l)}_{\omega} \) one must take the scalar product of the operator given by equation (28) with \( b^{(l)}_{\omega}(\mathbf{V}) \). One finds:

\[
C^{(0)}(\mathbf{X}, \tau) = 0 \tag{30}
\]

\[
C^{(1)}_i(\mathbf{X}, \tau) = -\Phi^{(0)}(\mathbf{X}, \tau) F^{mol}_i(\mathbf{X}, \tau) \tag{31}
\]

\[
C^{(2)}_{ij}(\mathbf{X}, \tau) = -\left[ \Phi^{(1)}_i(\mathbf{X}, \tau) F^{mol}_j(\mathbf{X}, \tau) + \Phi^{(1)}_j(\mathbf{X}, \tau) F^{mol}_i(\mathbf{X}, \tau) \right] \tag{32}
\]

Let us show that at equilibrium the molecular field can be expressed as a gradient. Following Marconi and Tarazona, we consider the relation, valid at thermodynamic equilibrium:

\[
\int d\mathbf{X}' \rho(\mathbf{X}', \tau) g_2(\mathbf{X}, \mathbf{X}'|\rho) \partial_{\mathbf{X}} U(|\mathbf{X} - \mathbf{X}'|) = \partial_{\mathbf{X}} \frac{\delta F^{exc}[\rho(\mathbf{X}, \tau)]}{\delta \rho(\mathbf{X}, \tau)} \tag{33}
\]

where \( F^{exc} \) is the free energy excess over the ideal gas, so that the molecular field is of the form sought. Consequently, we express the first non vanishing component of the interaction as

\[
C^{(1)}_i(\mathbf{X}, \tau) = \sigma^d \rho(\mathbf{X}, \tau) \partial_{\mathbf{X}} \frac{\delta F^{exc}[\rho(\mathbf{X}, \tau)]}{\delta \rho(\mathbf{X}, \tau)} \tag{34}
\]

B. Hard sphere model

The hard sphere (HS) model can be viewed as a collection of hard, perfectly elastic objects. There is no intermolecular force acting on them except at the instant when two spheres are at distance \( \sigma \), the HS diameter. Thus HS, due to the coupling with the stochastic heat bath, behave like non-interacting Brownian particles between collisions. When two HS collide their velocities after the impact, denoted with a prime, are related to those before the impact (unprimed) velocities by

\[
\mathbf{v}'_1 = \mathbf{v}_1 - (\mathbf{v}_{12} \cdot \hat{\mathbf{b}})\hat{\mathbf{b}}
\]

\[
\mathbf{v}'_2 = \mathbf{v}_2 + (\mathbf{v}_{12} \cdot \hat{\mathbf{b}})\hat{\mathbf{b}}
\]

where \( \mathbf{v}_{12} = \mathbf{v}_1 - \mathbf{v}_2 \), \( \hat{\mathbf{b}} \) is the unit vector directed from particle 1 to particle 2.
Using the fact that, although the derivative of the intermolecular potential is ill-defined, the trajectories in phase space are well defined, Ernst and van Beijeren were able to derive the evolution equation of the N-particle distribution function \( f^{(N)}(\{x, v\}, t) \). They proved that the evolution of the \( \Gamma \) phase space distribution for a randomly driven HS fluid is governed by the following pseudo-Liouville equation

\[
\left( \frac{\partial}{\partial t} + \sum_n L^{(n)}_i \right) f^{(N)}(\{x, v\}, t) = \left( \sum_n L^{(n)}_{FP} + \sum_{n<m} \bar{T}(nm) \right) f^{(N)}(\{x, v\}, t)
\]

(36)

The second term on the right hand side of equation (36) contains the binary collision operator \( \bar{T}(mn) \) for HS which accounts for the impulsive hard core interactions and reads:

\[
\bar{T}(mn) = \sigma^{d-1} \int d\hat{\Omega}(\hat{v}_{mn}\hat{\beta})(\hat{v}_{mn} \cdot \hat{\beta}) \left[ \delta(x_{mn} - \hat{\beta})b^{**}_{mn} - \delta(x_{mn} + \hat{\beta}) \right]
\]

(37)

where \( \Theta \) is the Heaviside function which selects only particles approaching one another, \( v_{mn} = (v_m - v_n), x_{mn} = (x_m - x_n) \) and \( b^{**}_{mn} \) is the scattering operator defined for arbitrary function \( S(v_m, v_n) \) by

\[
b^{**}_{mn}S(v_m, v_n) = S(v'_m, v'_n)
\]

(38)

which for elastic HS acts on the velocities \( v_n \), and replaces them by the restituting velocities as defined by equation (35).

Again starting from equation (36) one obtains the first level of the BBGKY hierarchy for the reduced one-particle distribution function \( f^{(1)}(x, v, t) \) which is similar to equation (15). In the HS case the derivation is quite lengthy so that we merely quote the final result of Ernst and van Beijeren for the interaction term

\[
k(x_1, v_1, t) = \sigma^{d-1} \int dv_2 \int d\hat{\Omega}(\hat{\beta} \cdot v_{12}))(\hat{\beta} \cdot v_{12}) \times \{ f^{(2)}(x_1, v'_1, x_1 - \hat{\beta}, v'_2, t) - f^{(2)}(x_1, v_1, x_1 + \hat{\beta}, v_2, t) \}
\]

(39)

where the primes on the velocities denote scattered values determined from equation (55). Finally, we consider the so-called Revised Enskog Theory (RET) which consists in replacing \( f^{(2)} \), using the molecular chaos hypothesis,

\[
f^{(2)}(x_1, v_1, x_2, v_2, t)\delta(|x_{12} - \sigma|) = f^{(1)}(x_1, v_1, t)f^{(1)}(x_2, v_2, t)g_2(x_1, x_2|\rho)\delta(|x_{12} - \sigma|)
\]

where \( g_2(x_1, x_2|\rho) \) is the pair correlation function. It is worth noticing the difference with the mean-field approximation. Here, it is assumed that atoms are uncorrelated immediately prior to collision but are correlated after they collide, because collision itself generates correlations.

We turn hereafter to the nondimensional notation and use capital letters for the reduced variables. With the substitution (40) the collision integral \( K(X, V, \tau) \) can be represented by the following convolution product:

\[
K(X_1, V_1, \tau) = \int dV_2 \int d\hat{\Omega}(\hat{\beta} \cdot V_{12}))(\hat{\beta} \cdot V_{12}) \times \{ g_2(X_1, X_1 - \hat{\beta}|\rho)P(X_1, V'_1, \tau)P(X_1 - \hat{\beta}, V'_2, \tau) - g_2(X_1, X_1 + \hat{\beta}|\rho)P(X_1, V_1, \tau)P(X_1 + \hat{\beta}, V_2, \tau) \}
\]

(40)

We now turn to the evaluation of the coefficients of the collision integral via the Hermite expansion (25). Since this expansion involves an infinite number of coefficients, we need to resort to a suitable truncation scheme. A physically motivated prescription consists in choosing a restricted basis in the complete Hilbert-space of the functions \( h^{(2)}_i \). To this purpose we choose the following \( 2 + d \) functions

\[
\left\{ h^{(0)}(V), h^{(1)}_1(V), \tilde{h}^{(2)}(V) \right\}
\]

(41)

with \( \tilde{h}^{(2)}(V) = \sum_i h^{(2)}_{ii}(V) \), corresponding to the \( 2 + d \) hydrodynamic modes (density, current and energy) which in the absence of thermostat are conserved.

In order to project \( K(X, V, \tau) \) on this basis it is convenient to replace \( (V_1, V_2, \hat{\beta}) \to (V'_1, V'_2, -\hat{\beta}) \) so that the
projection can be written as

\[ C^{(l)}_{\Omega}(X, \tau) = \int dV_1 \int dV_2 \int d\hat{\theta}(\hat{\theta} \cdot V_{12}) \times [h^{(l)}_{\Omega}(V_{1}) - h^{(l)}_{\Omega}(V_{1})]g_{2}(X, X + \hat{\theta} | \rho)P(X, V_{1}, \tau)P(X + \hat{\theta}, V_{2}, \tau) \]  

Equation (42) still represents a cumbersome \((3d-1)\)-fold integral. However, by a change of variables and using simple properties of Gaussian integrals it is possible to perform \(2d\) integrations. In order to see that, we introduce the relative velocity and the center of mass velocity:

\[
\begin{align*}
Z &= V_1 - V_2 \\
Y &= \frac{V_1 + V_2}{2}
\end{align*}
\]

and notice that the Jacobian of transformation from \((V_1, V_2)\) to \((Y, Z)\) is unity, so that the integral becomes, using the Hermite representation of \(P(X, V, \tau)\),

\[
C^{(l)}_{\Omega}(X, \tau) = \int d\hat{\theta}g_{2}(X, X + \hat{\theta} | \rho) \int d²Y \frac{1}{\pi^{d/2}} e^{-Y^2} \int d²Z \frac{1}{\pi^{d/2}} e^{-Z^2} \Theta(\hat{\theta} \cdot Z)(\hat{\theta} \cdot Z) \left[ h^{(l)}_{\Omega}(Y + \frac{Z}{2} - (\hat{\theta} \cdot Z) \hat{\theta}) - h^{(l)}_{\Omega}(Y + \frac{Z}{2}) \right] \times \\
\left[ \Phi^{(0)}(X + \hat{\theta}, \tau) + \sum_{j} h^{(1)}_{j}(Y - \frac{Z}{2}) \Phi^{(1)}_{j}(X + \hat{\theta}, \tau) + \frac{1}{2} h^{(2)}(Y - \frac{Z}{2}) \Phi^{(2)}(X + \hat{\theta}, \tau) \right] \times \\
\left[ \Phi^{(0)}(X, \tau) + \sum_{k} h^{(1)}_{k}(Y + \frac{Z}{2}) \Phi^{(1)}_{k}(X, \tau) + \frac{1}{2} h^{(2)}(Y + \frac{Z}{2}) \Phi^{(2)}(X, \tau) \right] \]
\]

with \(\Phi^{(2)} = \sum_{i} \Phi^{(2)}_{ii}\). The integration over \(Z\) and \(Y\) can be performed straightforwardly with the results:

\[ C^{(0)}(X, \tau) = 0 \]  

\[
\begin{align*}
C^{(1)}_{i}(X, \tau) &= -\int d^{d}\hat{\theta} \hat{\sigma}_{i}g_{2}(X, X + \hat{\theta} | \rho) \left\{ \Phi^{(0)}(X, \tau)\Phi^{(0)}(X + \hat{\theta}, \tau) + \\
&+ \frac{2}{\sqrt{\pi}} \sum_{j=1}^{d} \hat{\sigma}_{j} \left[ \Phi^{(1)}_{j}(X, \tau)\Phi^{(0)}(X + \hat{\theta}, \tau) - \Phi^{(1)}_{j}(X + \hat{\theta}, \tau)\Phi^{(0)}(X, \tau) \right] + \\
&\Phi^{(0)}(X, \tau)\Phi^{(2)}(X + \hat{\theta}, \tau) + \Phi^{(2)}(X, \tau)\Phi^{(0)}(X + \hat{\theta}, \tau) + \\
&- \sum_{j, k=1}^{d} \left[ \frac{1}{2d} \delta_{j,k} \Phi^{(1)}_{j}(X, \tau)\Phi^{(1)}_{k}(X + \hat{\theta}, \tau) - \frac{3}{2} \delta_{j,k} \Phi^{(1)}_{j}(X + \hat{\theta}, \tau)\Phi^{(1)}_{k}(X, \tau) \right] + \\
&+ \frac{1}{\sqrt{\pi}} \sum_{j=1}^{d} \hat{\sigma}_{j} \left[ \Phi^{(1)}_{j}(X, \tau)\Phi^{(2)}_{j}(X + \hat{\theta}, \tau) - \Phi^{(1)}_{j}(X + \hat{\theta}, \tau)\Phi^{(2)}_{j}(X, \tau) \right] \right\} \]
\]
\[ C^{(2)}(\mathbf{X}, \tau) = - \int d^d \sigma g_2(\mathbf{X}, \mathbf{X} + \hat{\mathbf{b}}_j \rho) \times \]
\[
\left\{ \sum_{j=1}^{d} \tilde{\sigma}_j \left[ \Phi_j^{(1)}(\mathbf{X}, \tau) \Phi_j^{(0)}(\mathbf{X} + \hat{\mathbf{b}}, \tau) + \Phi_j^{(1)}(\mathbf{X} + \hat{\mathbf{b}}, \tau) \Phi_j^{(0)}(\mathbf{X}, \tau) \right] \right. \\
\frac{4}{\sqrt{\pi}} \left[ \Phi_0^{(0)}(\mathbf{X}, \tau) \tilde{\Phi}_2^{(2)}(\mathbf{X} + \hat{\mathbf{b}}, \tau) - \tilde{\Phi}_2^{(2)}(\mathbf{X}, \tau) \Phi_0^{(0)}(\mathbf{X} + \hat{\mathbf{b}}, \tau) \right] + \\
\left. \sum_{j=1}^{d} \tilde{\sigma}_j \left[ \Phi_j^{(1)}(\mathbf{X}, \tau) \tilde{\Phi}_2^{(2)}(\mathbf{X} + \hat{\mathbf{b}}, \tau) + \Phi_j^{(1)}(\mathbf{X} + \hat{\mathbf{b}}, \tau) \tilde{\Phi}_2^{(2)}(\mathbf{X}, \tau) \right] \right\} \\
\] (47)

Having now obtained the expressions of the collision matrix elements in the restricted hydrodynamic space, we could in principle insert these into the moment hierarchy equations \([44][46]\). However, the hierarchy is not closed and we need some prescription in order to truncate the expansion. In the following we shall consider a perturbative method to achieve this goal.

IV. MULTISCALE METHOD

The multiple time-scale approach\([46][49]\) represents a powerful perturbative method to determine the temporal evolution of the distribution function \(P(\mathbf{X}, \mathbf{V}, \tau)\) in the high friction limit, \(\Gamma^{-1} << 1\). Physically, such a limit means that many solute-solvent collisions take place while a solute particle travels a distance of the order of its radius. The method is perturbative and the relevant expansion parameter is the inverse dimensionless friction, \(\Gamma^{-1}\). By means of such a procedure Titulaer\([45]\), starting from the Kramers equation, has derived the Smoluchowski equation for a colloidal particle. The latter equation could have also been obtained, without resorting to the multiple time scale method, by simply taking the high friction limit in the microscopic Langevin equation, i.e. dropping the inertial term. However, the perturbative method allows to compute the corrections to the Smoluchowski equation when \(\Gamma\) is finite\([45]\).

To begin with, the moments \(\Phi^{(l)}_{\alpha, \beta}\), their time derivatives and the collision integral are expanded in powers of \(\Gamma^{-1} << 1\):

\[ \frac{\partial}{\partial \tau} = \frac{\partial}{\partial \tau_0} + \frac{1}{\Gamma} \frac{\partial}{\partial \tau_1} + \frac{1}{\Gamma^2} \frac{\partial}{\partial \tau_2} + ... \] (48)

\[ \Phi^{(l)}_{\alpha, \beta} = \phi^{(l)}_{\alpha, \beta} + \frac{1}{\Gamma} \phi^{(1)}_{\alpha, \beta} + \frac{1}{\Gamma^2} \phi^{(2)}_{\alpha, \beta} + ... \] (49)

\[ C^{(l)}_{\alpha, \beta} = c^{(l)}_{\alpha, \beta} + \frac{1}{\Gamma} c^{(1)}_{\alpha, \beta} + \frac{1}{\Gamma^2} c^{(2)}_{\alpha, \beta} + ... \] (50)

Let us remark that, in order to construct the solution, we have replaced the single physical space, \(\tau\), by a set of auxiliary time scales \((\tau_0, \tau_1, .., \tau_n)\) which are related to the original variable by the relations \(\tau_n = \Gamma^{-n} \tau\) and are treated as independent variables. Also, all time-dependent functions of \(\tau\) are replaced by auxiliary functions of \((\tau_0, \tau_1, ..)\). Once the equations corresponding to the various orders have been determined, we return to the original time variable and functions.

Following the method of reference\([44]\), the amplitudes \(\phi^{(n)}\) with \(n > 0\) are set equal to zero. Such a choice, although not unique, is sufficient to eliminate secular terms, i.e. terms containing a dependence on the slow time \(\tau_0\).

Expansions \([48][50]\) must, now, be inserted into equation \((17)\) in order to identify on both sides of the resulting equation terms belonging to the same order in the expansion parameter \(\Gamma^{-1}\) and in the Hermite polynomials. We do not report the lengthy but straightforward derivation but merely write down the set of equations which allows to relate all the amplitudes \(\phi^{(l)}_{\alpha, \beta}\) in terms of the evolution of the amplitude \(\phi^{(0)}_{\alpha, \beta}\).

The order \(\Gamma^0\) yields: \(\phi^{(0)}_{\alpha, \beta} \neq 0\) and \(\phi^{(l)}_{\alpha, \beta} = 0\ \forall l > 0\).

The first power \(\Gamma^{-1}\) instead gives three equations, which allow to determine the amplitudes of order 1:

\[ \frac{\partial}{\partial \tau_0} \phi^{(0)}_{\alpha, \beta} = 0, \] (51)
\[- \phi^{(1)}_{1,i} = D_i \phi^{(0)}_0 - c^{(1)}_{0,i} \] (52)

and

\[ \phi^{(2)}_{1,i} = 0 \] (53)

The following order $\Gamma^{-2}$ gives an equation for the partial $\tau_1$ derivative of the amplitude $\phi^{(0)}_0$ in terms of a spatial derivative of the amplitude $\phi^{(1)}_{1,i}$:

\[ \frac{\partial}{\partial \tau_1} \phi^{(0)}_0 = -\partial_X \phi^{(1)}_{1,i} \] (54)

Thus, using equation (52), we obtain

\[ \frac{\partial}{\partial \tau_1} \phi^{(0)}_0 = \partial_X [D_i \phi^{(0)}_0 - c^{(1)}_{0,i}] \] (55)

At the same order we also find the relation

\[ \frac{\partial}{\partial \tau_0} \phi^{(1)}_{1,i} = -\phi^{(1)}_{2,i} + c^{(1)}_{1,i} = 0 \] (56)

which using the fact that $\phi^{(1)}_{1,i}$ does not depend on $\tau_0$, being a functional of $\phi^{(0)}_0$, in view of equation (52) leads to the equation:

\[ \phi^{(1)}_{2,i} = c^{(1)}_{1,i} \] (57)

Finally, we find:

\[ \phi^{(l)}_n = 0 \ \forall \ l > 1 \] (58)

To order $\Gamma^{-3}$ we need to consider only the relation:

\[ \frac{\partial}{\partial \tau_2} \phi^{(0)}_0 = -\partial_X \phi^{(1)}_{2,i} = -\partial_X c^{(1)}_{1,i} \] (59)

which allows to express the partial derivative of $\phi^{(0)}_0$ with respect to $\tau_2$ in terms of the collision integral.

We restore, now, the original time derivative:

\[ \frac{\partial}{\partial \tau} \phi^{(0)}_0 = (1 - \Gamma) \frac{\partial}{\partial \tau_1} \phi^{(0)}_0 + \frac{1}{\Gamma} \frac{\partial}{\partial \tau_2} \phi^{(0)}_0 \] (60)

and using equations (55) and (59) we arrive at

\[ \frac{\partial}{\partial \tau} \phi^{(0)}_0 (X, \tau) = \frac{1}{\Gamma} \nabla_X \left[ (\nabla_X - F(X)) \phi^{(0)}_0 (X, \tau) - c^{(1)}_{0} (X, \tau) - \frac{1}{\Gamma} c^{(1)}_{1} (X, \tau) \right] \] (61)

As one can see, at this order in the perturbative expansion only the component $\nu = 1$ of the collision operator appears in equation (61). We need to give an explicit representation of $c^{(1)}_{n,i}$ in order to have a closed evolution equation.

In the Vlasov model the procedure is straightforward: in fact, given eq. (31), the amplitudes $c^{(1)}_{n,i}$ only depend on the $\phi^{(0)}_0$, i.e. the density profile. Since such a quantity is of order $\Gamma^0$ in our small parameter expansion, it follows that there is no correction of order $\Gamma^{-1}$. Only at order $\Gamma^{-2}$, which is beyond the scope of the present treatment, one finds a correction to the evolution equation in the Vlasov model.
In the hard-sphere model, instead, we have the two following terms:

\[ c^{(1)}_{0,i}(\mathbf{X}, \tau) = -\int d\hat{\mathbf{b}}\hat{\mathbf{b}}\hat{g}_2(\mathbf{X}, \mathbf{X} + \hat{\mathbf{b}})\phi_0^{(0)}(\mathbf{X}, \tau)\phi_0^{(0)}(\mathbf{X} + \hat{\mathbf{b}}, \tau) \]  

\[ c^{(1)}_{1,i}(\mathbf{X}, \tau) = -\frac{2}{\sqrt{\pi}}\int d\hat{\mathbf{b}}\hat{\mathbf{b}}\hat{g}_2(\mathbf{X}, \mathbf{X} + \hat{\mathbf{b}})\times \]

\[ \sum_{j=1}^{d}\hat{\sigma}_j[\phi_{1,j}^{(1)}(\mathbf{X}, \tau)\phi_0^{(0)}(\mathbf{X} + \hat{\mathbf{b}}, \tau) - \phi_{1,j}^{(1)}(\mathbf{X} + \hat{\mathbf{b}}, \tau)\phi_0^{(0)}(\mathbf{X}, \tau)] \]

\[ \phi_{1,j}^{(1)}(\mathbf{X}, \tau) = -\left(\partial_{X_j} - F_i(\mathbf{X})\right)\phi_0^{(0)}(\mathbf{X}, \tau) + c^{(1)}_{0,i}(\mathbf{X}, \tau). \]

We show next that if we keep only the term \( c^{(1)}_{0,i} \) and drop the term \( c^{(1)}_{1,i} \) of order \( \Gamma^{-1} \) in equation (61) we recover the time dependent DDF equation. In fact, using the following expression for the HS impulsive force:

\[ \partial_{X_i}U_{HS}(|X - X'|) = -\hat{\sigma}_i\delta(|X - X'| - 1), \]

where \( U_{HS}(|X - X'|) \) is the HS pair potential, we can rewrite eq. (62) as

\[ c^{(1)}_{0,i}(\mathbf{X}, \tau) = \int d\mathbf{X}'\hat{g}_2(\mathbf{X}, \mathbf{X}'|\phi_0^{(0)}(\mathbf{X}, \tau)\phi_0^{(0)}(\mathbf{X}', \tau)\partial_{X_i}U_{HS}(|\mathbf{X} - \mathbf{X}'|) \]

or, using relation (33), in the equivalent form:

\[ c^{(1)}_{0,i}(\mathbf{X}, \tau) = \phi_0^{(0)}(\mathbf{X}, \tau)\partial_{X_i}\frac{\delta F^{\text{exc}}_{HS}([\mathbf{X}, \tau])}{\delta \phi_0^{(0)}(\mathbf{X}, \tau)} \]

where \( F^{\text{exc}}_{HS} \) is the excess contribution to the hard sphere free energy over the ideal gas value. Finally, we remark that terms of higher order in \( \Gamma^{-1} \) representing dynamical corrections to the overdamped result, such as \( c^{(1)}_{1,i}(\mathbf{X}, \tau) \), are functionals of \( \phi_0^{(0)}(\mathbf{X}, \tau) \), but cannot be expressed as functional derivatives of the free energy. They play a role only when the system is out of equilibrium, i.e. when currents are present.

**V. DISCUSSION**

In this paper we have derived the DDFT equation for the noise averaged density \( \rho(\mathbf{x}, t) \) relative to a system of particles with inertia and driven by a stochastic heat-bath. The starting point is the many particle Kramers equation for the phase space distribution which corresponds to the Langevin equations of motion. Such a microscopic model describes fluids, where, due to the interactions with the solvent, the momentum and energy reach equilibrium on a faster scale than the slowly varying number density. In more detail, we employed the standard BBGKY hierarchy to derive an exact evolution equation for the one particle distribution in terms of the two-particle distribution function. In the case of a soft intermolecular potential we have applied the so-called Vlasov approximation to derive a closed equation for the distribution function. On the other hand, in the case of hard spheres, in order to truncate the BBGKY hierarchy, we employed the RET approximation, which is tantamount to factoring the two particle correlation into the product of two one-particle phase space distributions times the equal time equilibrium configurational two particle correlation function. The resulting equation is similar to the Enskog-Boltzmann equation for the one body phase-space distribution augmented by a Fokker-Plank term accounting for the heat-bath.

In practical applications a realistic intermolecular potential can always be approximated by a hard-sphere potential and a soft potential. Hence, by a slight modification of the theory presented here, one can treat the hard-core repulsion with the method illustrated in section III.B, whereas the soft term is treated according to the method of section III.A, assuming that the processes induced by these forces proceed without interfering.

The further approximation of this paper is to use an expansion in the inverse friction parameter to eliminate the modes associated with momentum and energy fluxes. In order to avoid the appearance of secular terms this procedure
is carried out using a multiple-time scale analysis.

Interestingly, the method proposed yields, to leading order in the inverse friction parameter, an equation identical to that obtained in the DDF theory. Moreover, the merit of the present approach is the possibility to describe systems subject to externally imposed temperature gradients or inelastic non conserving interactions. Finally, the theory allows to compute higher order corrections, whose next order to DDF theory represents the coupling between the density and the momentum current. Given the above, our result could be employed to study the dynamics of systems where inertial and structural effects result in a non trivial interplay, such as for systems undergoing Poiseuille flow or under shear. Candidate systems are colloidal suspensions and dense confined fluids.

Finally, we wish to comment that the present theory can be useful for obtaining information about the relaxation of the structural properties, but does not allow to study hydrodynamic phenomena. In fact, Galilean invariance and conservation of momentum are explicitly violated by our model. The Langevin coupling dampens the absolute velocities due to the presence of a solvent at rest in the laboratory frame. However, the conservation of momentum could be enforced by introducing a translationally invariant thermostat which damps the relative instead of the absolute momenta of particles. Actually, this strategy is at the basis of the Dissipative Particle Dynamics (DPD) and could be embedded in the framework of the present approach.

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APPENDIX A: HERMITE POLYNOMIALS

The \( \nu \)-dimensional Hermite tensor polynomials, \( h^{(\nu)}(V) \), introduced in equation (19) are tensorial generalizations of the standard Hermite polynomials. These are defined through the formula

\[
h^{(\nu)}(V) \equiv (-1)^{\nu} e^{V^2/2} \partial_{V_\alpha_1} \ldots \partial_{V_\alpha_\nu} e^{-V^2/2}
\]

Explicitly the first polynomials read

\[
\begin{align*}
h^{(0)}(V) &= 1 \\
h^{(1)}(V) &= V_i \\
h^{(2)}_{ij}(V) &= (V_i V_j - \delta_{ij}) \\
h^{(3)}_{ijk}(V) &= [(V_i V_j V_k - (V_i \delta_{jk} + V_j \delta_{ik} + V_k \delta_{ij}))] \\
h^{(4)}_{ijkl}(V) &= [V_i V_j V_k V_l - (V_i V_j \delta_{kl} + V_i V_k \delta_{jl} + V_i V_l \delta_{jk} + V_j V_k \delta_{il} + V_j V_l \delta_{ik} + V_k V_l \delta_{ij}) + (\delta_{ij} \delta_{kl} + \delta_{ik} \delta_{jl} + \delta_{il} \delta_{jk})]
\end{align*}
\]

The tensor polynomials are orthonormal with respect to the weight \( \omega(V) \) defined by equation (20),

\[
\int dV \omega(V) h^{(\mu)}(V) h^{(\nu)}(V) = \delta^{(\mu \nu)}_{\alpha \beta}
\]

where \( \delta^{(\mu \nu)}_{\alpha \beta} \) is zero unless \( \mu = \nu \) and the subscript \( \alpha \) is a permutation of the subscript \( \beta \).

REFERENCES

1. R. Evans, Adv. Phys. 28 143 (1979).
2. R. Evans, in Fundamentals of Inhomogeneous Fluids, ed. D. Henderson, Dekker, New York, (1992), ch. 3.
3. J-P. Hansen and I.R. McDonald, Theory of Simple Liquids, Academic, London, (2006), 3rd ed.
4. L.E. Reichl, A Modern Course in Statistical Physics, University of Texas Press, Austin, (1980).
5. H.J. Kreuzer, Non-equilibrium Thermodynamics and its Statistical Foundations Oxford University Press, New York (1981).
6. S. R. de Groot and P. Mazur, Non-equilibrium Thermodynamics (Dover, New York, 1984).
7. J.A. McLennan, Introduction to Non Equilibrium Statistical Mechanics, (Prentice Hall, Indiana, 1988).
8. M. von Smoluchowski, Ann.Phys., 48, 1103 (1916).
9 C. Gardiner, *Handbook of Stochastic methods for Physics, Chemistry and in the Natural Sciences* (Springer-Verlag, Berlin, 1994).
10 H. Risken, *The Fokker-Planck Equation* (Springer-Verlag, Berlin, 1984).
11 T. Munakata, Phys. Rev. E **50**, 2347 (1994).
12 U. Marini Bettolo Marconi and P. Tarazona, J. Chem. Phys. **110**, 8032 (1999) and J. Phys.: Condens. Matter **12**, 413 (2000).
13 J. Dzubiella and C.N. Likos, J. Phys.: Condens. Matter **15**, L147 (2003).
14 A.J. Archer and R. Evans, J. Chem. Phys. **121**, 4246 (2004).
15 F. Penna and P. Tarazona, J. Chem. Phys. **68**, 1766 (2003).
16 F. Penna, J. Dzubiella and P. Tarazona, Phys. Rev. E **68**, 061407 (2003).
17 A.J. Archer, J. Phys.: Condens. Matter **17**, 1405 (2005).
18 M. Rex, H. Löwen and C.N. Likos, Phys. Rev. E **72**, 021404 (2005).
19 M. Rex, C.N. Likos, H. Löwen and J. Dzubiella, Mol. Phys. **104**, 527 (2006).
20 H.A. Kramers, Physica A, **7**, 284 (1940).
21 N. van Kampen, *Stochastic Processes in Physics and Chemistry* (North-Holland, Amsterdam, 1992).
22 U. Marini Bettolo Marconi and P. Tarazona, J. Chem. Phys. **124**, 164901 (2006).
23 A.J. Archer, J. Phys.: Condens. Matter **xx** (2006).
24 K. Kawasaki and J.D. Gunton, Phys. Rev. A **8**, 2048 (1973).
25 A. Yoshimori, Phys. Rev. E **71**, 031203 (2005).
26 D.S. Dean, J. Phys. A. **29**, L613 (1996).
27 K. Kawasaki, Physica A **208**, 35 (1994).
28 K. Kawasaki, Transport Theory and Statistical Physics **24**, 755 (1995).
29 K. Kawasaki, J. Phys.: Condens. Matter **12**, 6343 (2000).
30 K. Kawasaki, J. Phys.: Condens. Matter **14**, 2265 (2002).
31 K. Kawasaki, J. Stat. Phys. **123**, 711 (2006).
32 A.J. Archer and M. Rauscher, J. Phys. A: Math. Gen. **37**, 9325 (2004).
33 H. van Beijeren and M.H. Ernst, Physica A, **68**, 437 (1973), **70**, 225 (1973).
34 A. Santos, J.M. Montanero, J.W. Dufty and J.J. Brey, Phys. Rev. E, **57**, 1644 (1998) and J. W. Dufty, A. Santos, and J. Brey, Phys. Rev. Lett. **77**, 1270 (1996).
35 J.P. Lutsko, J. Chem. Phys. **120**, 6325 (2004).
36 U.M. Titulaer, Physica A, **91**, 321 (1978) and Physica A **100**, 234 (1980).
37 G. Wilemski, J. Stat. Phys. **14**, 153 (1976).
38 A. Nayfeh, *Perturbation Methods* (Wiley, New-York, 1973).
39 C. Bender and S.A. Orszag, *Advanced Mathematical Methods for Scientists and Engineers*, (McGraw-Hill, New York, 1978).
40 L. Bocquet, Am. J. Phys., **65**, 140 (1997).
41 J. Piasecki, L. Bocquet and J.P. Hansen, Physica A **218**, 125 (1995).
42 P. Espanol, Phys. Rev. E **52**, 1734 (1995).
43 Sadri Hassani, *Foundations of Mathematical Physics*, (Prentice-Hall International, London, 1991).