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SIMULATING NANOFLUIDS VIA THE WEIGHTED DENSITY LATTICE BOLTZMANN APPROACH

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The structure and transport of neutral and charged fluids under nanoscopic confinement are derived from the kinetic and microscopic perspective. As compared to lumped parameter approaches, the strategy is to resolve the collision between particles for hard-core forces and to use a mean field treatment for soft- and long-ranged forces. The numerical strategy adapts the Lattice Boltzmann (LB) scheme to handle interatomic and electrostatic interactions.

Keywords: Nanofluidics; transport properties of liquids; Planck–Nernst–Poisson equation.

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1. Introduction

Different physical phenomena emerge at the nanoscale giving the opportunity to unveil new phenomena and develop new branches of sciences and technologies going under the name of Nanoscience and Nanotechnology, respectively.[1–3] A large portion of nanoscopic devices operate by the action of pressure gradients or electric fields. The latter is a very effective mean of transporting species and heat in tiny spaces. In addition, a proper treatment of charged nanofluids is crucial in order to understand the translocation of charged biomolecules, such as DNA, and the motion of the accompanying electrolytes in narrow channels.[4,5] This topic is currently attracting considerable interest as a mean to perform fast genetic sequencing. At the same time, a large scientific community is devoted to studying the motion of charged biomolecules in cellular environments.

As of today, an accurate theory for transport and structure under nonequilibrium conditions is still missing. Under nanoconfinement, the assumptions leading to the standard macroscopic continuum description do not hold any longer, in fact when a small number of molecules is enclosed in a very small volume the mean free path becomes of the order of the interatomic distance and the linear size of the container.

In this scenario, one has to consider a microscopic description of matter. In fact, while the knowledge of the bulk transport coefficients is sufficient to study fluids under standard homogeneous conditions, this is not the case when the separation between the atomic scale and the scale of the phenomenon under investigation are comparable.

In the last few years we have explored methods to study fluids under nanoconfinement.[6–9] Our treatment combines different areas of liquid state theory, namely kinetic and density functional theory (DFT) and their implementation as an effective numerical method via the Lattice Boltzmann (LB) approach. The method focuses on the evolution of the singlet distribution function by separating the long-lived hydrodynamic modes from the fast kinetic ones and by invoking a coarse-graining ansatz.

There are several benefits stemming from the present approach: (i) the theory has thermodynamic consistency and produces accurate interatomic density/velocity correlations,[16,17] (ii) the equations for the moments have the correct structure, as compared with a dynamics that relies only on the free-energy landscape, (iii) the approach provides analytic expressions from the transport coefficients; (iii) the numerical solution is stable and reliable and, as shown below, is more efficient than atomic simulations for systems with large disparity in concentrations.

2. From One-Component Fluid to Electrolytic Solutions

We consider the following kinetic equation for the distribution function $f(\mathbf{r}, \mathbf{v}, t)$ with a collision kernel which fully represents the nonlocal repulsive interactions between hard spheres of diameter σ:

$$\partial_t f + v_i \partial_i f + \frac{F_i}{m} \frac{\partial}{\partial v_i} f = \Omega^{RET}[f, f], \tag{1}$$

where

$$\begin{aligned}\Omega^{RET}[f, f] = {} & \sigma^2 \int d\mathbf{v}_2 \int d\hat{k} \Theta(\hat{\mathbf{k}} \cdot \mathbf{v}_{12})(\hat{\mathbf{k}} \cdot \mathbf{v}_{12})[G(\mathbf{r}, \mathbf{r} - \hat{\mathbf{k}}\sigma, \mathbf{v}', \mathbf{v}_2') \\ & - G(\mathbf{r}, \mathbf{r} + \hat{\mathbf{k}}\sigma, \mathbf{v}, \mathbf{v}_2)].\end{aligned} \tag{2}$$

$G(\mathbf{r}_1, \mathbf{r}_2, \mathbf{v}_1, \mathbf{v}_2, t) = g_2(\mathbf{r}_1, \mathbf{r}_2, t) f(\mathbf{r}_1, \mathbf{v}_1, t) f(\mathbf{r}_2, \mathbf{v}_2, t)$ is the approximate two-body distribution function and the primed velocities are defined by the relations $\mathbf{v}' = \mathbf{v} - (\hat{\mathbf{k}} \cdot \mathbf{v}_{12})\hat{\mathbf{k}}$ and $\mathbf{v}_2' = \mathbf{v}_2 + (\hat{\mathbf{k}} \cdot \mathbf{v}_{12})\hat{\mathbf{k}}$, with $\mathbf{v}_{12} = \mathbf{v}_1 - \mathbf{v}_2$. G contains the configurational pair correlation function $g_2([n])$ that depends functionally on the density and reflects the Enskog treatment of correlations.

The hydrodynamic fields density, velocity and temperature are given by:

$$\begin{pmatrix} n \\ n\mathbf{u} \\ \frac{3}{2} n k_B T \end{pmatrix} = \int d\mathbf{v} \begin{pmatrix} 1 \\ \mathbf{v} \\ \frac{m(\mathbf{v}-\mathbf{u})^2}{2} \end{pmatrix} f(\mathbf{r},\mathbf{v},t), \tag{3}$$

where k_B is the Boltzmann constant, and the corresponding moments of the collision operator are:

$$\begin{pmatrix} 0 \\ \mathbf{C} \\ Q \end{pmatrix} = \int d\mathbf{v} \begin{pmatrix} 1 \\ m(\mathbf{v}-\mathbf{u}) \\ \frac{m(\mathbf{v}-\mathbf{u})^2}{2} \end{pmatrix} \Omega(\mathbf{r},\mathbf{v},t). \tag{4}$$

In order to reduce the complexity of Eqs. (1) and (2) we separate the fast degrees of freedom, which give a minor contribution to the observed properties, from the slow hydrodynamic ones, which on the contrary are crucial.[10] The collision operator is projected onto the hydrodynamic subspace spanned by the functions $\{1, \mathbf{v}, v^2\}$ and onto the complementary kinetic subspace:

$$\Omega = \mathcal{P}_{\text{hydro}}\Omega + (I - \mathcal{P}_{\text{hydro}})\Omega \tag{5}$$

with

$$\mathcal{P}_{\text{hydro}}\Omega = \frac{1}{k_B T}\phi_M \left[(\mathbf{v}-\mathbf{u}) \cdot \mathbf{C} + \left(\frac{m(\mathbf{v}-\mathbf{u})^2}{3k_B T} - 1 \right) Q \right]. \tag{6}$$

The second term is approximated as a BGK term[18]

$$(I - \mathcal{P}_{\text{hydro}})\Omega = -\omega_0 (f - f^{\text{eq}}), \tag{7}$$

where $f^{\text{eq}} = n[\frac{m}{2\pi k_B T}]^{3/2} \exp(-\frac{m(\mathbf{v}-\mathbf{u})^2}{2k_B T})$ is the local equilibrium distribution and ω_0 is a phenomenological collision frequency, chosen so as to reproduce the kinetic contribution to the viscosity.

By applying these approximations to the complicated multidimensional integrals, the interaction becomes:

$$\Omega_{RET} \simeq -\omega_0 (f - f^{\text{eq}}) + \frac{f^{\text{eq}}(n,\mathbf{u})}{n k_B T} \left[(\mathbf{v}-\mathbf{u}) \cdot \mathbf{C} + \left(\frac{m(\mathbf{v}-\mathbf{u})^2}{3k_B T} - 1 \right) Q \right] \tag{8}$$

an enormous simplification with respect to (2) that satisfies the correct balance equations for n, $\mathbf{u}$ and T. While this term treats exactly the collisions for the hydrodynamic modes, it approximates the nonhydrodynamic modes by means of the BGK relaxation term that acts directly only on the kinetic modes. It is still unproven that the scheme obeys an H-theorem, as compared to other approaches.[11,12]

An accurate analysis shows that $C_i(\mathbf{r},t)$ comprises three types of forces, the gradient of the nondissipative potential of mean force, a viscous force and a force due to thermal variations. In the case of a multicomponent fluid a drag force is also present, which appears when two species have different fluid velocities. The decomposition is given by dissipative and nondissipative contributions:

$$\mathbf{C} = n(\mathbf{F}^{\mathrm{mf}} + \mathbf{F}^{\mathrm{viscous}} + \mathbf{F}^{T}), \tag{9}$$

where

$$F_i^{\mathrm{mf}}(\mathbf{r},t) = -k_B T\sigma^2 \int d\hat{k} k_i g_2(\mathbf{r},\mathbf{r}+\sigma\mathbf{k},t) n(\mathbf{r}+\sigma\mathbf{k},t), \tag{10}$$

$$\begin{aligned} F_i^{\mathrm{viscous}}&(\mathbf{r},t) \\ &= 2\sigma^2\sqrt{\frac{mk_BT}{\pi}}\int d\hat{k}k_ik_jg_2(\mathbf{r},\mathbf{r}+\sigma\mathbf{k},t)n(\mathbf{r}+\sigma\mathbf{k},t)(u_j(\mathbf{r}+\sigma\mathbf{k})-u_j(\mathbf{r})), \end{aligned} \tag{11}$$

$$F_i^{T}(\mathbf{r},t) = -\frac{\sigma^2}{2}\int d\hat{k}k_ig_2(\mathbf{r},\mathbf{r}+\sigma\mathbf{k},t)n(\mathbf{r}+\sigma\mathbf{k},t)k_B[T(\mathbf{r}+\sigma\mathbf{k},t)-T(\mathbf{r},t)]. \tag{12}$$

The effective fields at position $\mathbf{r}$ depend on integrals of $n(\mathbf{r},t)$, $\mathbf{u}(\mathbf{r},t)$ and $T(\mathbf{r},t)$ on a spherical surface of diameter σ centered at $\mathbf{r}$. Under equilibrium conditions $\mathbf{F}^{\mathrm{mf}}$ is the gradient of the potential of mean force, that is the gradient of excess over ideal part of chemical potential $\mathbf{F}^{\mathrm{mf}}(\mathbf{r},t) = -\nabla\mu_{\mathrm{exc}}(\mathbf{r},t)$. Being expressed as a thermodynamic force, it relates to an underlying free energy, whose analytic form is ultimately encoded by the form of g_2. However, the viscous and thermal forces cannot be related to an underlying free-energy. In this respect, the theory has full thermodynamic consistency and describes forces which have entropic, depletion, electrostatic or Van der Waals counterparts at equilibrium.[19,20] The pair correlation function at contact $g_2(\mathbf{r},\mathbf{r}+\sigma\hat{\mathbf{k}},t|n)$ is conveniently given by the Fisher–Methfessel prescription, by estimating the pair correlation of a homogeneous HS fluid at the density $\bar{n}(\frac{\mathbf{r}+\mathbf{r}'}{2})$ defined by $\bar{n}(\mathbf{r},t) = \frac{3}{4\pi\sigma^3}\int_{|\mathbf{r}-\mathbf{r}'|<\sigma} d\mathbf{r}' n(\mathbf{r}+\mathbf{r}',t)$.

In Eq. (8) there is no explicit reference to the transport coefficients. In fact, a detailed analysis shows that the kinetic system has the correct equilibrium behavior and less trivial, self-consistent transport properties with respect to simple BGK dynamics. Under homogeneous conditions, the viscosity is $\eta = \frac{1}{\omega_0}k_BTn + \frac{4}{15}\sqrt{m\pi k_BT}n^2\sigma^4g_2(\sigma^+)$, the thermal conductivity is $\lambda = [\frac{5}{2}\frac{1}{m\omega_0}nk_B^2T + \frac{2}{3}\sqrt{m\pi k_BT}g_2(\sigma^+)n^2\sigma^4\frac{k_B}{m}]$ while the parameter ω_0, is interpreted as the collision frequency between spheres of equal diameter σ so that $\omega_0 = n\sigma^2\sqrt{2k_BT/m}$.

Let us now illustrate the generalization to electrolytic solutions, being composed of basically three species, a neutral solvent and two ionic species of opposite charges. When studying the motion of charged biomolecules by electrophoretic forces, the strength of entropic, coulombic and viscous forces arising from the electrolytic environment need to be assessed with care.

The theoretical approach is suitably generalized to the multicomponent case, such as two-component mixtures[8,9] or ternary mixtures of positive and negative ions immersed in a solvent of neutral particles. We label with the superscript 0 the solvent and with ± the electrolytes of valence $z^{\pm} = \pm 1$. We assume the dielectric permittivity ϵ to be constant everywhere. The collision operator is written as:

$$\begin{aligned}\sum_{\beta}\Omega^{\alpha\beta}(\mathbf{r},\mathbf{v},t) \approx -\omega_0[f^{\alpha}(\mathbf{r},\mathbf{v},t) - f_{\perp}^{\mathrm{eq},\alpha}(\mathbf{r},\mathbf{v},t)]&\\ + \frac{f^{\mathrm{eq},\alpha}(\mathbf{r},t)}{nk_BT}\cdot(\mathbf{v}-\mathbf{u}(\mathbf{r},t))\mathbf{\Phi}^{\alpha}(\mathbf{r},\mathbf{v},t)&\\ - \frac{ez^{\alpha}}{m}\nabla\psi(\mathbf{r})\cdot\frac{\partial}{\partial\mathbf{v}}f^{\alpha}(\mathbf{r},\mathbf{v},t),&\end{aligned}$$

where the distribution $f^{\mathrm{eq},\alpha}(\mathbf{r},\mathbf{v},t)$ is the local equilibrium distribution of the species α and $f_{\perp}^{\mathrm{eq},\alpha}(\mathbf{r},\mathbf{v},t)$ is a local distribution modified as to give the correct diffusion behavior of the mixture.[8] The quantity $\mathbf{\Phi}^{\alpha}$ represents the sum of the internal forces of nonelectrostatic nature acting on species α of the type (10)–(12) plus a frictional force between the ions and the solvent proportional to $\mathbf{F}^{\pm,\mathrm{drag}} = -\gamma^{\pm}(\mathbf{u}^{\pm}-\mathbf{u})$ with $\gamma^{\pm} \approx \frac{8}{3}\sqrt{\pi m k_B T}g_{0\pm}n^0\sigma^2$ and $g_{0\pm}$ the bulk ion-solvent pair correlation function evaluated at contact. Finally, the electric potential ψ satisfies Poisson equation, $\nabla^2\psi = -\frac{e\sum z_{\alpha}n^{\alpha}}{\epsilon}$ and the ionic currents are expressed in terms of the microscopic parameters:

$$\mathbf{J}^{\pm} = -\frac{1}{\gamma^{\pm}}n^{\pm}\nabla\mu^{\pm} - \frac{1}{\gamma^{\pm}}ez^{\pm}n^{\pm}\nabla\psi + n^{\pm}\mathbf{u} \tag{13}$$

that, used in conjunction with the continuity equation $\partial_t n^{\pm} + \nabla\cdot\mathbf{J}^{\pm} = 0$, *de facto* extends the Planck–Nernst–Poisson equation to the presence of convective[13] and thermodynamic forces.

3. Numerical Method

The kinetic equations described above are amenable to numerical solution within the LB framework. The devised method has been applied to simulate simple fluids as well as to mixtures of particles having unequal sizes, repulsive short-range hard-sphere potentials and weak attractive long-range interactions.[7,8] The approach was further applied to electrolytic solutions in devices.[6,7] While one can work out the case of thermal currents via suitable high-order lattice schemes, we have preferred to work in isothermal conditions for the sake of simplicity.

The method is an adaptation of the conventional LB to the presence of hard sphere collisions. It relies on computing hard-core collisional forces and, for charged fluids, to solve the Poisson equation. The inclusion of hard sphere collisions is based on computing the surface integrals of Eqs. (10) and (11) via numerical quadratures. To this aim, the mesh spacing δx must be chosen to be a fraction of the hard-sphere diameter, typically $\sigma = 4\delta x$. The spatial quadratures provide $O(\delta x^3)$ accuracy, while this is sufficient for many purposes isotropic schemes can be included.[14]

The populations are evolved by a second-order accurate trapezoidal rule. In addition, we compensate the harsh internal forces by auxiliary fields, as detailed in Ref. 15, in order to minimize parasitic currents. This approach is based on the use of

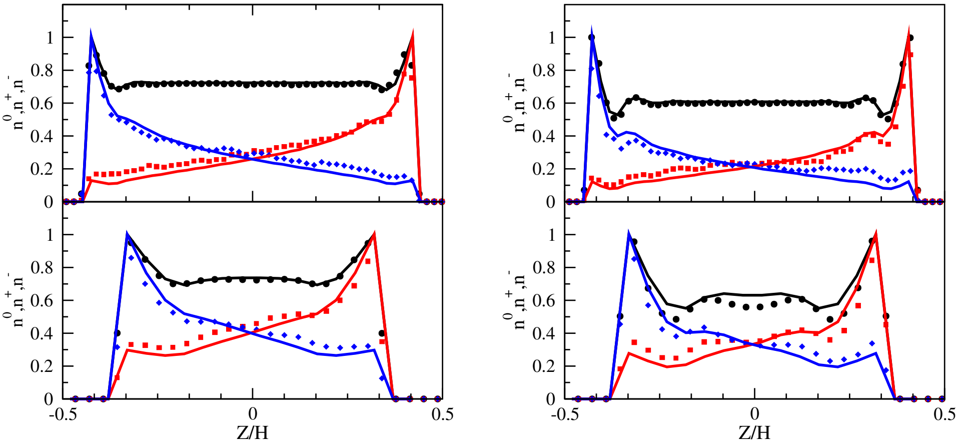

Fig. 1. (Color online) Density profiles as obtained from the electrokinetic LB method (continuous lines) and MD simulations (dotted lines).

an auxiliary set of populations and improves the accuracy and robustness of the scheme, without altering the equations for the hydrodynamic fields. A comparison at equilibrium between the LB results and Molecular Dynamics (MD) data is shown in Fig. 1 and illustrates the high accuracy of the present scheme. Being a microscopic approach to fluids, one question regards if the numerical scheme is competitive with atomic-based simulation techniques, such as MD, where in fact, one solves Newton equations virtually without approximations. The answer comes from two crucial facts: the first is the absence of noise in the deterministic LB scheme as compared to the need for averaging in MD. While the effect of fluctuating forces in nanoscopic systems is still the object of debate, the probabilistic nature of the Boltzmann approach is a strategic asset over the atomistic treatment. Second, the case of solutions with large disparity in concentrations, as typical in electrolytic devices, is hardly accessible to MD. In fact, the same averaging limitations arises when focusing on a few important atoms in a sea of other particles.

In conclusion, separating hydrodynamic from nonhydrodynamic modes is a strategic advantage to describe nanofluids and to understand the interplay between structure and dynamics. While at first glance our kinetic equations resemble a standard theory based on gradients of proper hydrodynamic fields, in reality they hold full thermodynamic consistency without being based on an underlying free-energy model. The approach leads to a practical simulation method to study confined fluids under different conditions.

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