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Hydrodynamic properties of confined fluids

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Abstract. In the present work, we study the dynamical properties of fluids confined at molecular scales. First, we show that, for a fluid confined between two parallel solid walls, the phenomenological hydrodynamic description of bulk fluids holds down to nanoscopic scales, once *appropriate boundary conditions* at the solid walls are applied. Then, we investigate the influence of confinement on the self-diffusion coefficient (in the direction parallel to the walls) in a fluid slab. We have computed the effect of confinement on the mode-coupling contribution to the diffusion coefficient. These finite-size corrections are shown to reduce the diffusion constant by an amount $-(\sigma/h)\log(h/\sigma)$, where h is the thickness of the fluid slab and σ the atomic size. This behaviour can be interpreted in terms of the suppression of long-wavelength modes in the backflow effect, due to confinement.

1. Introduction

The properties of liquids confined in very narrow spaces have been the object of much interest during the last two decades, thanks to the considerable development of surface force apparatus (SFA) techniques. While static properties are now rather well understood (see e.g. [6]), the dynamics of confined systems have been investigated more recently [1, 16]. Two types of observation have been made. Very thin films (of a few molecular diameters) exhibit strongly enhanced apparent viscosities, or even exotic ‘stick–slip’ behaviour [5, 11]. On the other hand, thicker films can be described using the Navier–Stokes equations, supplemented by the usual ‘no-slip’ boundary condition (BC) [2] at the solid surface [3, 8]. However some adjustments (in particular for the effective thickness of the fluid) are needed to fit correctly the experimental results. This arbitrariness raises the problem of the microscopic foundations of the no-slip BC. Indeed, while bulk hydrodynamics is known to be correct even at very small length scales [15], the no-slip BC might not be appropriate for thin films, in which boundary conditions can be expected to have measurable effects. It is the purpose of this work to demonstrate that the arbitrariness in the choice of hydrodynamic boundary conditions at a liquid–solid interface can be avoided, and that, under some reasonable assumptions, the appropriate BC can be determined from first-principles microscopic calculations.

2. Phenomenological description of thin films

Up to now, microscopic descriptions (using e.g. kinetic theory) of the dynamics of a fluid flowing past a solid wall have only been proposed for very specific models of fluid and wall–fluid interactions [9, 7]. Therefore, it is usual in fluid dynamics to bypass the complexity

of the microscopic problem by imposing a boundary condition on the velocity field. At macroscopic scales, experimental evidence indicates that the no-slip BC is fully appropriate for the description of the flow of simple liquids. However, as shown in reference [10], any ‘microscopic’ BC reduces on a macroscopic scale to the no-slip BC. Hence the validity of this description at a nanometric scale is not established. In this work, we consider the simplest generalization of the no-slip BC that allows for a velocity slip at the fluid–wall interface:

$$\left. \frac{\partial v_\alpha(\mathbf{r}, t)}{\partial z} \right|_{z=z_{wall}} = \frac{1}{\delta_{wall}} v_\alpha(\mathbf{r}, t) \Big|_{z=z_{wall}} \quad (\alpha = x, y). \quad (1)$$

where $\mathbf{v}(\mathbf{r}, t)$ is the velocity field, δ_{wall} is the slipping length and z_{wall} the location of the hydrodynamic boundary. The two phenomenological parameters δ_{wall} and z_{wall} depend on the microscopic details of the wall–fluid interface (fluid density, wall corrugation, ...) and characterize the dissipation at the interface.

Our aim is to prove the validity of this description in terms of a generalized BC and to determine the relevant boundary parameters for model systems. To this end, we focus on the *equilibrium fluctuations* in a fluid confined between two solid walls (parallel to the xy plane). BC as defined in equation (1) are assumed to hold at both fluid–solid interfaces. The starting point of our analysis is that, according to Onsager’s principle of linear regression of fluctuations [12], the dynamics of small fluctuations around an equilibrium state can be described by the macroscopic equation of motion, including in our case the boundary conditions. Phenomenological forms of the time-dependent correlation functions can then be computed, which carry all the information contained in the BC. In practice, we consider the fluctuations of the transverse momentum density parallel to the walls $j(z, t) = \sum_{i=1}^N v_{x,i}(t) \delta(z - z_i(t))$ (N is the number of fluid particles) and the corresponding correlation function $C(z, z', t) = \langle j(z, t) j(z', 0) \rangle$. According to Onsager’s assumption, this correlation function evolves in time according to the Navier–Stokes equations, supplemented by the BC (1) at both walls. In the case of transverse momentum, the NS equations reduce to a diffusion equation inside the fluid slab, $(\partial_t - \nu \partial_z^2) C(z, z', t) = 0$, completed by the two BC (1), $\partial_n C(z, z', t)|_{z=z_{wall}} = (1/\delta_{wall}) C(z, z', t)|_{z=z_{wall}}$, with $n = z$ ($n = -z$) for the lower (upper) wall. In this equation, ν is the kinematic viscosity of the *unconfined bulk* fluid. The general solution of these equations can be found in terms of a sum over the eigenmodes of the system [4]. This analysis thus provides a phenomenological expression for the transverse momentum correlation function in a confined fluid. Since the bulk kinematic viscosity can be obtained from independent calculations, the only parameters that enter our description are the BC parameters.

The validity of the BC can now be tested by comparing the phenomenological form for the time-dependent correlation functions $C(z, z', t)$ with ‘exact’ results for the same functions obtained from molecular dynamics (MD) simulations of a particular model. The results of this study can be summarized as follows. (i) We obtained a very good agreement between the phenomenological and computed correlation functions. This agreement allowed us to validate the proposed BC (1) and unambiguously determine the BC parameters, δ_{wall} and z_{wall} for various wall–fluid geometries. (ii) The intrinsic character of the BC parameters has been checked, in order to verify that they do not depend on the presence of the second interface. (iii) The phenomenological description of the fluid dynamics was found to remain valid for fluid slab of thickness of 8 atomic diameters, which shows that a hydrodynamic description of confined fluids holds down to nanoscopic scales once appropriate BC are applied. (iv) Quantitatively, two interesting results emerge from this study. First, the slipping length is found to decrease very rapidly with corrugation which validates a no-slip

BC for realistic walls. On the other hand, the hydrodynamic position of the interface z_{wall} was found to be always of the order of the thickness of one layer of fluid atoms. This shows that the BC has to be applied at a surface inside the fluid, separated from the solid by about one layer of fluid atoms. An inspection of particle trajectories did not reveal any indication of crystallization or locking in this layer. This result is in perfect agreement with recent experimental observations [8] for a variety of simple liquids.

3. Transport properties in confined liquids

Finally, we consider the influence of confinement on the transport coefficient of the confined fluids, and more especially on the diffusion constant D_{\parallel} (parallel to the walls). Physically, our previous study showed that confinement modifies the relaxation of hydrodynamic modes. On the other hand, these modes are known to play a fundamental role in the determination of the transport coefficient, as explicitly appears in the Green–Kubo (GK) relations. As a consequence, the so-called ‘mode-coupling’ contribution to the transport coefficient should be very sensitive to confinement effects.

The GK relation for diffusion connects D_{\parallel} to the velocity autocorrelation function (ACF), $D = \int_0^{+\infty} dt \langle v_x(t)v_x(0) \rangle$. In the long-time limit, it is known [15, 13, 14], that the diffusion of the initially injected momentum $mv_x(0)$ (and mainly its transverse part) determines the relaxation of the velocity ACF. Using the results of the first part of this work, where the transverse part of the momentum ACF has been computed for a fluid confined between two walls, we adapted the simple mode-coupling approach of references [13, 14] to obtain

$$\begin{aligned} \langle v_x(t)v_x(0) \rangle_{t \rightarrow \infty} &\sim t^{-1} \exp\left(-\nu \left(\frac{\pi}{h}\right)^2 t\right) \\ (D_{\parallel}(h) - D_{bulk})/D_{bulk} &= -\left(\frac{A \log(h/\sigma) + B}{(h/\sigma)}\right) + \mathcal{O}(1/h^2) \end{aligned} \quad (2)$$

where h is the film thickness, σ the particle diameter, D_{bulk} the bulk diffusion constant and A and B two (positive) numerical constants. For the sake of simplicity, a no-slip BC was assumed to apply at both walls. These results can be given a simple interpretation. Indeed, the essential effect of the confinement is to suppress the long-wavelength modes (of wavevector $k_z \leq 1/h$) and the diffusion constant is reduced by the contribution of these modes in the bulk mode-coupling formula for D [13]. In other words, the backflow induced by each particle is cut off by the boundaries and the mobility of fluid particles is decreased accordingly. This simple argument could be applied to other transport coefficients (viscosity, rotational diffusion, . . .) and to other geometries, to obtain the corresponding functional form of the size dependence.

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