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# Dynamic density functional theory versus kinetic theory of simple fluids

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## Abstract

By combining methods of kinetic and density functional theory, we present a description of molecular fluids which accounts for their microscopic structure and thermodynamic properties as well as their hydrodynamic behavior. We focus on the evolution of the one-particle phase space distribution, rather than on the evolution of the average particle density which features in dynamic density functional theory. The resulting equation can be studied in two different physical limits: diffusive dynamics, typical of colloidal fluids without hydrodynamic interaction where particles are subject to overdamped motion resulting from coupling with a solvent at rest, and inertial dynamics, typical of molecular fluids. Finally, we propose an algorithm to solve numerically and efficiently the resulting kinetic equation by employing a discretization procedure analogous to the one used in the lattice Boltzmann method.

## 1. Introduction

Understanding transport phenomena and their interplay with the structural properties of liquids in strongly inhomogeneous systems is of major importance in many fields such as microfluidics, materials science and physiology and has several technological applications, ranging from pharmaceuticals to ternary oil recovery [1]. Much progress has been achieved in the last 30 years concerning the equilibrium properties of liquids in the presence of confining geometries or structured substrates. One of the major tools for exploring inhomogeneous classical fluids is density functional theory (DFT), yielding thermodynamic (free energy, phase coexistence, osmotic pressure) and structural properties (density and composition profiles) within the same framework [2, 3]. Such a method presents many advantages: it is highly versatile, variational, lends itself to approximations guided by physical insight and is universally applicable to the study of the properties of all real fluids under a wide variety of thermodynamic and geometric conditions. In view of the great success of the DFT, a dynamic DFT (DDFT) has been proposed to describe the dynamics of the density profile  $n(\mathbf{r}, t)$  possibly due to a time dependent external potential or to a sudden change of the control parameters [4, 5].

The typical DDFT equation is a continuity equation for the number density:

$$\frac{\partial n(\mathbf{r}, t)}{\partial t} + \nabla \cdot \mathbf{J}(\mathbf{r}, t) = 0 \quad (1)$$

supplemented by a prescription relating the particle flux,  $\mathbf{J}$ , to the density itself obtained by using the specific properties of the dynamics of the system. In the case of a colloid–solvent system without hydrodynamic interaction, one ideally traces out the solvent microscopic degrees of freedom and mimics their influence on the solute particles via Brownian dynamics induced by a heat bath stochastic term. Under this assumption one can derive a simple relation between  $\mathbf{J}$  and  $n$ . On the other hand, in the case of molecular fluids, the absence of the fast degrees of freedom of the solvent seems to preclude such a possibility. It is necessary to recognize that the minimal set of collective variables which are relevant in the dynamical description of a fluid corresponds to the locally conserved fields, namely the number of particles, momentum and energy density. One can represent their evolution at a mesoscopic level by means of a set of hydrodynamic equations, which require the specification of the currents associated with momentum and

the energy densities in terms of the hydrodynamic variables via the so-called phenomenological constitutive relations. However, if one requires a microscopic level of description similar to the one achieved by DDFT it is necessary to choose a kinetic approach and consider the time evolution of the one-particle phase space distribution,  $f(\mathbf{r}, \mathbf{v}, t)$ . Doing this it is also possible to bridge hydrodynamics and microscopic structural theories of fluids. The method avoids the difficulty of computing separately the velocity moments of the distribution function because it considers directly the evolution of  $f$ . The derived equations can then be solved numerically by means of the lattice Boltzmann (LB) method, a well-known method widely used in computational fluid dynamics [6]. The resulting theory is able to predict structure and thermodynamics with an accuracy comparable to that of DDFT, but has the advantage of describing transport properties more realistically [7, 8]. In addition we shall show that from the present kinetic approach it is possible to derive both the DDFT for colloids and the transport equation describing molecular fluids. The two descriptions depart when one specifies the interaction of the fluid with the heat bath. In the first case, the heat bath is fixed, breaks the Galilei invariance of the system and damps the momentum and energy transport. In the second case, the internal degrees of freedom act as a heat bath co-moving with the fluid and restoring the local equilibrium.

The present paper is organized as follows: in section 2 we shall briefly review the DDFT for a colloid–solvent solution by considering its derivation from an approach based on the evolution of the one-particle phase space distribution. In section 3 we switch to the case of a molecular liquid and obtain a simplified transport equation which accommodates within the same framework thermodynamic and structural properties, inertial effects of the fluid (sound waves, shear modes) and transport coefficients. In section 4 we give a brief account of the numerical method used to solve the transport equation. Finally, in section 5 we present the conclusions.

## 2. Microscopic description

Let us consider first a system of great practical interest,  $N$  particles, of mass  $m$ , positions  $\mathbf{r}_i$  and velocities  $\mathbf{v}_i$ , immersed in a solvent. Since the solvent particles are in general much lighter and smaller than the host particles, the degrees of freedom of the solvent can be eliminated by applying a suitable coarse graining procedure. The resulting total force acting on each colloidal particle is the sum of the interactions with other colloidal particles, of the external fields and of a stochastic force represented as a Langevin process, which combines a frictional force proportional to the velocity with respect to the solvent with a stochastic white noise forcing  $-\gamma^{\text{solv}}\mathbf{v}_i + \xi_i$ . Since both terms originate from the solvent their amplitudes are related by the following fluctuation–dissipation relation,  $\langle \xi_i^\alpha(t) \xi_j^\beta(s) \rangle = 2\gamma^{\text{solv}} m k_B T^{\text{solv}} \delta_{ij} \delta^{\alpha\beta} \delta(t-s)$ , where the superscript ‘solv’ indicates the origin of the friction and of the thermostating medium. The particles interact through a pair

potential  $U$  and are subject to a force field  $\mathbf{F}_{\text{ext}}$ :

$$\begin{aligned} \frac{d\mathbf{r}_i}{dt} &= \mathbf{v}_i \\ m \frac{d\mathbf{v}_i}{dt} &= \left[ \mathbf{F}_{\text{ext}}(\mathbf{r}_i) - \sum_{j(\neq i)} \nabla_{\mathbf{r}_i} U(|\mathbf{r}_i - \mathbf{r}_j|) \right] \\ &\quad - m\gamma^{\text{solv}} \mathbf{v}_i + \xi_i(t). \end{aligned} \quad (2)$$

It is straightforward to derive the associated linear Kramers–Fokker–Planck [9] evolution equation for the  $6N$ -dimensional phase space probability density distribution  $f_N(\{\mathbf{r}, \mathbf{v}\}, t)$ , where  $\{\mathbf{r}, \mathbf{v}\}$  indicates a  $6N$ -dimensional phase space point:

$$\begin{aligned} &\left( \frac{\partial}{\partial t} + \sum_i \left[ \mathbf{v}_i \cdot \nabla_{\mathbf{r}_i} + \left[ \frac{\mathbf{F}_{\text{ext}}(\mathbf{r}_i)}{m} \right. \right. \right. \\ &\quad \left. \left. \left. - \frac{1}{m} \sum_{j(\neq i)} \nabla_{\mathbf{r}_i} U(|\mathbf{x}_i - \mathbf{x}_j|) \right] \cdot \nabla_{\mathbf{v}_i} \right] \right) f_N(\{\mathbf{r}, \mathbf{v}\}, t) \\ &= \gamma^{\text{solv}} \sum_i \left[ \nabla_{\mathbf{v}_i} \cdot \mathbf{v}_i + \frac{k_B T^{\text{solv}}}{m} \nabla_{\mathbf{v}_i}^2 \right] f_N(\{\mathbf{r}, \mathbf{v}\}, t). \end{aligned} \quad (3)$$

Notice that we switched from a description in terms of trajectories of the particles to a probabilistic representation in terms of  $f_N$ . This can be justified in two possible ways: the probabilistic description is: (a) the result of an ensemble averaging of the trajectories over a noise ensemble or (b) follows from an averaging over initial conditions. Case (a) applies to the damped stochastic dynamics ( $\gamma^{\text{solv}} > 0$ ) typical of a colloidal suspension, while case (b) applies to the Hamiltonian dynamics characteristic of an atomic liquid,  $\gamma^{\text{solv}} = 0$ , when equation (3) reduces to the Liouville equation.

The information contained in  $f_N$  is fully microscopic since it describes the microstate of the system. However, one recognizes that after an initial many-body regime, whose duration is of the order of the duration of a collision event, such a representation becomes redundant and it is possible to contract the description from  $6N$  dimensions to only six dimensions, that is, from the phase space distribution of  $N$  particles to the one-particle phase space distribution,  $f(\mathbf{r}, \mathbf{v}, t)$ . In this stage, termed the kinetic regime, the one-body distribution relaxes towards a local Maxwellian and its evolution can be represented by the following equation:

$$\begin{aligned} &\left( \frac{\partial}{\partial t} + \mathbf{v} \cdot \nabla + \frac{\mathbf{F}_{\text{ext}}(\mathbf{r})}{m} \cdot \frac{\partial}{\partial \mathbf{v}} \right) f(\mathbf{r}, \mathbf{v}, t) \\ &= \mathcal{Q}(\mathbf{r}, \mathbf{v}, t) + \mathcal{B}^{\text{solv}}(\mathbf{r}, \mathbf{v}, t). \end{aligned} \quad (4)$$

This equation contains the streaming terms in the left-hand side, whereas in the right-hand side  $\mathcal{Q}$  is the interaction term:

$$\mathcal{Q}(\mathbf{r}, \mathbf{v}, t) = \frac{1}{m} \nabla_{\mathbf{v}} \cdot \int d\mathbf{r}' \int d\mathbf{v}' f_2(\mathbf{r}, \mathbf{v}, \mathbf{r}', \mathbf{v}', t) \nabla_{\mathbf{r}'} U(|\mathbf{r} - \mathbf{r}'|) \quad (5)$$

and  $\mathcal{B}^{\text{solv}}$  represents the heat bath term:

$$\mathcal{B}^{\text{solv}}(\mathbf{r}, \mathbf{v}, t) = \gamma^{\text{solv}} \left[ \frac{k_B T^{\text{solv}}}{m} \frac{\partial^2}{\partial \mathbf{v}^2} + \frac{\partial}{\partial \mathbf{v}} \cdot \mathbf{v} \right] f(\mathbf{r}, \mathbf{v}, t). \quad (6)$$

To proceed further one makes the approximation that the two-particle distribution function,  $f_2$ , can be expressed as a product

of one-particle distribution functions times the positional pair correlation function  $g$ :

$$f_2(\mathbf{r}, \mathbf{v}, \mathbf{r}', \mathbf{v}', t) \approx f(\mathbf{r}, \mathbf{v}, t) f(\mathbf{r}', \mathbf{v}', t) g(\mathbf{r}, \mathbf{r}') \quad (7)$$

so that equation (4) becomes a closed non-linear equation for the one-particle distribution. This is a crucial assumption, since it decouples the evolution of  $f(\mathbf{r}, \mathbf{v}, t)$  from the evolution of the higher order multiparticle distribution functions. Many particle correlations are, however, retained through the structural information contained in the positional pair correlation function  $g(\mathbf{r}, \mathbf{r}')$ . As an approximation, we shall assume that  $g(\mathbf{r}, \mathbf{r}')$  is a nonlocal function of the profile  $n(\mathbf{r}, t)$ , depends on time only through the density profile and has the same form as in a nonuniform equilibrium state whose density is  $n(\mathbf{r}, t)$ .

For  $\gamma^{\text{solv}} > 0$ , one can simplify equation (4) further and derive an equation involving only the ensemble averaged particle density, by using the fact that momentum and energy of the colloidal particles are not conserved, so that the currents become rapidly ‘slaved’ to the density, i.e. the evolution is completely determined in terms of  $n(\mathbf{r}, t)$  and its derivatives. That occurs because the velocities of the particles rapidly relax towards the equilibrium distribution, in a time of the order of the inverse friction time  $\tau^{\text{solv}} = 1/\gamma^{\text{solv}}$ . This is the case when the non-dimensional ratio  $v_T \tau^{\text{solv}}/\sigma \ll 1$ , where  $\sigma$  is the typical size of the particles and  $v_T$  is the thermal velocity, since the particles undergo a small displacement in a time  $\sim \tau^{\text{solv}}$ . The only relevant evolution on timescales larger than  $\tau^{\text{solv}}$  concerns the spatial distribution of the particles. This is the reason why the DDFT gives a sufficiently accurate description of colloidal systems.

To be concrete, let us define the velocity moments of  $f(\mathbf{r}, \mathbf{v}, t)$  by multiplying equation (4) by  $1, m\mathbf{v}, m(\mathbf{v} - \mathbf{u})^2/2$ , respectively, and integrating w.r.t.  $\mathbf{v}$ , obtaining the continuity equation

$$\partial_t n(\mathbf{r}, t) + \nabla \cdot (n(\mathbf{r}, t) \mathbf{u}(\mathbf{r}, t)) = 0 \quad (8)$$

the momentum balance equation

$$mn(\mathbf{r}, t)[\partial_t u_j(\mathbf{r}, t) + u_i(\mathbf{r}, t) \partial_i u_j(\mathbf{r}, t)] + \partial_i P_{ij}^{(K)}(\mathbf{r}, t) - F_j(\mathbf{r})n(\mathbf{r}, t) - C_j^{(1)}(\mathbf{r}, t) = b_j^{(1)}(\mathbf{r}, t) \quad (9)$$

and the kinetic balance equation

$$\frac{3}{2}k_B n(\mathbf{r}, t)[\partial_t T(\mathbf{r}, t) + u_i(\mathbf{r}, t) \partial_i T(\mathbf{r}, t)] + P_{ij}^{(K)}(\mathbf{r}, t) \partial_i u_j(\mathbf{r}, t) + \partial_i q_i^{(K)}(\mathbf{r}, t) - C^{(2)}(\mathbf{r}, t) = b^{(2)}(\mathbf{r}, t) \quad (10)$$

where the local fluid density is

$$n(\mathbf{r}, t) = \int d\mathbf{v} f(\mathbf{r}, \mathbf{v}, t) \quad (11)$$

the local fluid velocity,  $\mathbf{u}$ , is

$$n(\mathbf{r}, t) \mathbf{u}(\mathbf{r}, t) = \int d\mathbf{v} \mathbf{v} f(\mathbf{r}, \mathbf{v}, t) \quad (12)$$

and the local fluid kinetic energy density is:

$$e^{\text{kin}}(\mathbf{r}, t) = \frac{d}{2} k_B n(\mathbf{r}, t) T(\mathbf{r}, t) = \frac{m}{2} \int d\mathbf{v} (\mathbf{v} - \mathbf{u})^2 f(\mathbf{r}, \mathbf{v}, t). \quad (13)$$

We have introduced the kinetic component of the pressure tensor

$$P_{ij}^{(K)}(\mathbf{r}, t) = m \int d\mathbf{v} f(\mathbf{r}, \mathbf{v}, t) (\mathbf{v} - \mathbf{u})_i (\mathbf{v} - \mathbf{u})_j \quad (14)$$

and of the heat flux vector:

$$q_i^{(K)}(\mathbf{r}, t) = \frac{m}{2} \int d\mathbf{v} f(\mathbf{r}, \mathbf{v}, t) (\mathbf{v} - \mathbf{u})^2 (\mathbf{v} - \mathbf{u})_i. \quad (15)$$

Notice that  $P_{ij}^{(K)}$  and  $q_i^{(K)}$  cannot in general be expressed in terms of the hydrodynamic moments introduced so far. We also have two terms stemming from the interaction

$$C_i^{(1)}(\mathbf{r}, t) = m \int d\mathbf{v} \mathcal{Q}(\mathbf{r}, \mathbf{v}, t) v_i = -\frac{1}{m} n(\mathbf{r}, t) \nabla_i \frac{\delta \mathcal{F}^{\text{nonideal}}[n(\mathbf{r}, t)]}{\delta n(\mathbf{r}, t)} = -\partial_j P_{ij}^{(C)}(\mathbf{r}, t) \quad (16)$$

$$C^{(2)}(\mathbf{r}, t) = \frac{m}{2} \int d\mathbf{v} \mathcal{Q}(\mathbf{r}, \mathbf{v}, t) (\mathbf{v} - \mathbf{u})^2. \quad (17)$$

The second equality in (16) relates  $C_i^{(1)}$  to a functional derivative of the nonideal part of the free energy, whereas the third equality connects it to a spatial derivative of the potential part of the stress tensor. It is important to notice that  $C_i^{(1)}$  and  $C^{(2)}$  vanish in a uniform system. Finally we specify the terms stemming the coupling with the heat bath

$$b_i^{(1)}(\mathbf{r}, t) = m \int d\mathbf{v} (v - u)_i \mathcal{B}^{\text{solv}}(\mathbf{r}, \mathbf{v}, t) = -m \gamma^{\text{solv}} n(\mathbf{r}, t) u_i(\mathbf{r}, t) \quad (18)$$

$$b^{(2)}(\mathbf{r}, t) = \frac{m}{2} \int d\mathbf{v} (\mathbf{v} - \mathbf{u})^2 \mathcal{B}^{\text{solv}}(\mathbf{r}, \mathbf{v}, t) = \gamma^{\text{solv}} [3k_B T^{\text{solv}} - m \langle \mathbf{v}^2 \rangle] n(\mathbf{r}, t). \quad (19)$$

The presence of  $b_i^{(1)}$  and  $b^{(2)}$  in equations (9) and (10) determines a fast equilibration process of the momentum current  $n\mathbf{u}$  and of the local temperature  $T$  towards their stationary values. This fact is used to contract the description from the five fields appearing in equations (8)–(10) to the single field appearing in the DDFT equation. The rigorous mathematical procedure to derive this result employs the multiple timescale analysis [10–12], exploiting the timescale separation between the zero mode associated with the density fluctuations and the remaining modes, including the momentum and energy fluctuations which are fast relaxing due to the friction with the solvent. Physically speaking, the heat bath renders possible the contraction from the phase space to the configurational space because it rapidly ‘washes out’ any possible deviation of the distribution function from the Gaussian. The larger the friction the faster the restoring process towards the Maxwellian. We shall not go through the details of such a derivation, which can be found in [10, 12], and merely quote the final result:

$$\partial_t n(\mathbf{r}, t) = \frac{1}{m\gamma} \sum_i \nabla_i [k_B T \nabla_i n(\mathbf{r}, t) - F_i(\mathbf{r})n(\mathbf{r}, t) - C_i^{(1)}(\mathbf{r}, t)]. \quad (20)$$

It is possible to compute inertial corrections to such an equation by employing systematically the multiple timescale

analysis, which is tantamount to an inverse friction expansion, but this procedure does not help in the case of molecular fluids where the inverse friction parameter  $1/\gamma^{\text{solv}}$  diverges, and only internal dissipation mechanisms are at work. A salient feature of molecular liquids is that they support hydrodynamical modes, as a result of local conservation laws of particle number, momentum and energy, which are eventually damped due to internal friction and heat transport mechanisms. Hence it is necessary to apply a strategy which preserves the translational invariance of the system and does not select a particular reference frame where the solvent is at rest [13, 14].

### 3. Molecular fluids

The key difference between colloidal systems and molecular fluids is that in the former the equilibration is due to the heat bath externally imposed by the solvent whilst in the latter equilibration is realized via viscosity and heat conduction among the same fluid elements. In molecular fluids typical relaxation times of hydrodynamic modes diverge as  $k^{-2}$  for excitations of wavevector  $k \rightarrow 0$ , whereas the relaxation times of non-hydrodynamic modes are shorter and finite in the same limit. Our treatment of equation (4) must retain such a feature while accounting for the structural and thermodynamic properties with an accuracy comparable to DDFT [15]. For  $\gamma^{\text{solv}} = 0$ , we recast equation (4) as:

$$\begin{aligned} \partial_t f(\mathbf{r}, \mathbf{v}, t) + \mathbf{v} \cdot \nabla f(\mathbf{r}, \mathbf{v}, t) + \frac{\mathbf{F}^{\text{ext}}(\mathbf{r})}{m} \cdot \frac{\partial}{\partial \mathbf{v}} f(\mathbf{r}, \mathbf{v}, t) \\ = \mathcal{K}(\mathbf{r}, \mathbf{v}, t) + \mathcal{B}^{\text{int}}(\mathbf{r}, \mathbf{v}, t) \end{aligned} \quad (21)$$

where

$$\begin{aligned} \mathcal{K}(\mathbf{r}, \mathbf{v}, t) \equiv \frac{f_{\text{loc}}(\mathbf{r}, \mathbf{v}, t)}{k_B n(\mathbf{r}, t) T(\mathbf{r}, t)} \left( (\mathbf{v} - \mathbf{u}) \cdot \mathbf{C}^{(1)}(\mathbf{r}, t) \right. \\ \left. + \left( \frac{m(\mathbf{v} - \mathbf{u})^2}{3k_B T(\mathbf{r}, t)} - 1 \right) C^{(2)}(\mathbf{r}, t) \right) \end{aligned} \quad (22)$$

and

$$f_{\text{loc}}(\mathbf{r}, \mathbf{v}, t) = n(\mathbf{r}, t) \left[ \frac{m}{2\pi k_B T(\mathbf{r}, t)} \right]^{3/2} \exp\left(-\frac{m(\mathbf{v} - \mathbf{u})^2}{2k_B T(\mathbf{r}, t)}\right). \quad (23)$$

The two terms in the right-hand side of equation (21) represent a suitable decomposition of  $\mathcal{Q}(\mathbf{r}, \mathbf{v}, t)$ . The idea is to treat the contribution of  $\mathcal{Q}$  from hydrodynamic modes separately from the non-hydrodynamic kinetic modes. The term  $\mathcal{K}$  guarantees that the local transfer of momentum and energy is not altered. The part  $\mathcal{B}^{\text{int}}$  is chosen so that it does not contribute explicitly to the evolution of the hydrodynamic modes nor to the structure of the fluid, i.e. it does not appear in equations (9) and (10). For this reason it can be treated within a simple relaxation approximation, as shown below. We have deliberately employed the same symbol  $\mathcal{B}$  as used for the solvent heat bath, to stress the fact that even in this case a thermalizing mechanism for the hydrodynamic modes exists and stems from the interplay between these modes and the non-hydrodynamic modes. The role of  $\mathcal{B}^{\text{int}}$  is to reproduce in an approximate and simple fashion the fast relaxation process of  $f$

towards the local equilibrium distribution  $f_{\text{loc}}$ . The following BGK relaxation approximation [16] for the non-hydrodynamic components of  $\mathcal{Q}$  meets the requirements of leaving unaltered the balance equations

$$\mathcal{B}^{\text{int}}(\mathbf{r}, \mathbf{v}, t) \equiv -\nu_0 [f(\mathbf{r}, \mathbf{v}, t) - f_{\text{loc}}(\mathbf{r}, \mathbf{v}, t)] = -\nu_0 \delta f(\mathbf{r}, \mathbf{v}, t) \quad (24)$$

where  $\nu_0$  is a microscopic relaxation rate of the order of the Enskog collision rate,  $\omega_E = 4\sqrt{\pi}n\sigma^2 v_T$ , where  $\sigma$  is a molecular diameter and  $v_T = \sqrt{k_B T/m}$ . Since by construction both  $f(\mathbf{r}, \mathbf{v}, t)$  and  $f_{\text{loc}}(\mathbf{r}, \mathbf{v}, t)$  correspond to the same values of  $n, \mathbf{u}, T$ , one obtains that  $b_i^{(1)}$  and  $b^{(2)}$ , associated with  $\mathcal{B}^{\text{int}}$ , vanish. In conclusion, the balance equations for the hydrodynamic moments generated by equation (21) with the ansatz (24) meet all the requirements imposed by the translational invariance of the system and thus possess the correct long-wavelength hydrodynamic behavior.

Before particularizing the description we wish to comment on a similarity between the DDFT and the present approach. It was found in DDFT that the free energy always decreases with time:

$$\frac{d\mathcal{F}[n]}{dt} = - \int d\mathbf{r} n(\mathbf{r}, t) \left[ \nabla \cdot \frac{\delta \mathcal{F}[n]}{\delta n(\mathbf{r}, t)} \right]^2 \leq 0.$$

In the present case instead we have that the entropy, defined as

$$S[f] = -k_B \int d\mathbf{r} d\mathbf{v} f(\mathbf{r}, \mathbf{v}, t) \ln f(\mathbf{r}, \mathbf{v}, t)$$

increases with time  $\frac{dS[f]}{dt} \geq 0$ , which is a statement of the  $H$ -theorem.

Using the special form of  $\mathcal{B}^{\text{int}}$  it is possible to obtain perturbatively an approximation for  $\delta f$  and the transport coefficients at low density. In the spirit of the Chapman–Enskog method [17] we insert the trial distribution  $f_{\text{loc}}(\mathbf{r}, \mathbf{v}, t)$  into the left-hand side of equation (21) and neglect the term  $\mathcal{K}$ . Using equations (8)–(10) to eliminate the time derivatives of the fields we arrive at the following explicit representation of  $\delta f$ :

$$\begin{aligned} \delta f(\mathbf{r}, \mathbf{v}, t) = -\frac{1}{\nu_0} \frac{f_{\text{loc}}(\mathbf{r}, \mathbf{v}, t)}{k_B T(\mathbf{r}, t)} \left[ \left( \frac{m(\mathbf{v} - \mathbf{u})^2}{2k_B T(\mathbf{r}, t)} - \frac{5}{2} \right) \right. \\ \times (v_i - u_i) \partial_i k_B T(\mathbf{r}, t) \\ \left. + m \left( (v_i - u_i)(v_k - u_k) - \frac{(\mathbf{v} - \mathbf{u})^2}{3} \delta_{ik} \right) \partial_i u_k(\mathbf{r}, t) \right] \end{aligned} \quad (25)$$

which is valid in the low density limit and to first order in the gradients of  $\mathbf{u}$  and  $T$ . By substituting  $\delta f$  in equations (14) and (15) and with the help of the definitions

$$P_{ij}^{(K)} = -\eta^{(K)} (\nabla_i u_j + \nabla_j u_i - \frac{2}{3} \nabla \cdot \mathbf{u})$$

and

$$q_i^{(K)} = -\lambda^{(K)} \nabla_i T$$

we compute the associated kinetic contributions to the viscosity

$$\eta^{(K)} = \frac{m v_T^2}{\nu_0} n \quad (26)$$

and to the heat conductivity

$$\lambda^{(K)} = \frac{5}{2} \frac{v_T^2}{v_0} k_B n. \quad (27)$$

In order to obtain the ‘potential’ contribution to the transport coefficients one needs an explicit representation of  $C_i^{(1)}$  and  $C^{(2)}$ , which can be studied either in the random phase approximation (RPA) [18] consisting of combining equations (5) and (7) or in the revised Enskog theory (RET), which applies to hard sphere fluids and to piecewise constant potentials.

Within the RPA one finds  $C^{(2)}(\mathbf{r}, t) = 0$  and

$$C_i^{(1)}(\mathbf{r}, t) = n(\mathbf{r}, t) F_i^{\text{mol}}(\mathbf{r}, t) \quad (28)$$

where we have introduced the self-consistent molecular field:

$$F_i^{\text{mol}}(\mathbf{r}, t) = - \int d\mathbf{r}' n(\mathbf{r}', t) g(\mathbf{r}, \mathbf{r}') \frac{\partial}{\partial r_i} U(|\mathbf{r} - \mathbf{r}'|). \quad (29)$$

Concerning the RPA, we wish to comment that it can treat fluids characterized by slowly varying potentials, like ultra-soft potentials used to model the steric repulsion between polymers or long range attractive interactions. It can describe qualitatively their multiphase behavior, but does not give a suitable representation of their transport properties in the high density region, as it is evident from the vanishing of  $C^{(2)}(\mathbf{r}, t)$ . In fact, the RPA treatment of correlations, while accounting for thermodynamical properties, does not contribute to their hydrodynamical properties.

Sharp repulsive interactions cannot be accounted for as a molecular field because they imply strong correlations between the relative positions and the relative velocity.

On the contrary, one can obtain a satisfactory representation of both structural and transport properties of hard sphere fluids. A very accurate treatment of how the hard sphere interaction contributes to the evolution of the phase space distribution is provided by the RET [19] which approximates the collisional integral as:

$$\begin{aligned} \mathcal{Q}_{\text{RET}}[f](\mathbf{r}, \mathbf{v}_1, t) &= \sigma^{d-1} \int d\mathbf{v}_2 \int d\hat{\sigma} \Theta(\hat{\sigma} \cdot \mathbf{v}_{12}) (\hat{\sigma} \cdot \mathbf{v}_{12}) \\ &\times \{ g_{\text{hs}}(\mathbf{r}, \mathbf{r} - \sigma \hat{\sigma}) f(\mathbf{r}, \mathbf{v}'_1, t) f(\mathbf{r} - \sigma \hat{\sigma}, \mathbf{v}'_2, t) \\ &- g_{\text{hs}}(\mathbf{r}, \mathbf{r} + \sigma \hat{\sigma}) f(\mathbf{r}, \mathbf{v}_1, t) f(\mathbf{r} + \sigma \hat{\sigma}, \mathbf{v}_2, t) \} \end{aligned} \quad (30)$$

where  $g_{\text{hs}}(\mathbf{r}, \mathbf{r}')$  is the hard sphere pair correlation function and  $\sigma$  is the hard sphere diameter. The primes on velocities denote scattered values after the collision and  $\mathbf{v}_{12} \equiv (\mathbf{v}_1 - \mathbf{v}_2)$ ,  $\hat{\sigma}$  is the unit vector directed from particle 1 to particle 2, and

$$\mathbf{v}'_1 = \mathbf{v}_1 - (\hat{\sigma} \cdot \mathbf{v}_{12}) \hat{\sigma}$$

$$\mathbf{v}'_2 = \mathbf{v}_2 + (\hat{\sigma} \cdot \mathbf{v}_{12}) \hat{\sigma}.$$

The difference from the Boltzmann equation is that the two distribution functions are evaluated at different positions. Such a difference in positions at collision allows the instantaneous transfer of momentum and energy between two particles. This collisional transfer is much faster and more effective than the translational transfer and becomes dominant as density increases.

The salient feature which differentiates RPA and RET is the presence of velocity correlations in the latter approximation. In fact it is assumed that the velocities of two particles are uncorrelated immediately prior to collision but are correlated after they collide, because collision itself generates correlation.

From equation (30) we can obtain  $C_i^{(1)}$  and  $C^{(2)}$  once  $f(\mathbf{r}, \mathbf{v}, t)$  is known. Interestingly one derives a simple relation for  $C^{(2)}$  in terms of the hydrodynamic variables:

$$C^{(2)}(\mathbf{r}, t) = -\nabla_i q_i^{(C)}(\mathbf{r}, t) - P_{ij}^{(C)}(\mathbf{r}, t) \nabla_i u_j(\mathbf{r}, t) \quad (31)$$

where  $q_i^{(C)}$  and  $P_{ij}^{(C)}$  are the collisional components of the heat flux vector and of the pressure tensor, respectively. The two terms in the previous formula account for the transfer of thermal energy via collisional transfer and the viscous dissipation due to the presence of velocity gradients, but such a connection is valid only for the hard sphere case, where there is no potential energy contribution.

However, it is also possible, as shown in [8], to obtain these quantities explicitly by approximating in equation (30)  $f(\mathbf{r}, \mathbf{v}, t)$  by  $f_{\text{loc}}(\mathbf{r}, \mathbf{v}, t)$ , that is, by neglecting  $\delta f$  in the integrals. This approximation allows one to express  $C_i^{(1)}(\mathbf{r}, t)$  and  $C^{(2)}(\mathbf{r}, t)$  by means of appropriate convolution integrals involving finite spatial differences of  $n(\mathbf{r}, t)$ ,  $\mathbf{u}(\mathbf{r}, t)$ , and  $T(\mathbf{r}, t)$ . It is such a dependence on the hydrodynamic fields that gives a nontrivial result for the transport coefficients. In fact, one finds that in the limit of slowly varying inhomogeneities the present theory reduces to the Longuet-Higgins–Pople theory of transport coefficients [20]. This level of approximation yields the following collisional contributions to the shear viscosity:

$$\eta^{(C)} = \frac{4}{15} \sqrt{\pi} m v_T \sigma^4 n^2 g_{\text{hs}}(\sigma) \quad (32)$$

and to the heat conductivity:

$$\lambda^{(C)} = \frac{2}{3} \frac{k_B}{m} \sqrt{\pi} m v_T \sigma^4 n^2 g_{\text{hs}}(\sigma). \quad (33)$$

To conclude, in the HS case we obtain a formula for the shear viscosity by taking into account only the distortion of the singlet distribution function from the uniform Maxwellian. For more general interactions the potential contribution to  $\eta$  dominates over the one-body contribution in liquids at high densities and one has to consider the distortion of the doublet distribution function which is completely neglected in the present treatment [21].

#### 4. Numerical method in a nutshell

This section is included to illustrate how the microscopic description presented above can be applied in practical situations where the system under scrutiny is spatially inhomogeneous. In such a case, the transport equation (21) still represents a formidable numerical problem for the evolution of  $f(\mathbf{r}, \mathbf{v}, t)$  on a six-dimensional space. A possible method of solution is represented by focusing on the set of partial

differential equations for the hydrodynamic moments (8)–(10), but these require the specification of complex boundary conditions and constitutive relations.

An appealing alternative is to solve equation (21) directly by using a discretization of velocities on a mesh [22–25], a technique known as the lattice Boltzmann equation (LBE), which deals directly with the phase space distribution function and provides a well-tested and robust method of solution [6].

In order to illustrate the scheme, we first project the phase space distribution function over an orthonormal basis spanned by the tensorial Hermite polynomials  $\{H_{\underline{\alpha}}^{(l)}\}$ :

$$f(\mathbf{r}, \mathbf{v}, t) = \omega(\mathbf{v}) \sum_{l=0}^{\infty} \frac{1}{l! v_T^{2l}} \phi_{\underline{\alpha}}^{(l)}(\mathbf{r}, t) H_{\underline{\alpha}}^{(l)}(\mathbf{v}) \quad (34)$$

where  $\omega(\mathbf{v}) = (2\pi v_T^2)^{-3/2} e^{-\mathbf{v}^2/2v_T^2}$  and the Hermite coefficients  $\phi_{\underline{\alpha}}^{(l)}(\mathbf{r}, t)$ , using the orthonormal relation

$$\int \omega(\mathbf{v}) H_{\underline{\alpha}}^{(l)}(\mathbf{v}) H_{\underline{\beta}}^{(m)}(\mathbf{v}) d\mathbf{v} = (v_T)^{l+m} \delta_{lm} \delta_{\underline{\alpha}\underline{\beta}} \quad (35)$$

can be obtained by:

$$\phi_{\underline{\alpha}}^{(l)}(\mathbf{r}, t) = \int f(\mathbf{r}, \mathbf{v}, t) H_{\underline{\alpha}}^{(l)}(\mathbf{v}) d\mathbf{v}. \quad (36)$$

The exact infinite series representation of  $\bar{f}(\mathbf{r}, \mathbf{v}, t)$  is approximated by a function  $f(\mathbf{r}, \mathbf{v}, t)$  obtained by retaining in equation (34) only terms up to  $l = K$ , so that the complete and truncated distributions have the same coefficients up to Hermite order  $K$ . At this stage, a Gauss–Hermite quadrature formula is employed in order to evaluate the expansion coefficients,  $\phi_{\underline{\alpha}}^{(l)}(\mathbf{r}, t)$ , recognizing that  $\bar{f}(\mathbf{r}, \mathbf{v}, t) H_{\underline{\alpha}}^{(l)}(\mathbf{v})/\omega(\mathbf{v}) = p(\mathbf{r}, \mathbf{v}, t)$  is a polynomial in  $\mathbf{v}$  with a degree  $\leq 2K$ , and using the nodes  $\mathbf{c}_p$  and the weights  $w_p$  of a quadrature of order  $2G \geq K$ , with  $p = 1, \dots, Q$ . Using the result

$$\int d\mathbf{v} \omega(\mathbf{v}) p(\mathbf{r}, \mathbf{v}, t) = \sum_{p=0}^G w_p p(\mathbf{r}, \mathbf{c}_p, t) \quad (37)$$

one obtains

$$\phi_{\underline{\alpha}}^{(l)}(\mathbf{r}, t) = \int d\mathbf{v} \bar{f}(\mathbf{r}, \mathbf{v}, t) H_{\underline{\alpha}}^{(l)}(\mathbf{v}) = \sum_{p=0}^G f_p(\mathbf{r}, t) H_{\underline{\alpha}}^{(l)}(\mathbf{c}_p) \quad (38)$$

where

$$f_p(\mathbf{r}, t) \equiv \bar{f}(\mathbf{r}, \mathbf{c}_p, t) \frac{w_p}{\omega(\mathbf{c}_p)}. \quad (39)$$

Notice that  $f_p(\mathbf{r}, t)$  contains the same information as the continuous velocity distribution  $\bar{f}(\mathbf{r}, \mathbf{v}, t)$ , so that the continuous phase space distribution is replaced by a  $Q$ -dimensional array,  $\bar{f}(\mathbf{r}, \mathbf{v}, t) \rightarrow f_p(\mathbf{r}, t)$ . The  $Q$  nodes connect neighboring mesh points  $\mathbf{r}$  on a lattice through the discrete velocities  $\mathbf{c}_p$ , mirroring the hopping of particles between mesh points, generally augmented by a null vector  $\mathbf{c}_0$  accounting for particles at rest. The specific form of the lattice velocities and weights depends on the order of accuracy of the method and reflects the required Hermite order, as described

in the following and thoroughly discussed in [26]. The LB algorithm exploits the Cartesian mesh to rearrange populations over spatial shifts corresponding to a first-order fully explicit temporal update,

$$\partial_t f_p(\mathbf{r}, t) + \mathbf{c}_p \cdot \partial_{\mathbf{r}} f_p(\mathbf{r}, t) \simeq \frac{f_p(\mathbf{r} + \mathbf{c}_p \Delta t, t + \Delta t) - f_p(\mathbf{r}, t)}{\Delta t} \quad (40)$$

where  $\Delta t$  is the time step.

Similarly, one expands the collisional and BGK contributions featuring in the right-hand side of equation (21) and writes the following expressions:

$$\mathcal{B}^{\text{int}}(\mathbf{r}, \mathbf{v}, t) \rightarrow \mathcal{B}_p^{\text{int}}(\mathbf{r}, t) \equiv \bar{\mathcal{B}}^{\text{int}}(\mathbf{r}, \mathbf{c}_p, t) \frac{w_p}{\omega(\mathbf{c}_p)} \quad (41)$$

and

$$\mathcal{K}(\mathbf{r}, \mathbf{v}, t) \rightarrow \mathcal{K}_p(\mathbf{r}, t) \equiv \bar{\mathcal{K}}(\mathbf{r}, \mathbf{c}_p, t) \frac{w_p}{\omega(\mathbf{c}_p)}. \quad (42)$$

Using the specific form of the BGK term the LB algorithm reads

$$f_p(\mathbf{r} + \mathbf{c}_p \Delta t, t + \Delta t) = \left(1 - \frac{\Delta t}{\tau}\right) f_p(\mathbf{r}, t) + \frac{\Delta t}{\tau} f_p^{\text{eq}}(\mathbf{r}, t) + [\mathcal{K}_p(\mathbf{r}, t) + \mathcal{B}_p(\mathbf{r}, t)] \Delta t. \quad (43)$$

The resulting population dynamics of  $f_p$  is able to virtually reproduce any target macroscopic evolutions to high accuracy. In the absence of explicit collisional terms, and owing to the hyperbolic nature of the evolution equation, the LB method approximates the Navier–Stokes equation in the nearly incompressible limit. In addition, the LB method is completely flexible in terms of the mesh spacing  $\Delta x$  that can be tuned in order to resolve the details of the microscopic interactions, as for the spatial convolution in the collisional terms. Therefore, the error introduced in the spatial discretization does not represent a critical issue.

The specific form of the discrete velocities and weights depends on the order of accuracy of the method [26]. They are also designed to preserve mass, momentum and local isotropy by satisfying the rules  $\sum_p w_p c_{pi} = 0$ ,  $\sum_p w_p c_{pi} c_{pj} = v_T^2 \delta_{ij}$ ,  $\sum_p w_p c_{pi} c_{pj} c_{pk} = 0$  and  $\sum_p w_p c_{pi} c_{pj} c_{pk} c_{pl} = v_T^4 (\delta_{ik} \delta_{jl} + \delta_{il} \delta_{jk})$ , where  $w_p$  is a set of normalized weights and  $v_T = 1/\sqrt{3}$  is the mesh sound speed.

The exact local equilibrium distribution function contains an infinite number of terms in its Hermitian representation, but since we consider a truncation to second order Hermite polynomials we have

$$f_p^{\text{eq}} = w_p n(\mathbf{r}, t) \left[ 1 + \frac{c_{pi} u_i(\mathbf{r}, t)}{v_T^2} + \frac{(c_{pi} c_{pj} - v_T^2 \delta_{ij}) u_i(\mathbf{r}, t) u_j(\mathbf{r}, t)}{2v_T^4} \right] \quad (44)$$

corresponding to a low-Mach ( $O[Ma^3]$ ) expansion of the local Maxwellian. On the other hand, by keeping only the momentum component of the collisional contribution,  $\mathcal{C}^{(1)}(\mathbf{r}, t)$ , one writes the following discretized form:

$$\mathcal{K}_p = -w_p \frac{1}{m} \left[ \frac{c_{pi} C_i^{(1)}(\mathbf{r}, t)}{v_T^2} + \frac{(c_{pi} c_{pj} - v_T^2 \delta_{ij}) u_i(\mathbf{r}, t) C_j^{(1)}(\mathbf{r}, t)}{v_T^4} \right]. \quad (45)$$

Similarly, the contribution arising from heat conduction,  $C^{(2)}(\mathbf{r}, t)$ , could be included within the same framework. However, a thermal version of the LB scheme requires inclusion up to third- or fourth order Hermite polynomials.

Once the populations  $f_p$  are known, they are used to compute hydrodynamic moments, both entering the equilibrium and in sampling the macroscopic evolution. The fluid density, momentum current and local temperature read

$$\begin{aligned} n(\mathbf{r}, t) &= \sum_p f_p(\mathbf{r}, t) \\ n(\mathbf{r}, t)\mathbf{u}(\mathbf{r}, t) &= \sum_p f_p(\mathbf{r}, t)\mathbf{c}_p \\ \frac{3k_B}{m}n(\mathbf{r}, t)T(\mathbf{r}, t) &= \sum_p f_p(\mathbf{r}, t)\mathbf{c}_p^2. \end{aligned} \quad (46)$$

A Chapman–Enskog analysis shows that the relaxation time  $\tau$  is related to the kinetic component of the shear viscosity via

$$\eta^{(K)} = nmv_T^2 \left( \tau - \frac{\Delta t}{2} \right) \quad (47)$$

i.e. the physical value, found in equation (26), subtracted by a contribution of numerical origin.

For hard spheres, the radial distribution function  $g(\mathbf{r}, \mathbf{r}')$  appearing in the evaluation of  $\mathbf{C}_i^{(1)}(\mathbf{r}, t)$  and  $\mathbf{C}^{(2)}(\mathbf{r}, t)$  associated with the RET approximation is obtained according to the Fischer and Methfessel construction [27]. At first, one defines a coarse-grained density  $\bar{n}(\mathbf{r}, t)$  via a uniform smearing over a sphere of radius  $\sigma/2$ , and the coarse-grained packing fraction is  $\bar{\eta}(\mathbf{r}, t) = \pi\sigma^3\bar{n}(\mathbf{r}, t)/6$ . The actual pair correlation,  $g_{\text{hs}}(\mathbf{r}, \mathbf{r} + \boldsymbol{\sigma})$ , is replaced by its equilibrium value at the given smoothed density

$$g_{\text{hs}}(\mathbf{r}, \mathbf{r} + \boldsymbol{\sigma}) \simeq [1 - \bar{\eta}(\mathbf{r} + \boldsymbol{\sigma}/2)/2 + \bar{\eta}^2(\mathbf{r} + \boldsymbol{\sigma}/2)/4] / [1 - \bar{\eta}(\mathbf{r} + \boldsymbol{\sigma}/2)]^3.$$

In order to evaluate the surface integrals, we choose  $\sigma$  to be an even multiple of the lattice spacing and employ an 18-point quadrature over a spherical surface [28]. With this choice, the elements arising from  $g_{\text{hs}}$  and the hydrodynamic moments are taken from six on-lattice quadrature points while the elements arising from the remaining 12 off-lattice points are constructed via a linear interpolation from the surrounding on-lattice elements.

The numerical method has been tested to determine the shear viscosity of a uniform system and an excellent agreement was found with the theoretical prediction equation (32). In addition we have considered the flow of a hard sphere system induced in a slit by the presence of a uniform field parallel to the walls. The observed velocity profiles had the expected parabolic behavior for wall distances sufficiently larger than the hard sphere diameter and moderately low densities, but displayed pronounced oscillations for larger densities and the average streaming velocity decreased as a consequence of mutual steric hindrance among particles.

Regarding the stability of the method, LB is subjected to numerical instability whenever the flow velocity becomes larger than a certain threshold, function of the relaxation time,

the wavenumber [26] and the stiffness of intermolecular forces. However, the stability range can always be widened by taking a smaller  $\Delta x$ . In fact, a generic upper bound for the variation of populations due to the forcing term is  $\delta f/f \sim f_p/w_p \sim \Delta t\mathcal{K}_p \ll 1$ .

The advantages of the LB method over the solution of the coupled hydrodynamic equations are evident:

- The convective term  $\mathbf{u}(\mathbf{r}, t) \cdot \nabla$  does not need to be computed explicitly.
- Solution of the Poisson equation for the pressure is not needed.
- The boundary conditions are handled in an easier way, for instance by imposing simple collision rules on the local velocity distribution at the boundary, such as bounce-back in order to reproduce a no-slip condition.
- A relatively small number of velocity and spatial mesh points are sufficient for many purposes.
- The two-body interparticle potential can be quite arbitrary and in the case of a slowly varying attractive tail it can be modeled via the RPA. Such an approximation, although not contributing to the shear viscosity, allows to study phase coexistence.

## 5. Conclusions

Starting from a microscopic level we have obtained a governing equation for  $f(\mathbf{r}, \mathbf{v}, t)$  describing both equilibrium structural properties and transport properties. The essential difference between the DDFT and the present method consists in the fact in the former the dynamical evolution of the fluid system is treated only in configurational space and the fundamental variable is the one-particle density, whereas in the latter the dynamics is studied in phase space and the corresponding quantity is the phase space density distribution. The use of such a distribution enables us to consider the microscopic details of the molecular collisions and analyze transport properties on a quantitative basis.

The DDFT equation can be obtained as a particular case, when the heat bath term is externally imposed and has a viscous character forcing the velocity distribution to attain its global equilibrium form in a time much shorter than the time needed to reach the configurational equilibrium. As a result, the DDFT does not describe sound waves in liquids, but only diffusive modes. In the case of molecular fluids instead, the timescales characterizing the equilibration times of the hydrodynamic fields can be comparable and diverge as the wavelength of the modes tends to infinity, as a result of the translational invariance and absence of a fixed solvent. The kinetic equation (21) by construction reproduces this aspect and the mechanism restoring the global equilibrium in the fluid is purely due to the presence of gradients in the hydrodynamic fields and not to the fields themselves. Hydrodynamic versus non-hydrodynamic mode splitting proves a convenient route. As far as similarities are concerned, both methods use the same equilibrium structural information as their key ingredient and the same adiabatic treatment of two-particle correlation

necessary to decouple the one-particle from the multiparticle dynamics.

Other popular approaches within the LB framework have been put forward to treat inhomogeneous fluids, but they differ from ours in the derivation of the interaction terms. Most of these methods, such as the Swift–Osborne–Yeomans [29] and the effective pseudopotential methods by Shan–Chen [22], do not utilize a microscopic level, but rather start from a coarse-grained level and assume the validity of a local thermodynamics. In our opinion, we find it rewarding to be able to derive in unified way both DDFT and a transport equation and to discriminate them on the basis of the thermostating mechanism.

The major limitation of the present treatment is the assumption underlying the Boltzmann equation that particles are uncorrelated before collisions, resulting in a Markovian dynamics. In the case of hard spheres, the RET approximation represents an improvement over the Boltzmann treatment by taking into account the nonlocal character of the momentum and energy transfer, but without incorporating the time correlations which are responsible for memory effects. Even the RET approach is local in time with no memory of the past history. The deficiency of the theory becomes more acute when treating soft potentials, where the interaction is not instantaneous as in the hard sphere case. For continuous interaction, it is not possible to consider the dynamics as composed of two separate stages, namely instantaneous collisions followed by free-streaming trajectories, as in the case of hard spheres. The interactions have a finite duration and a second interaction can take place before the first one is completed. Some authors have modeled the different regions of the attractive potential tails by means of sequence of square-well constant potentials so that the RET formalism could be applied [30]. However, this approach inherits from the hard sphere model the impulsive character of the interactions and therefore fails to reproduce memory effects. Alternatively, it has been observed [31] that the motion of the particles can be regarded as the combination of continuous momentum changes, assimilated to a Brownian motion in an average attractive field, and quasi-instantaneous collisions with large momentum binary exchanges, described as hard core collisions. Following these lines it seems possible to extend the present approach to the treatment of soft potentials.

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