Ab initio hydrodynamics
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ABSTRACT

Hydrodynamic phenomena are usually described in terms of fields, e.g., number/mass density, $\rho(x,t)$, momentum density, $\pi(x,t)$, energy density, $e(x,t)$, temperature, $T(x,t)$, etc., where x is a point in the ordinary $\Re^3$ space. $\rho(x,t)$, $e(x,t)$, and $\pi(x,t)$ obey conservation laws, which are supplemented by empirical constitutive laws (e.g., Fick's law and Fourier's Law) depending on the materials forming the system *via* the value of certain transport coefficients. It is further assumed that the system is locally at the equilibrium. By solving the complete set of equations with given initial conditions one obtains the relevant fields at any time t, thus fully characterizing the dynamics of the (continuum) system.

This macroscopic description is valid when the characteristic length and time scales of the process at hand are much larger than the atomistic/molecular ones. However, also in these conditions continuum hydrodynamics presents some problems: i) it cannot be checked that the local equilibrium hypothesis holds; ii) constitutive laws have a phenomenological origin, which accuracy must be checked case by case, iii) the value of the associated coefficients might be unavailable at the relevant conditions (pressure, temperature, etc.).

Alternatively to continuum methods one can use an *ab initio* atomistic/molecular approach. In this case, the system is described in terms of its constituents, atoms and/or molecules, and time-dependent statistical mechanics is used to obtain the time evolution of the system [1]. The main ingredient of this formulation is the time-dependent Probability Density Function (PDF), $m(\Gamma,t)$, with $\Gamma = (\mathbf{r},\mathbf{p})$ point of the $\Re^{3N}$ phase space and N number of particles in the system. Macroscopic fields are the ensemble average of suitable microscopic observables: $o(\mathbf{x},t) = \int d\Gamma \, o(\mathbf{x},\Gamma) \, m(\Gamma,t)$, in which we assumed that the observable does not depend explicitly on time. $o(\mathbf{x},\Gamma) = \hat{o}(\Gamma_i)\delta(\mathbf{r}_i - x)$ is the value of the atomistic observable associated to the macroscopic field computed on the atom(s) laying at **x**.

The main problem to transform this theoretical framework into a computational method is the sampling of the time-dependent PDF. In this talk I will describe how to (indirectly) sample this PDF by combining the dynamical approach to non-equilibrium molecular dynamics with techniques for the sampling of conditional PDF. I will illustrate the *ab initio* atomistic approach by applying it to the relaxation to the equilibrium of two interface systems: the bent interface between two immiscible liquids [2] and a step density gradient in a single component system [3]. In the first case we compared the results of our approach with more simplistic methods largely used in the literature. We show that standard approaches break some of the fundamental properties of the system under investigation. In the second case we compared ab initio atomistic and continuum results, obtaining a surprising good agreement also when the characteristic length of the interface is on the atomistic scale.

REFERENCES

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