Nonequilibrium inertial dynamics of colloidal systems

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(Received 14 December 2005; accepted 23 February 2006; published online 24 April 2006)

We consider the properties of a one-dimensional fluid of Brownian inertial hard-core particles, whose microscopic dynamics is partially damped by a heat bath. Direct interactions among the particles are represented as binary, instantaneous elastic collisions. Collisions with the heat bath are accounted for by a Fokker-Planck collision operator, whereas direct collisions among the particles are treated by a well known method of kinetic theory, the revised Enskog theory. By means of a time multiple time-scale method we derive the evolution equation for the average density. Remarkably, for large values of the friction parameter and/or of the mass of the particles we obtain the same equation as the one derived within the dynamic density functional theory (DDF). In addition, at moderate values of the friction constant, the present method allows to study the inertial effects not accounted for by DDF method. Finally, a numerical test of these corrections is provided.
 [DOI: 10.1063/1.2188390]

I. INTRODUCTION

Over the last few years suspensions of interacting Brownian particles have been the subject of vivid theoretical interest due to new accurate experiments probing their properties at nanoscale, down to the effects of the correlation shells and layering structures in the density distribution. There is a great variety of systems and problems of fundamental and applied interest, including dense polymer solutions in good solvents,[1] the sedimentation of latex spheres, to produce materials with engineered optical gaps,[2] the design of microfluidic devices, to handle colloidal particles,[3–5] or the crowding effects in the cellular cytoplasm.[6] Whenever the systems may be considered to be at thermodynamical equilibrium, the theoretical analysis of such structures may be efficiently done within the density functional formalism, with well tested approximations to include the effects of the repulsive and attractive interactions between the particles, although the inclusion of hydrodynamic (velocity dependent) interactions is still an open challenge. The theoretical study of the dynamical properties of colloidal particles suspended in a solution of lighter particles is a much harder problem, often studied through the Langevin approach to Brownian motion,[7–9] with the lighter particles represented by a bath providing a damping force, with friction constant γ, and a thermalizing stochastic noise.

Two levels of description, both based on the Fokker-Planck equation, can be employed to analyze the Langevin model for Brownian motion. In the first, the so-called Kramers equation[10] which governs the evolution of the joint probability distribution of position and velocity, one keeps track both of velocities and positions of the particles, whereas in the second, the Smoluchowski equation,[11] one considers only the evolution of the probability distribution of position. In fact, the velocity distribution relaxes in a time span of the order of the inverse of the damping constant toward its equilibrium form and afterward remains stationary, so that the Kramers phase-space description becomes somehow redundant and one can restrict attention on the evolution of the spatial distribution, governed by the Smoluchowski equation. However, the passage from the Kramers phase-space description to the Smoluchowski positional description requires the adiabatic elimination of the fast velocity variable. Even for the simplest case of ideal noninteracting particles, the correct procedure was understood only in the late seventies due to the work of Wilemski[12] and Titulaer.[13] In particular, Titulaer showed that a modified Smoluchowski equation can be derived from Kramers equation by means of a systematic γ^{-1} expansion of the Chapman-Enskog type. He obtained the corrections to the standard Smoluchowski equation in terms of γ for an arbitrary time independent external potential. More recently, Bocquet[14] and Piasecki *et al.*[15] gave a pedagogical discussion of such a derivation using the multiple time-scale method.[16,17] The corrections to the Smoluchowski equation for large, but finite, values of γ represent the effects of the underlying inertial dynamics, over the fully damped limit, in which at any time the velocity of a particle, averaged over the realization of the random noise, is proportional to the external potential force $\langle v(t)\rangle \sim F(x(t))$ with no inertial memory of the value of $\langle v(t')\rangle$ for $t' < t$. In the noninteracting case these corrections to the Smoluchowski equation produce a gradient of the external force, which determines a nonuniform acceleration of the particle and renormalizes the effective diffusion constant.

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In this present paper, we are interested in the role played by the forces between the particles, in particular, by those having a short range character, such as the impulsive forces between hard spheres; which have been usually neglected in previous studies. We want to answer the question whether inertial effects matter, in the dynamics of a system of interacting colloidal particles, and which are the corrections to the Smoluchowski equation in that case. Interactions are expected to modify the motion of the particles by restricting their trajectories, by inducing different accelerations, and correlating their velocities and positions. In the case of an overdamped dynamics, i.e., when $\gamma \to \infty$, we presented[18] a dynamic equation that governs the probability density of finding a particle in a given position. Starting from the Smoluchowski equation for the distribution function of the positions of N particles, we introduced a closure based on the assumption that the dynamical pair correlations could be approximated by those of a reference equilibrium system characterized by the same density profile as the nonequilibrium system. The resulting self-consistent description for the average density was encoded in a deterministic dynamical density functional (DDF) equation,

$$\frac{\partial \rho(x,t)}{\partial t} = D\,\nabla\left[\nabla\rho(x,t) + \rho(x,t)\,\nabla\left(\frac{\delta\beta\mathcal{F}_{\mathrm{ni}}[\rho]}{\delta\rho(x,t)} + \beta V_{\mathrm{ext}}(x)\right)\right], \tag{1}$$

where $\beta\mathcal{F}_{\mathrm{ni}}[\rho]$ is the nonideal part of the free energy functional, $\beta V_{\mathrm{ext}}(x)$ is the external potential, both in $\beta=(k_BT)^{-1}$ units.[19] The diffusion coefficient satisfies the Einstein relation $D=k_BT/m\gamma$, where m is the mass of the colloidal particles, T the absolute temperature, k_B the Boltzmann constant, and γ the friction constant. Notice that the essence of any DDF approach is to set an approximate scheme in which the dynamic two-particle distribution function $\rho_2(x,x',t)$, required to include the interaction's effects in the time derivative of $\rho(x,t)$, is taken as fully determined by the instantaneous value of that density distribution, as already done in earlier treatments such as the Enskog[20] method and its revisions.[21] The exact time evolution of $\rho(x,t)$ in interacting systems could only be obtained from the knowledge of the full previous history of the density distribution,[22] but from the practical point of view, the use of DDF approximations seems to be well supported by the comparison of their predictions with Brownian dynamics simulations.[19,23,24]

Can we extend such a description to the case of systems, where the dynamics is not overdamped? One would expect a richer dynamics as compared to the purely diffusive dynamics of Eq. (1). Does the momentum of the particles play a role? The one-particle phase-space distribution function $P[x,v,t]$ is the natural candidate to replace the density $\rho(x,t)$ in this extended description. Of course, the Boltzmann equation for $P[x,v,t]$, which predates all nonequilibrium kinetic equations, applies only to very dilute gases and does not incorporate the interaction with a heat bath. We shall consider both these aspects and show that it is possible to derive Eq. (1) as the leading term of a γ^{-1} expansion, starting from the full inertial dynamics. The leading corrections are also obtained as the next terms in the expansion. In the present paper we investigate numerically and analytically the problem in the simplified version of a one-dimensional colloidal fluid driven by a heat bath at fixed temperature. Although it may appear that the one-dimensional model employed is not of direct practical relevance, our motivation derives not only from the great simplification of the resulting algebra and computer codes, but also from recent experimental work for colloidal particles in very narrow channels.[25]

An outline of this article is as follows: We open Sec. II with a presentation of the microscopic model of inertial interacting particles subject to stochastic dynamics. We then introduce the evolution equation for the single-particle phase-space distribution function obtained by combining the effect of dissipative collisions with the heat bath, which gives rise to a Kramers-Fokker-Planck contribution, with the effect of interparticle collisions, described by an Enskog collision term. At this stage, we separate the space dependence from the velocity dependence of the phase-space distribution functions by using the eigenfunctions of the Fokker-Planck operator as basis functions. As a result of such a projection procedure we obtain an infinite nonlinear system of coupled equations for the velocity moments of the phase distribution function. In Sec. III by means of the method of multiple scales we construct a uniform expansion in the inverse friction parameter and obtain the equation of evolution for the particle density. In Sec. IV we explore the consequences of such an equation with a simple application and discuss its relation with the DDF equation. Finally in Sec. V we draw the conclusions.

II. ENSKOG-FOKKER-PLANCK EQUATION

Let us consider a system of heavy particles suspended in a solution of lighter particles. Due to their smaller mass, the solvent particles perform rapid motions so that their influence on the heavy particles can be described by a stochastic force. As a result of such elimination of microscopic degrees of freedom one can represent the motion heavy particles by means of stochastic Langevin dynamics. Here we consider a system of N particles moving in one dimension, under the action of an external force $f_e(x)$ and interacting elastically with a pair potential energy $U(x-x')$. The equations of motions are

$$\frac{dx_i}{dt} = v_i, \tag{2}$$

$$m\frac{dv_i}{dt} = -m\gamma v_i + f_e(x_i) - \sum_{j\neq i}\frac{\partial U(x_i-x_j)}{\partial x_i} + \xi_i(t), \tag{3}$$

including the effects of the solvent with the linear friction coefficient γ and the stochastic white noise with zero average and correlation,

$$\langle \xi_i(t)\xi_j(s)\rangle = 2\gamma m k_B T\delta_{ij}\delta(t-s), \tag{4}$$

T is the "heat-bath temperature" and $\langle\cdot\rangle$ indicates the average over a statistical ensemble of realizations.[26,27] The elimination in (3) of the rapid bath variables $\xi_i(t)$ leads to the Fokker-Planck equation,[7,8] in terms of the probability distri-

bution function $P(x,v,t)$ for the position and velocity variables,

$$\frac{\partial}{\partial t}P(x,v,t)+\left[v\frac{\partial}{\partial x}+\frac{f_e(x)}{m}\frac{\partial}{\partial v}\right]P(x,v,t)$$
$$=\gamma\left[\frac{\partial}{\partial v}v+\frac{T}{m}\frac{\partial^2}{\partial v^2}\right]P(x,v,t)+\mathcal{C}[x,v,t,P_2]. \quad (5)$$

The left-hand side (lhs) is the Liouville operator for the ideal gas, under the external force $f_e(x)$, the first term in the right-hand side (rhs) represents the heat bath as the standard Fokker-Planck collision operator, and the last term represents the effect of the interactions among the particles, as a generic collision operator,

$$\mathcal{C}[x,v,t,P_2]=\frac{1}{m}\frac{\partial}{\partial v}\int dx'\int dv'\frac{\partial U(x-x')}{\partial x}\times P_2(x,v,x',v',t), \quad (6)$$

This operator $\mathcal{C}$ satisfies the first equation of the Bogoliubov-Born-Green-Kirkwood-Yvon (BBGKY) hierarchy,[28] which connects the evolution of the n-particle distribution function to the distribution function for $(n+1)$ particles. For interacting particles, the evolution equation (5) for the one-particle distribution function $P(x,v,t)$ depends on the two-particle distribution $P_2(x,v,x',v',t)$, and some approximate closure is required to obtain a workable scheme.

Whenever $U(x-x')$ is a smooth function of the particle separation, like for the ultrasoft repulsive potentials used to model the steric repulsion between polymers[1] or in the long range attractive interactions from dispersion or screened ionic forces, we may follow a mean-field approximation $P_2(x,v,x',v',t)\approx P(x,v,t)P(x',v',t)$, which reduces (5) to a partial differential equation for the one-particle distribution,[29,30] and the effects of the particle interactions may be directly integrated over velocities, with the density distribution $\rho(x,t)=\int dvP(x,v,t)$ and included as a molecular field, $f_m(x,t)=-\int dx'[\partial U(x-x')/\partial x]\rho(x',t)$, to be added to $f_e(x)$ in the lhs of (5), as a self-consistent, $\rho(x,t)$ dependent, force field.

On the other hand, sharp repulsive contributions between the particles cannot be included as a molecular field, since they imply very strong correlations between the relative position $(x-x')$ and the relative velocity $(v-v')$ over the range of the repulsive force; so that $P_2(x,v,x',v',t)$ goes sharply to zero when $x-x'$ goes into the repulsive core. For hard-rod particles of length σ, there is an infinite force acting on an infinitesimal range around $x-x'=\pm\sigma$, and the collision operator $\mathcal{C}[x,v,t,P_2]$ is exactly represented[31] by the following operator:

$$K_E[x_1,v_1,t]=\sum_{s=\pm1}\int dx_2\int dv_2\Theta(v_{12}s)(v_{12}s)[\delta(x_{12}-s\sigma)\times b_{12}-\delta(x_{12}+s\sigma)]P_2[x_1,v_1,x_2,v_2,t], \quad (7)$$

where Θ is the Heaviside function, $v_{12}=(v_1-v_2)$, $x_{12}=(x_1-x_2)$, and b_{12} is the scattering operator defined for arbitrary function $X(v_1,v_2)$ by

$$b_{12}X(v_1,v_2)=X(v_1',v_2'), \quad (8)$$

which for hard rods swaps the velocities $b_{12}X(v_1,v_2)=X(v_2,v_1)$ thus generating a correlation between relative position and relative velocity. The representation (7) formally integrates (6) over the instant of collision and substitutes the direct effect of the force by the change from the precollisional to the postcollisional velocities.

A standard approximation of the collision term (7) is to assume that atoms are uncorrelated immediately prior to collision, which is the essence of Boltzmann's "molecular chaos hypothesis" but are correlated after they collide, because the collision itself generates correlations.[32] The revised Enskog theory (RET), developed by van Beijeren and Ernst,[21] truncates the infinite BBGKY hierarchy by factorizing

$$P_2(x_1,v_1,x_2,v_2,t)=g_2[x_1,x_2;\rho]P(x_1,v_1,t)P(x_2,v_2,t), \quad (9)$$

The spatial pair distribution function $g_2[x_1,x_2;\rho]$ reflects the local positional correlations in the fluid. For particles with both short-range repulsions and long-range tails, the simplest approximation would be to split the generic collision operator K_E in (6) into a molecular field representation of the soft interactions and an effective hard-rod description (7) of the core repulsion, following the usual treatment for equilibrium properties, which goes back to van der Waals, and is still the most used scheme within the density functional formalism.

In the case of one dimensional elastic hard rods the RET provides the following expression for the collision integral:

$$K_E[x_1,v_1,t]=\sum_{s=\pm1}\int dv_2\Theta(v_{12}s)(v_{12}s)\{g_2[x_1,x_1-s\sigma;n]\times P[x_1,v_1',t]P[x_1-s\sigma,v_2',t]-g_2[x_1,x_1+s\sigma;n]\times P[x_1,v_1,t]P[x_1+s\sigma,v_2,t]\}. \quad (10)$$

Whereas in Enskog's formulation the pair correlation function at contact was assumed to be that of an equilibrium fluid evaluated at the local density at some point in between the colliding atoms, in the RET instead the contact value of g_2 is assumed: (i) to be a nonlocal equilibrium functional of the local density, (ii) to depend on time only through the density $\rho(x,t)$, and (iii) to have the same form as in a nonuniform equilibrium state whose density profile is $\rho(x,t)$. Fortunately, in the case of a one-dimensional hard-rod system the exact expression for the equilibrium pair correlation at contact is known given any arbitrary equilibrium density profile and reads[33]

$$g_2[x\pm\sigma;\rho]=\frac{1}{1-\eta(x\pm\sigma/2)}. \quad (11)$$

The density dependence occurs entirely via the local packing fraction $\eta(x,t)=\int_{x-\sigma/2}^{x+\sigma/2}dx'\rho(x',t)$.

At this stage it is convenient to introduce the following dimensionless variables:

$$\tau\equiv t\frac{v_T}{\sigma},\quad V\equiv\frac{v}{v_T},\quad X\equiv\frac{x}{\sigma},\quad \Gamma=\gamma\frac{\sigma}{v_T}, \quad (12)$$

$$F_e(X) \equiv \frac{\sigma f_e(x)}{m\upsilon_T^2}, \quad F_m(X,\tau) \equiv \frac{\sigma f_m(x,t)}{m\upsilon_T^2}, \tag{13}$$

$$\tilde{P}(X,V,\tau) \equiv \sigma\upsilon_T P(x,\upsilon,t), \quad K(X,V,\tau) \equiv \sigma^2 K_E(x,\upsilon,t), \tag{14}$$

where $\upsilon_T = \sqrt{k_B T/m}$.

In situations where $\Gamma \gg 1$ particles lose memory of their initial velocities after a time span which is of the order of the inverse of the friction coefficient γ so that the velocity distribution soon becomes a Maxwellian. On the other hand, during the same interval the coordinates of the particles suffer a negligible change, as one can see comparing the product of the thermal velocity υ_T by γ^{-1} with the typical molecular size σ. In this limit the Smoluchowski description of a system of noninteracting particles, which takes into account only the configurational degrees of freedom, turns out to be adequate. However, for intermediate values of Γ inertial effects may come into play. The question is how do we recover a description similar to that provided by the DDF approach starting from a phase description? On physical grounds one could directly neglect the inertial term in Eq. (3) and consider only the evolution of the position distribution, as the DDF does, but such an approach does not give a clue on how the inertial effects can modify the dynamics.

Accordingly, Kramers' evolution equation for the phase-space distribution function can be rewritten with the help of relations (12) and (13) and with the definition of effective field $F(X,\tau) = F_e(X) + F_m(X,\tau)$ as

$$\frac{1}{\Gamma}\frac{\partial \tilde{P}(X,V,\tau)}{\partial \tau} = L_{FP}\tilde{P}(X,V,\tau) - \frac{1}{\Gamma}V\frac{\partial}{\partial X}\tilde{P}(X,V,\tau) - \frac{1}{\Gamma}F(X,\tau)\frac{\partial}{\partial V}\tilde{P}(X,V,\tau) + \frac{1}{\Gamma}K(X,V,\tau), \tag{15}$$

having introduced the "Fokker-Planck" operator $L_{FP}\tilde{P}(X,V,\tau) = (\partial/\partial V)[\partial/\partial V + V]\tilde{P}(X,V,\tau)$, whose eigenfunctions $H_\nu(V)H_\nu(V) \equiv (1/\sqrt{2\pi})(-1)^\nu(\partial^\nu/\partial V^\nu)\exp(-\frac{1}{2}V^2)$ have nonpositive integer eigenvalues $\nu = 0,-1,-2,\ldots$. Solutions of Eq. (15), where position and velocity dependence of the distribution function are separated, can be written as

$$\tilde{P}(X,V,\tau) \equiv \sum_{\nu=0}^{\infty} \phi_\nu(X,\tau)H_\nu(V). \tag{16}$$

Moreover, by multiplying $K(X,V,\tau)$ by $(1/n!)H_n(V)/H_0(V)$ and integrating with respect to V, one represents the collision term as

$$\tilde{K}(X,V,\tau) \equiv \sum_{\nu=0}^{\infty} C_\nu(X,\tau)H_\nu(V). \tag{17}$$

After substituting (16) and (17) into Eq. (15) we find

$$\sum_\nu \left[\frac{\partial \phi_\nu(X,\tau)}{\partial \tau} + \Gamma\nu\phi_\nu(X,\tau) - C_\nu(X,\tau)\right]H_\nu(V) + \left[\frac{\partial \phi_\nu(X,\tau)}{\partial X} - F(X)\phi_\nu(X,\tau)\right]H_{\nu+1}(V) + \nu\frac{\partial \phi_\nu(X,\tau)}{\partial X}(\delta_{\nu,0}-1)H_{\nu-1}(V) = 0. \tag{18}$$

Finally, by equating the coefficients of the same basis functions H_ν, we obtain an infinite hierarchy of equations which differs from standard Brinkman's expansion[34] by the presence of collision terms.

A. Physical interpretation of the expansion

Before considering in detail the method of solution, we digress on the physical interpretation of our equations. By identifying $\phi_0(X,\tau)$ with the dimensionless particle density $n = \rho\sigma$, $\phi_1(X,\tau)$ with the momentum flow density J_υ, and $\phi_2 = E_k - n/2$ with the deviation from the thermalized value of the kinetic energy, E_k being the kinetic energy density, expressed in reduced units, we can rewrite the first three equations,

$$\frac{\partial n(X,\tau)}{\partial \tau} = -\frac{\partial J_\upsilon(X,\tau)}{\partial X}, \tag{19}$$

$$\frac{\partial J_\upsilon(X,\tau)}{\partial \tau} = -\Gamma J_\upsilon(X,\tau) + F(X,\tau)n(X,\tau) - 2\frac{\partial E_k(X,\tau)}{\partial X} + C_1(X,\tau), \tag{20}$$

$$\frac{\partial E_k(X,\tau)}{\partial \tau} = -2\Gamma\left[E_k(X,\tau) - \frac{1}{2}n(X,\tau)\right] - \frac{\partial J_k(X,\tau)}{\partial X} + F(X,\tau)J_\upsilon(X,\tau) + C_2(X,\tau), \tag{21}$$

where the kinetic energy flow is defined as $J_k \equiv \int dV V^3 \tilde{P}(X,V,\tau)$.

Using the result derived in Appendix B we can express the coefficients $C_n(X,\tau)$ as divergences. First we introduce[35] the kinetic pressure $\Pi_k = 2E_k$ and second identify the collisional contributions to the pressure and to the energy current via

$$\frac{\partial \Pi_c(X,\tau)}{\partial X} = -C_1(X,\tau), \quad \frac{\partial J_c(X,\tau)}{\partial X} = -C_2(X,\tau). \tag{22}$$

We arrive at

$$\frac{\partial J_\upsilon(X,\tau)}{\partial \tau} = -\Gamma J_\upsilon(X,\tau) + F(X,\tau)n(X,\tau) - \frac{\partial[\Pi_k(X,\tau) + \Pi_c(X,\tau)]}{\partial X} \tag{23}$$

and

$$\frac{\partial E_k(X,\tau)}{\partial \tau} = -2\Gamma\left[E_k(X,\tau) - \frac{1}{2}n(X,\tau)\right] + F(X,\tau)J_v(X,\tau) - \frac{\partial[J_k(X,\tau)+J_c(X,\tau)]}{\partial X}, \tag{24}$$

where the presence of the source term $n(X,\tau)/2$ maintains the fluid at constant temperature. Notice that properties (22) are consequences of the local conservation of momentum and energy during the collisional process. In one-dimensional elastic systems in addition to mass, impulse, and energy all higher moments of the velocity distribution are conserved quantities under collisions, because $K(X,V,\tau)$ is a divergence.

If the hierarchy of moment equations is truncated by supplementing the constitutive equations, one recovers the analogue of hydrodynamic equations with dissipation. We also remark that in a uniform bulk system the collisional contribution to the pressure coincides with the pressure excess over the ideal gas pressure, since $\Pi_c(X,\tau)=n^2/(1-n)$, having used Eq. (B4) and the contact value $g_2^b=1/(1-n)$ of the bulk pair correlation.

B. Exact solution for the free ideal gas

We illustrate the nature of the solutions by a simple example, namely, the free expansion of a system where the collisional terms and the molecular force field are dropped. Let us remark, that even in that simple case, the time evolution of the inhomogeneous ideal gas, is not well described by any simple truncation of the hierarchy, for instance setting $\phi_3(X,\tau)=0$ in order to obtain a closed system of equations for the first three weight functions. The exact eigenfunctions of Kramers' equation are known, and they can be expressed as infinite series of the form

$$\tilde{P}^{(\mu)}(X,V,\tau) = \exp(-\mu\Gamma\tau)\exp\left[-\frac{A_+}{\Gamma}\frac{\partial}{\partial x}\right]\left(1+\frac{A_-}{\Gamma}\frac{\partial}{\partial x}\right)^{\mu} \times H_\mu(V)\phi_0^{(\mu)}(X,\tau), \tag{25}$$

where A_+ and A_- are the raising and lowering operators on the Fokker-Planck (FP) velocity eigenfunctions, respectively, $A_\pm H_\nu(V)=H_{\nu\pm1}(V)$. The functions $\phi_0^{(\mu)}(X,\tau)$, which fully define $\tilde{P}^{(\mu)}(X,V,\tau)$, may be any generic solutions of the diffusion equation,

$$\frac{\partial}{\partial\tau}\phi_0^{(\mu)}(X,\tau) = \frac{1}{\Gamma}\frac{\partial^2}{\partial X^2}\phi_0^{(\mu)}(X,\tau), \tag{26}$$

which produces the time dependence to be scaled as $\tau_1 \equiv \tau/\Gamma$. Therefore, for $\Gamma \gg 1$ there is a clear separation between the *fast* time dependence of the exponential decay $\exp(-\mu\Gamma\tau)$ and the *slow* dependence of the function $\phi_0^{(\mu)} \times(X,\tau)$. The eigenfunction associated with $\mu=0$ has the explicit form

$$\tilde{P}^{(0)}(X,V,\tau) = \exp\left[-\frac{A_+}{\Gamma}\frac{\partial}{\partial x}\right]\phi_0^{(0)}(X,\tau) = H_0(V)\phi_0^{(0)} - \frac{H_1(V)}{\Gamma}\frac{\partial\phi_0^{(0)}}{\partial X} + \frac{H_2(V)}{2!\Gamma^2}\frac{\partial^2\phi_0^{(0)}}{\partial X^2} + \cdots \tag{27}$$

and represents a slowly decaying density inhomogeneity $\phi_0^0(X,\tau_1)$ with small (order $1/\Gamma$, $1/\Gamma^2,\ldots$), *slaved* perturbations of momentum, energy, etc., whose shapes are given by the successive derivatives of the density distribution with respect to X. Similarly, the eigenfunction associated with $\mu=1$ has the explicit representation

$$\tilde{P}^{(1)}(X,V,\tau) = \exp(-\Gamma\tau)\left[\left(H_1(V)\phi_0^{(1)} - \frac{H_2(V)}{\Gamma}\frac{\partial\phi_0^{(1)}}{\partial X} + \frac{H_3(V)}{2!\Gamma^2}\frac{\partial^2\phi_0^{(1)}}{\partial X^2} + \ldots\right) + \frac{1}{\Gamma}\left(H_0(V)\frac{\partial\phi_0^{(1)}}{\partial X} - \frac{H_1(V)}{\Gamma}\frac{\partial^2\phi_0^{(1)}}{\partial X^2} + \ldots\right)\right], \tag{28}$$

where the first line in the rhs has the interpretation of a current inhomogeneity $\phi_0^{(1)}(X,\tau/\Gamma)$, which *slaves* higher order (energy, etc.) perturbations with decreasing amplitudes $(1/\Gamma,\ldots)$, while the second line in the rhs has the same structure of the $P^{(0)}(X,V,\tau)$ eigenfunction with amplitude $\phi_0^{(0)}=\Gamma^{-1}\partial_X\phi_0^{(1)}$, and both terms have the fast decay of the exponential prefactor. The physical interpretation of such a combination is that an initially pure current fluctuation, described by $H_1(V)\phi_1(X,0)$ would die very fast, as $\exp(-\Gamma\tau)$, but leaving behind a density fluctuation proportional to $\Gamma^{-1}\partial_X\phi_1^{(1)}(X,0)$, which would evolve with the *slow time* τ_1. The particular combination in (28) is such that it completely cancels those remnant density fluctuations, i.e., it orthogonalizes $P^{(1)}(X,V,\tau)$ to $P^{(0)}(X,V,\tau)$, and leaves a purely fast decaying form.

The structure of the higher order eigenvalues follows the same pattern, $P^{(2)}(X,V,\tau)$ is an energy fluctuation, decaying as $\exp(-2\Gamma\tau)$, but it has to contain diagonalizing terms proportional to $\Gamma^{-1}P^{(1)}$ and to $\Gamma^{-2}P^{(0)}$, to leave no slower remnant behind. With arbitrary choice of $\phi_0^{(\nu)}(X,0)$, for $\nu=0,1,2,\ldots$, we may describe any initial distribution of the ideal gas, whose time evolution would be given by the superposition of the decaying modes. These "excited" $\mu>0$ modes decay with a fast transient decay toward the only slowing decaying $\mu=0$ mode, which contains τ_1 as the only relevant time scale. Such a separation between fast decaying exponential modes and a slow diffusive mode should be much more generic than the particular realization in the free ideal gas. Indeed, it emanates from the structure of Eq. (15), where the heat-bath term is associated with the diagonal operator of the form $\Gamma L_{FP}=-\Gamma\nu$, which contains a null matrix element ($\nu=0$), while the remaining elements are proportional to Γ. The nondiagonal contributions (given by the streaming terms for the ideal gas and by collisions in gen-

eral) are independent of Γ. In the limit $\Gamma \gg 1$, the generic structure of the eigenfunctions, reflects the properties of the eigenfunctions of the ΓL_{FP} operator, with corrections of order $1/\Gamma$, that is, combinations of exponential decays $\exp(-\nu\Gamma\tau)$ and slow functions, evolving with $\tau_1 = \tau/\Gamma$, or slower. Therefore, from an arbitrary initial condition, the system would have a fast transient decay toward a slow mode, made of a density distribution, accompanied of slaved current, energy, etc., fluctuations, with magnitude proportional to inverse powers of Γ. In the next section we work out the leading contributions of the collisions to that slow mode; taking into account their nonlinear character generates slower than τ_1 times scales, as the slow reaction to a slowly changing external force $F(X, \tau/\Gamma)$ would do.

III. MULTIPLE TIME-SCALE ANALYSIS

How can we construct the equivalent eigenfunction representation of Kramers' equation for a system of interacting particles? The method is provided by the multiple time-scale analysis, that we shall discuss hereafter. The multiple time-scale method is designed to deal with nonuniformities in systems with more than a time scale. It has been shown that a straightforward expansion of the Kramers equation in powers of the small parameter Γ^{-1} does not lead to a uniformly valid result.[14] In order to obtain a uniformly valid expansion, instead, makes use of the presence of two different time scales in the problem. The first scale is fast and corresponds to the time interval necessary to the velocities of the particles to relax to configurations consistent with their thermal equilibrium value. The second time scale is much longer and corresponds to the time necessary to the positions of the particles to assume their equilibrium configurations.

In the multiple time-scale analysis one determines the temporal evolution of the distribution function $\tilde{P}(X, V, \tau)$ in the regime $\Gamma^{-1} \ll 1$, by means of a perturbative method. In order to construct the solution one replaces the single physical time scale τ by a series of auxiliary time scales $(\tau_0, \tau_1, \ldots, \tau_n)$ which are related to the original variable by the relations $\tau_n = \Gamma^{-n}\tau$. Also the original time-dependent function $\tilde{P}(X, V, \tau)$ is replaced by an auxiliary function $\tilde{P}_a(X, V, \tau_0, \tau_1, \ldots)$ which depends on τ_n, which are treated as independent variables. Once the equations corresponding to the various orders have been determined, one returns to the original time variable and to the original distribution.

One begins by replacing the time derivative with respect to τ by a sum of partial derivatives,

$$\frac{\partial}{\partial \tau} = \frac{\partial}{\partial \tau_0} + \frac{1}{\Gamma}\frac{\partial}{\partial \tau_1} + \frac{1}{\Gamma^2}\frac{\partial}{\partial \tau_2} + \ldots . \tag{29}$$

First, the auxiliary function $\tilde{P}_a(X, V, \tau_0, \tau_1, \ldots)$ is expanded as a series of Γ^{-1},

$$\tilde{P}_a(X, V, \tau_0, \tau_1, \tau_2, \ldots) = \sum_{s=0}^{\infty} \frac{1}{\Gamma^s} \tilde{P}_a^{(s)}(X, V, \tau_0, \tau_1, \tau_2, \ldots). \tag{30}$$

Similarly, the collision operator is expanded as

$$C_\alpha(X, \tau) = \sum_{s=0}^{\infty} \frac{1}{\Gamma^s} C_{s,\alpha}(X, \tau_0, \tau_1, \tau_2, \ldots). \tag{31}$$

Next, each term $P_a^{(s)}$ is projected over the functions H_ν,

$$P_a^{(s)}(X, V, \tau_0, \tau_1, \ldots) = \sum_{\nu=0}^{\infty} \psi_{s\nu}(X, \tau_0, \tau_1, \tau_2, \ldots) H_\nu(V). \tag{32}$$

The term $C_{s,\alpha}$ represents the contribution of order Γ^{-s} to $C_\alpha(X, \tau)$,

$$C_{s,\alpha}(X, \tau) = \sum_{l+m=s} \sum_{\mu,\nu} g_2(X, X+1) G^{\alpha}_{\mu,\nu} \psi_{l\mu}(X, \tau) \psi_{m\nu}(X+1, \tau) - g_2(X, X-1) G^{\alpha}_{\nu,\mu} \psi_{l\mu}(X, \tau) \psi_{m\nu}(X-1, \tau). \tag{33}$$

One substitutes, now, the time derivative (29) and expressions (30)–(32) into Eq. (15) and identifying terms of the same order in Γ^{-1} in the equations one obtains a hierarchy of relations between the amplitudes $\psi_{s\nu}$. The advantage of the method over the naive perturbation theory is that secular divergences can be eliminated at each order of perturbation theory and thus uniform convergence is achieved.

We show, now, how the method works. We substitute Eqs. (29) and (30) into Eq. (15) and equate the coefficients of the same powers of Γ. To order Γ^0 one finds

$$L_{FP}\left[\sum_{\nu} \psi_{0\nu} H_\nu\right] = 0 \tag{34}$$

and concludes that only the amplitude ψ_{00} is nonzero.

Next, we consider terms of order Γ^{-1} and write

$$L_{FP}[\psi_{11} H_1 + \psi_{12} H_2] = \frac{\partial \psi_{00}}{\partial \tau_0} H_0 + D_X \psi_{00} H_1 - C_{0,1} H_1 - C_{0,2} H_2 - C_{0,3} H_3, \tag{35}$$

having introduced, for notational convenience, $D_X \equiv (\partial_X - F(X, \tau))$. Following the method of Ref. 13, the amplitudes with $\nu = 0$ and $s > 0$ 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 τ_0. By equating the coefficients multiplying the same H_ν we find that since

$$\frac{\partial \psi_{00}}{\partial \tau_0} = 0, \tag{36}$$

the amplitude ψ_{00} is not a function of τ_0. Therefore, also the amplitude ψ_{11}, which is given by the relation

$$\psi_{11} = -D_X \psi_{00} + C_{0,1}, \tag{37}$$

does not depend on τ_0, being a functional of ψ_{00}, both through the linear operator D_X and through the effective field $C_{0,1}$, whose explicit form is given in Sec. IV. The remaining two amplitudes, instead, vanish because to order Γ^{-1} the self-consistent terms vanish, $C_{0,2} = 0$ and $C_{0,3} = 0$,

$$\psi_{12} = \frac{1}{2}C_{0,2} = 0, \quad \psi_{13} = \frac{1}{3}C_{0,3} = 0. \tag{38}$$

In particular, the vanishing of $C_{0,2}$ is a consequence of the traceless form (for an elastic hard-rod system) of $G^2_{\mu,\nu}$ (see Appendix A). A similar property yields $C_{0,3}=0$.

To order Γ^{-2} we obtain the equation

$$\begin{aligned} L_{FP}[\psi_{21}H_1 + \psi_{22}H_2 + \psi_{23}H_3] &= \frac{\partial\psi_{11}}{\partial\tau_0}H_1 + \frac{\partial\psi_{00}}{\partial\tau_1}H_0 + D_X\psi_{11}H_2 + \partial_X\psi_{11}H_0 \\ &\quad - C_{1,1}H_1 - C_{1,2}H_2 - C_{1,3}H_3 \end{aligned} \tag{39}$$

from which we obtain the conditions

$$\frac{\partial\psi_{00}}{\partial\tau_1} = -\partial_X\psi_{11} \tag{40}$$

and

$$\frac{\partial\psi_{11}}{\partial\tau_0} = -\psi_{21} + C_{1,1}. \tag{41}$$

Notice that, since the lhs of Eq. (41) does not depend on τ_0, as discussed after Eq. (37), the rhs must vanish. Utilizing Eqs. (37) and (40) we write

$$\frac{\partial\psi_{00}}{\partial\tau_1} = \partial_X[D_X\psi_{00} - C_{0,1}]. \tag{42}$$

By carrying on the procedure to order Γ^{-3} we obtain

$$\frac{\partial\psi_{00}}{\partial\tau_2} = -\partial_X\psi_{21} = -\partial_X C_{1,1}, \tag{43}$$

where we have used Eq. (41) to eliminate ψ_{21}.

For the sake of completeness we write the third order correction Γ^{-3} and find

$$\frac{\partial\psi_{00}}{\partial\tau_3} = -\partial_X\left[(\partial_X F)(D_X\psi_{00} - C_{0,1}) + C_{2,1} - \frac{\partial C_{0,1}}{\partial\tau_1} - \partial_X C_{1,2}\right]. \tag{44}$$

The time derivative appearing in the rhs can be expressed in terms of spatial derivatives of the order parameter ψ_{00} using Eq. (42) and therefore could be computed.

As a check of the method we have reobtained perturbatively the exact solution in the ideal gas case. Moreover, Eq. (44) reduces to the modified Smoluchowski diffusion equation in a potential obtained by Titulaer,[13] who showed that, in the case of independent particles in a parabolic potential, it coincides with the exact solution up to order Γ^{-3}.

In the following, we shall truncate the expansion to second order. Collecting together the various terms and employing Eq. (29) to eliminate the time variables τ_0, τ_1, τ_2 and restore the original time variable τ we obtain the evolution equation,

$$\frac{\partial\psi_{00}}{\partial\tau} = \frac{1}{\Gamma}\partial_X\left[D_X\psi_{00} - C_{0,1} - \frac{1}{\Gamma}C_{1,1}\right]. \tag{45}$$

Clearly, the evolution equation (45) for the amplitude $\psi_{00}(X,\tau)$, representing the key result of the present paper, has to be supplemented with a prescription for $C_{0,1}$ and $C_{1,1}$ which is given explicitly in the next section. These terms represent collisions and involve the density and current amplitude, ψ_{00} and ψ_{11}, respectively. However, the latter quantity can be expressed by means of Eq. (45) as a functional of ψ_{00}. In this manner expression (37) forms a closed equation for the density profile.

It is worth to remark that, while in the original hierarchy Eq. (19) the various amplitudes were independent fields, the solution obtained in this section, being, in fact, the generalization to interacting systems of the zeroth eigenfunction of Kramers equation, imposes a constraint on each of the $\nu > 0$ components. We used this property as an internal check of the present extension to colliding particles. Employing the constraint provided by relations (37) and (40) into the first equations of the hierarchy (19), we have verified that to order Γ^{-2} indeed the method provides a solution. In other words the solution even in the presence of collisions can be represented only by the eigenfunction associated with the less negative eigenvalue.

IV. EVOLUTION EQUATION AND ITS DDF LIMIT

Let us solve, in the case of interacting particles, the evolution equation (45) for the amplitude $\psi_{00}(X,\tau)$, which corresponds to the density fluctuation. The collisional contributions of orders Γ^{-1} and Γ^{-2} are, respectively,

$$C_{0,1} = -\psi_{00}(X,\tau)\,[g_2(X,X+1)\psi_{00}(X+1,\tau) - g_2(X,X-1)\psi_{00}(X-1,\tau)]\} \tag{46}$$

and

$$\begin{aligned} C_{1,1} &= \frac{2}{\sqrt{\pi}}\psi_{00}(X,\tau)[g_2(X,X+1) \times \psi_{11}(X+1,\tau) + g_2(X,X-1)\psi_{11}(X-1,\tau)] \\ &\quad - \frac{2}{\sqrt{\pi}}\psi_{11}(X,\tau)[g_2(X,X+1)\psi_{00}(X+1,\tau) + g_2(X,X-1)\psi_{00}(X-1,\tau)], \end{aligned} \tag{47}$$

where we have employed the matrix elements $G^1_{0,0}=-1$, $G^1_{0,1}=2/\sqrt{\pi}$, and $G_{1,0}=-G_{0,1}$ and relation $\psi_{11}=-D_X\psi_{00}+C_{0,1}$ to evaluate these expressions. Notice that the self-consistent interaction term $C_{0,1}$ depends only on the amplitude $\psi_{00}(X,\tau)$ of the $H_0(V)$ component. It describes the contribution to the effective restoring force when the velocity distribution of the colliding particles is Maxwellian. The term $C_{1,1}$, instead, accounts for collisions between particles whose velocity deviates from the equilibrium thermal distribution. One may visualize, such a term by imagining the collision as occurring between a thermalized particle, i.e., a particle with zero average momentum and a particle carrying momentum. Indeed, the Langevin dynamics leading to the standard DDF equation describes only collision between per-

fectly thermalized particles. This can be seen by using Eq. (45) and neglecting the term $C_{1,1}$. One can recognize that the following equation:

$$\frac{\partial \psi_{00}(X,\tau)}{\partial \tau} = \frac{1}{\Gamma}\frac{\partial}{\partial X}\left\{\frac{\partial \psi_{00}(X,\tau)}{\partial X} - F(X,\tau)\psi_{00}(X,\tau) + \psi_{00}(X,\tau)[g_2(X,X+1)\psi_{00}(X+1,\tau) - g_2(X,X-1)\psi_{00}(X-1,\tau)]\right\} \tag{48}$$

represents the governing equation of the DDF method, expressed in dimensionless guise.

It is also worth to comment the fact that the short-range and the long-range contributions to the dynamics, contained in $C_{s,\nu}(X,\tau)$ and $F(X,\tau)$, respectively, do not appear on equal footing. This state of affairs is encountered also when studying the equilibrium properties of liquids and was first recognized by van der Waals. In the present dynamical approach we see that the difference originates in the fact that in the hard-core term $K(X,V,\tau)$ the velocity dependence of the distribution function $\tilde{P}(X,V,\tau)$ does not factorize as in the molecular field term. The effect of hard-core collision depends not only on the amplitude of the Maxwellian component of the velocity distribution but on the full velocity distribution. Therefore, as far as the system is not fully thermalized we observe a force which has no counterpart in equilibrium systems. However, as the system relaxes the term $C_{1,1}$ tends to zero, because its amplitude depends on the current $\psi_{11}(X,\tau)=-D_X\psi_{00}(X,\tau)+C_{0,1}(X,\tau)$ which vanishes at equilibrium.

A. Linear analysis

The following simple example may give an idea of the role of the corrections to the DDF equation. We compare the analytical results of our theory with those obtained by computer simulations of the model described by Eq. (3) for an ensemble of N hard particles stochastically driven, in a periodic box of size L.[36] Particle positions and velocities within two consecutive collisions are updated according to a second order discretization scheme for the dynamics in Eq. (3). Averages over 10^4 realizations of the noise were taken.

We perform the analysis of the evolution of a small initial perturbation $\Delta\rho(X,\tau)\sigma=(\psi_{00}(X,\tau)-\rho_0\sigma)$ and show that while the DDF predicts that the relaxation depends only on the time scale τ/Γ, hence is universal, the present theory leads to a violation of this scaling.

In the limit of vanishing perturbations, each Fourier component evolves independently, and decays to zero exponentially.[23]

The characteristic relaxation time can be ascertained by substituting in Eq. (45) the trial solution $\psi_{00}(X,\tau)=\rho_0\sigma+A(\tau)\cos(kX)$ and keeping only linear terms. The resulting equation reads

$$\frac{\partial A(\tau)}{\partial \tau} = -\frac{\alpha(K)}{\Gamma}A(\tau) + O(A^2), \tag{49}$$

and has an exponential solution with a wavelength dependent decay time,

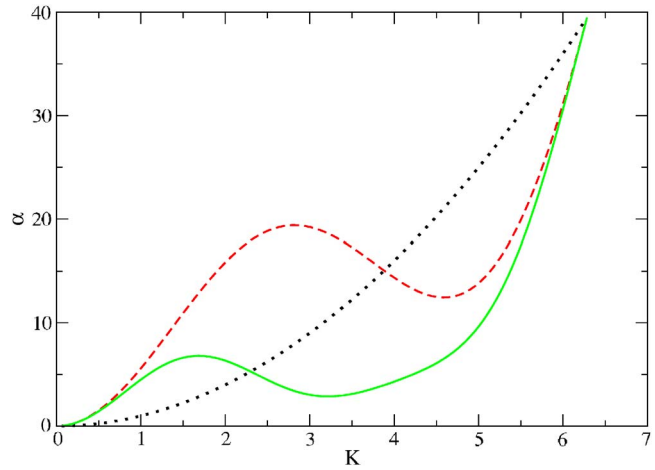

FIG. 1. Exponential relaxation time corresponding to a sinusoidal density modulation of wave vector K. The uniform background is $\rho_0\sigma=0.6$. The dashed line represents the DDF results, while the continuous line represents the result of the present theory with $\Gamma=10$ and the dots the noninteracting system.

$$\frac{\alpha(K)}{\Gamma} = \frac{1}{\Gamma}\frac{K^2}{S(K)}(1-\epsilon(K)) \tag{50}$$

where $S(K)$ is the hard-rod equilibrium structure factor

$$S(K) = \left[1 + 2p_o\sigma\frac{\sin(K)}{K} + 4(p_o\sigma)^2\frac{\sin^2(K/2)}{K^2}\right]^{-1}, \tag{51}$$

with $p_o=\rho_0/(1-\rho_0\sigma)$, being the pressure of the uniform one-dimensional (1D) fluid divided by k_BT. In physical units the decay time associated with the wave vector $q=K/\sigma$ reads $Dq^2(1-\epsilon)/S(q\sigma)$, where for the self-diffusion coefficient D, we use the result for isolated Brownian spheres, given by the Stokes-Einstein equation,

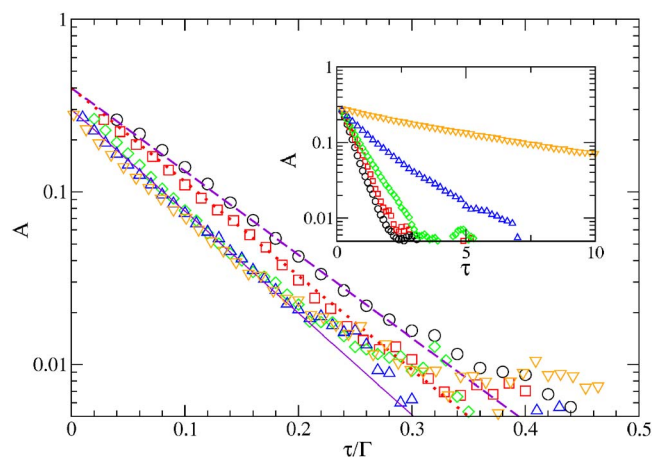

FIG. 2. Initial stage of the temporal evolution of the amplitude decay of a sinusoidal modulation for different values of the dimensionless parameter Γ. The DDF theory would predict a collapse of the data when using the time scale τ/Γ, whereas the present theory predicts a Γ dependence. The circles represent the numerical results relative to $\Gamma=5$, square symbols refer to $\Gamma=7$, diamonds to $\Gamma=10$, upper triangles $\Gamma=20$, and down triangles to $\Gamma=100$. In the inset we report the same data using the original time scale τ. The straight lines correspond to the values of the relaxation time predicted by the linearized solution.

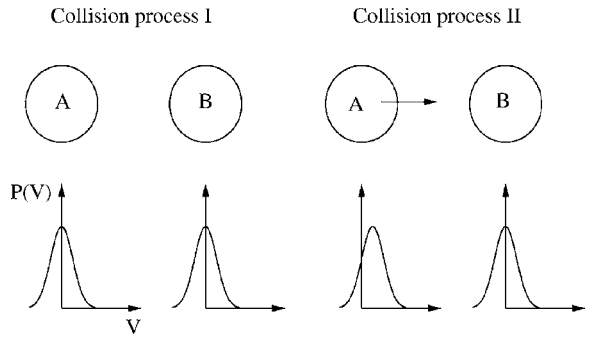

FIG. 3. Sketch of the two different collision processes contributing to the term $C_{0,1}$ (process I) and to the term $C_{1,1}$ (process II).

$$D = \frac{k_B T}{6\pi\eta\sigma}, \tag{52}$$

η being the viscosity of the suspending fluid. The correction to the DDF result $\epsilon(K)$, appearing in Eq. (51), reads

$$\epsilon(K) = \frac{8p_o\sigma}{\Gamma\sqrt{\pi}}\sin^2\left(\frac{K}{2}\right) = \frac{4\omega_E}{\gamma}\sin^2\left(\frac{K}{2}\right) \tag{53}$$

and depends on the ratio $8p_o\sigma/\Gamma\sqrt{\pi}=4(\omega_E/\gamma)$ between the Enskog collision frequency and the heat-bath characteristic frequency. For a uniform one-dimensional hard-rod system the collision frequency is

$$\omega_E = 2\frac{v_T}{\sqrt{\pi}}p_o = 2\sqrt{\frac{k_B T}{m\pi}}p_o. \tag{54}$$

The prediction of the present theory for the variation of the relaxation time with respect to the wave vector of the perturbation is shown in Fig. 1 and compared with the DDF result.

Figure 2 illustrates the comparison between the theoretical predictions and numerical simulations in the case of an initial sinusoidal perturbation of period $K=2\pi/1.4$ and several values of the dimensionless friction Γ. Instead of the data collapse predicted by DDF we observe deviations in the short-time regime. Only for large value of Γ, i.e., in the overdamped limit, we recover universality.

In particular, one observes a slower relaxation of density fluctuations. The larger the collision frequency, the slower the decay. In other words the theory predicts that, at fixed Γ, collisions render the relaxation process slower. What is the physical origin of this slowing down? One can think that a current of momentum can occur either via a particle displacement, i.e., a density change, or through collisional transfer. However, in the latter case the momentum can travel a distance σ without paying any price to the frictional force $-m\gamma v$. Such a mechanism renders this relaxation "channel" slower. The two types of relaxation processes are sketched in Fig. 3. The first process dominates when the system is close to equilibrium when the velocity distribution is well described by a Maxwellian. In the second collision process, which is more relevant far from equilibrium, the two distributions have the same temperature, but not the same momentum.

Two facts are worth to mention: (a) the correction has a kinetic origin as can be seen from the presence of the mass in the last member of Eq. (55). When $m\to\infty$ the correction vanishes, being the inertial effect negligible. On the contrary, in the case of overdamped dynamics, $\epsilon(K)\to 0$, the mass does not appear explicitly in the diffusion coefficient D and only geometrical factors such as $S(K)$ play a role. Secondly, the correction increases as the particle size σ increases.

V. CONCLUSIONS

We have considered the nonequilibrium colloidal dynamics of a system of hard rods of mass m driven by a uniform heat bath. The evolution depends on the nondimensional parameter Γ^{-1}, proportional to the time span occurring to the velocity distribution to reach its equilibrium value and on the packing fraction. This evolution is described by a Kramers equation for the phase-space density $P(X,V,\tau)$ supplemented by a collision term, treated within the revised Enskog theory. Since the momentum degrees of freedom equilibrate much faster than the positional degrees of freedom it is reasonable to look for a description which contains only the latter variables. By employing the multiple time-scale method we have performed the Γ^{-1} expansion of the Kramers-Enskog equation and obtained a modified Smoluchowski-Enskog equation for the density field. We found that the collision term gives a nonlocal coupling between density, momentum, and energy fluctuations. However, the density field slaves the remaining fields. To lowest order in Γ^{-1} the present method yields the same evolution equation for the density as the one obtained within the DDF approach. The present derivation does not require the existence of any equilibrium density functional, but is based on kinetic theory arguments. Therefore, it can be applied to generic nonequilibrium systems, where the RET closure of the evolution equation for the phase-space distribution is physically sound. However, containing as a key ingredient the same equilibrium pair correlation as the DDF, the matching between the two methods is not too surprising.

As discussed by Archer and Evans[19] if the thermal equilibration occurs mainly via the solvent the deviations from the DDF should be negligible. Nevertheless, for atomic fluids the harshly repulsive potential might concur appreciably to the relaxation process and lead to significant effects which are beyond the limits of the DDF approach.

Besides reproducing known results the present derivation provides systematic corrections to the DDF equation accounting for the deviation of the velocity distribution from the Maxwellian. Hence, it can describe situations very far from thermodynamic equilibrium or even situations where a steady but nonequilibrium state exists.

The present method quite naturally lends itself to the following future applications and extensions: (a) hard-core systems whose spatial dimensionality is larger than one, (b) systems of particles experiencing inelastic collisions, such as granular gases, where free energy functional approaches are not applicable[31] and the RET closure provides a valid alternative, (c) systems having a nonuniform temperature profile[37,38] where the standard isothermal DDF approach can-

not be applied, and (d) inclusion of higher order corrections in the inverse friction expansion Γ^{-1} accounting for currents associated with higher moments of the velocity distribution.

ACKNOWLEDGMENTS

We wish to thank F. Cecconi for providing the numerical code on which our simulations are based and G. Costantini for help with the plots. This work was supported by the Ministerio de Educación y Ciencia of Spain Grant No. SAB2003-0207. One of the authors (U.M.B.M.) thanks the Departamento de Fisica Téorica de la Materia Condensada of the Universidad Autonoma de Madrid for hospitality.

APPENDIX A: COLLISION INTEGRALS

We consider explicitly the first three coefficients C_α featuring in the series expansion (17),

$$C_\alpha(X,\tau) = \int_{-\infty}^{\infty} dV \mu_\alpha(V) K(X,V,\tau), \tag{A1}$$

with $\mu_0=1$, $\mu_1=V$, and $\mu_2=(V^2-1)/2$. Using the definition of K given by Eq. (11) one finds the expressions

$$\begin{aligned} C_\alpha(X,\tau) &= g_2(X,X+1)\Big\{\int_{-\infty}^{\infty} dV \mu_\alpha(V) \\ &\quad \times \Big[\int_{-\infty}^{0} du u \tilde{P}(X,V,\tau)\tilde{P}(X+1,u+V,\tau) \\ &\quad + \int_0^{\infty} du u \tilde{P}(X,u+V,\tau)\tilde{P}(X+1,V,\tau)\Big]\Big\} \\ &\quad - g_2(X,X-1)\Big\{\int_{-\infty}^{\infty} dV \mu_\alpha(V) \times \Big[\int_{-\infty}^{0} du u \tilde{P}(X,u \\ &\quad + V,\tau)\tilde{P}(X-1,V,\tau) + \int_0^{\infty} du u \tilde{P}(X,V,\tau)\tilde{P}(X \\ &\quad - 1,u+V,\tau)\Big]\Big\}. \end{aligned} \tag{A2}$$

After substituting expansion (16) into Eq. (A2) and integrating over velocities one obtains

$$\begin{aligned} C_\alpha(X,\tau) &= g_2(X,X+1)\sum_{\mu,\nu} G^\alpha_{\mu,\nu}\phi_\mu(X,\tau)\phi_\nu(X+1,\tau) \\ &\quad - g_2(X,X-1)\sum_{\mu,\nu} G^\alpha_{\nu,\mu}\phi_\mu(X,\tau)\phi_\nu(X-1,\tau), \end{aligned} \tag{A3}$$

where the matrix elements $G^\alpha_{\mu,\nu}$ are given by

$$\begin{aligned} G^\alpha_{\mu,\nu} &= \int_{-\infty}^{\infty} dV \mu_\alpha(V)\Big[\int_{-\infty}^{0} du u H_\mu(V) H_\nu(u+V) \\ &\quad + \int_0^{\infty} du u H_\nu(V) H_\mu(u+V)\Big]. \end{aligned} \tag{A4}$$

The integral $C_0(X,\tau)=0$ is zero, as required by the conservation of the number of particles during a collision, and indeed all $G^0_{\mu,\nu}=0$ vanish. The explicit form of the $G^\alpha_{\mu,\nu}$ for $\mu,\nu=0,1,2$ and $\alpha=1,2$ are given by the following matrices:

$$G^1_{\mu,\nu} = \begin{matrix} -1 & 2/\sqrt{\pi} & -1 \\ -2/\sqrt{\pi} & 1 & -1/\sqrt{\pi} \\ -1 & 1/\sqrt{\pi} & 0 \end{matrix}$$

and

$$G^2_{\mu,\nu} = \begin{matrix} 0 & -1/2 & 2/\sqrt{\pi} \\ -1/2 & 0 & 1/2 \\ -2/\sqrt{\pi} & 1/2 & 0 \end{matrix}.$$

APPENDIX B: A USEFUL IDENTITY

We prove hereafter that the collision kernel $K(X,V,\tau)$ and thus the expansion coefficients $C_n(X,\tau)$ can be expressed as divergences. To this purpose we employ the following identity:[39]

$$\begin{aligned} S(X,X+Y) - S(X-Y,X) &= \int_0^1 dz \frac{\partial}{\partial z} S(X-(1-z)Y,X+zY) \\ &= \frac{\partial}{\partial X}\int_0^1 dz S(X-(1-z)Y,X+zY) \end{aligned} \tag{B1}$$

and identify

$$\begin{aligned} S(X,X+Y) &= -g_2(X,X+Y)\int_{-\infty}^{\infty} dV_2(V_1-V_2) \\ &\quad \times \{\Theta(V_1-V_2)P(X,V_1,\tau)P(X+Y,V_2,\tau) \\ &\quad + \Theta(V_2-V_1)P(X+Y,V_1,\tau)P(X,V_2,\tau)\} \end{aligned} \tag{B2}$$

and setting $Y=1$ rewrite Eq. (11) with the help of Eq. (B2) as

$$\begin{aligned} K(X,V_1,\tau) &= -\frac{\partial}{\partial X}\int_0^1 dz g_2(X-(1-z)Y,X+zY) \\ &\quad \times \int_{-\infty}^{\infty} dV_2(V_1-V_2)\{\Theta(V_1-V_2) \\ &\quad \times P(X-(1-z)Y,V_1,\tau) \\ &\quad \times P(X+zY,V_2,\tau) + \Theta(V_2-V_1) \\ &\quad \times P(X+zY,V_1,\tau)P(X-(1-z)Y,V_2,\tau)\}. \end{aligned} \tag{B3}$$

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