Final Report

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I. INTRODUCTION

In recent years the experimental study of the flow of liquids in nanometric structures has become an important and rapidly evolving discipline driven by technological applications, such as lab-on-a-chip (LOC) systems , electrophoresis and electro-osmotic pumping. The mixing and separation of different molecules according to their size or chemical and transport properties is a major issue in chromatography, nanofluidic logic gates and electrokinetics. Many applications are foreseen also in biotechnologies, because very small quantities are sufficient for analysis and synthesis, includuding the possibilty of isolating and analyzing or manipulating a single molecule in a single nanochannel or surface with nanoscale features [1, 2].

These rapid technological advances require a better theoretical understanding of the fluid properties in confined geometries and under non equilibrium conditions. At the nanoscale new areas of physics, chemistry and materials science come in. The systems become more surface-like and molecules never explore a bulk-like environment. Because inhomogeneities have a greater impact some interesting phenomena arise. Whereas a large body of information has been accumulated in the last thirty years concerning the physics inhomogeneous fluids under thermodynamic equilibrium conditions [3], the state of the art of flowing fluids is not so advanced [4–6].

It is crucial to understand how the interplay between the various forces occurs and how it changes when we go from macrosystems to nanosystems. It is clear from dimensional considerations that their relative importance changes with the typical dimensions of the systems and we expect that the smaller the sample under scrutiny the more important the role of surface forces with respect to bulk force. Not only nanoscale flows are dominated by viscous effects where turbulence is not present because they are laminar, but since frequent molecule-channel wall collisions occur besides molecule-molecule collisions we expect a modified frictional resistence [7].

The generalization of fluid dynamics from pure to multicomponent fluids fluid mixtures composed of different components or species requires the introduction of some new concepts. While traditional computational fluid methods involve some ad-hoc extrapolation of Navier-Stokes equation to confining geometries, our approach is based on a a microscopic kinetic equation which incorporates the effects of the inhomogeneities in its structure.

The major difference with respect to one component fluids is the phenomenon of concentration diffusion. We shall study a multicomponent kinetic equation [8–12] which has been considered in the past by several authors with the specific goal of computing the transport coefficients from a microscopic approach. Many of these studies, which were based on the Boltzmann equation or on its extension to the dense case, the Boltzmann-Enskog equation, require some analytical and numerical effort, so that a simpler treatment of the interactions has been proposed. A very popular approximation is represented by the phenomenological Bhatnagar-Gross-Krook (BGK) equation whose merit is to reduce the complexity of the original Boltzmann collision kernel $\Omega^{\alpha\beta}$ between species α and β by introducing a simple relaxation-time ansatz [13, 14]. The BGK, in spite of being even less accurate than original the Boltzmann equation, has enjoyed a great popularity especially in conjunction with applications of the Lattice Boltzmann method (LBM) thanks to the simple treatment of the collision kernel leading to a considerable speed up of the numerics [15] .

However, it must be said that in the multicomponent case the choice of the form of the BGK relaxation term is not unique and hard to infer from the original $\Omega^{\alpha\beta}$, that it aims to approximate and that in the literature about the subject one finds a variety of proposals [16–20].

In order to describe with a sufficient accuracy the fluid structure at length scales comparable with the size of the particles, necessary to take into account the presence of inho-

mogeneities, we shall resort to methods similar to those of density functional theory (DFT) employed in the study of equilibrium and non equilibrium properties [21–24]. In the case of hard-core fluids the DFT and its dynamical extension gives excellent results and can be extended to more realistic fluids by using the van der Waals picture of decomposing the total interparticle potential into a short-range repulsive potential and a long-range attractive potential tail. The first is treated by means of a reference hard-sphere system whilst the second is considered within an RPA mean-field approximation. Such a decomposition can describe phase separating systems, wetting phenomena, two phase interfaces, but predicts transport coefficients of purely hard-core systems [25].

II. PURPOSE OF THE VISIT

The purpose of my visit was to study together with Dr. Simone Melchionna at EPFL, Lausanne a multicomponent extension of our recent theory of simple fluids [U.M.B. Marconi and S. Melchionna, Journal of Chemical physics, 131, 014105 (2009)] to describe miscible and immiscible liquid mixtures under inhomogeneous, non steady conditions typical of confined fluid flows.

III. DESCRIPTION OF THE WORK CARRIED DURING THE VISIT

The agenda during the visit focused on two things: the validation of the theory and the production of numerical code to solve the governing equation of our theory.

We first derived from a microscopic level the evolution equations of the phase space distribution function of each component in terms of a set of self consistent fields, representing both body forces and viscous forces (forces dependent on the density distributions in the fluid and on the velocity distributions, that is body forces and viscous forces). Secondly, we solved numerically the resulting governing equations by means of the Lattice Boltzmann method whose implementation contains some special features with respect to existing approaches. Our model incorporates hydrodynamic fow, diffusion, surface tension,and the possibility for global and local viscosity variations.

The hard core part of the interaction is treated within the revised Enskog theory (RET) [26] which considers the non-local character of the momentum and energy transfer and takes

into account the static spatial correlations among the particles but does not incorporate the time correlations which are responsible for memory effects and for hydrodynamic contributions to the transport coefficients [27].

With respect to the dynamical DFT [28] the present theory preserves the Galilei invariance of the fluid and therefore shows full hydrodynamic behavior in the limit of slowly varying fluctuations about the equilibrium reference state.

With the aim of deriving a practical numerical approximation to study mixtures in inhomogeneous situations we extended the method of Dufty and coworkers [29] to the multicomponent case. The method is a compromise between the RET, of which it retains the accuracy as far as the momentum and energy transfer are involved, and the much simpler BGK, which we employ to evolve the non-hydrodynamic moments of the distribution functions [30–32].

The final product of our theory is a coupled system of simplified equations for the density distributions of individual species describing both the streaming and the collisional stages which can be solved by an appropriate extension of the LBM algorithm to include both particle-particle interactions and particle-wall interactions. A simple analysis of the equations can be used to derive explicit expressions both for equilibrium thermodynamic quantities, such as pressure, compressibilities etc., and for non equilibrium transport coefficients. It is important to stress the difference between the present work and other LBM based approaches for non-ideal fluids, where only attractive interactions are accounted for by the so called Shan-Chen pseudo-potential, whose justification is purely mesoscopic, while transport coefficients enter as free parameters of the theory [33, 34].

We validated our model by studying the viscosity dependence of the mixture on concentration, packing fraction and size ratio and finally we considered the diffusivity of the mixture and the Poiseuille flow in a narrow channel.

IV.   CONCLUDING REMARKS AND FURTHER COLLABORATIONS

During my stay at EPFL I implemented a Lattice Boltzmann code for the mixture problem. All of the above would have not been such a success without the great support of Dr. Melchionna. Aside from the productive time at EPFL, I established many links to scientists at EPFL for further collaborations. There are two post-visit tasks that I intend to pursue. The extension of the theory to include long range forces and the detailed study

of the diffusion properties of the model.

The work carried on at EPFL will form the basis of a nice publication whose writing resulting from the short visit grant is already in an advanced stage of preparation.

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