Hydrodynamic Boundary Conditions and Correlation Functions of Confined Fluids

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A phenomenological description of the dynamical correlations in a fluid confined between two parallel solid walls, using a generalization of Onsager's theory of fluctuations, is presented. Besides the bulk viscosity, this description involves parameters characterizing the boundary conditions. Correlation functions obtained in equilibrium molecular dynamics simulations are very well described within this framework. Featureless walls yield perfect slip boundary conditions, while corrugated walls in most cases correspond to stick boundary conditions. Only for very small corrugation amplitudes is it necessary to introduce a finite slipping length.

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It is well known that the description of hydrodynamic flow requires two ingredients: the knowledge of the phenomenological transport coefficients, such as the shear viscosity η, that enter the Navier-Stokes equations, and boundary conditions (BCs) that permit one to uniquely solve these equations [1]. These two ingredients are essentially independent. The transport coefficients are intrinsic properties of the bulk fluid. They can in principle be obtained independently of any assumption concerning the BCs, by analyzing the spectrum of the light scattered by the fluid at rest. BCs, on the other hand, are a property of the interface between two different phases. In this work, we shall be interested in the particularly important case of the BC at a fluid-solid interface. In this case, experimental evidence indicates that, on macroscopic or mesoscopic length scales, the appropriate BC is one of "no slip"; i.e., the tangential velocity of the fluid vanishes at a fixed solid boundary. This condition does not have any microscopic justification, but can to some extent be justified by invoking the unavoidable roughness of the solid boundary on such length scales [2]. It is worth noticing, however, that other possible BCs were considered by pioneers in the field [3,4], and are indeed more appropriate than the no-slip BC in rarefied gases [5] and possibly in entangled polymer melts [6]. The simplest generalization of the no-slip BC introduces a slipping length δ. For a planar solid boundary located in the $z=z_0$ plane, this BC reads

$$\left.\frac{\partial v_\alpha(\mathbf{r},t)}{\partial z}\right|_{z=z_0} = \frac{1}{\delta} v_\alpha(\mathbf{r},t)|_{z=z_0}, \tag{1}$$

$\mathbf{v}(\mathbf{r},t)$ being the fluid velocity field and $\alpha=x,y$. This BC expresses the continuity of the viscous stress present in the fluid ($z>z_0$) with a frictional stress $\eta v_\alpha(z_0)/\delta$ localized at the solid boundary ($z=z_0$). It depends on *two parameters,* the slipping length δ and the position z_0 at which it is applied. From a macroscopic viewpoint, z_0 is just the location of the solid-liquid interface. Microscopically, however, the interface has a finite thickness, so that z_0 as well as δ must be interpreted as a phenomenological parameter.

In view of the practical success of the no-slip BC, the study of (1) might appear somewhat academic (although it is of importance in the study of contact line motion [7]). With the development of the surface force apparatus (SFA) [8], it has recently become possible to study hydrodynamic flow on microscopic length scales [9–11]. These studies indicate that unless the length scale of the experiment is smaller than about ten molecular diameters, macroscopic hydrodynamics with no-slip BCs applies, provided some freedom is allowed in the choice of the surface at which the BC is applied. Nonequilibrium molecular dynamics (MD) simulations [12–14] of Couette or Poiseuille flows between planar surfaces confirmed this result, but could also be interpreted by using (1) with a finite slipping length [13]; δ is in this case defined as the distance from the first atomic layer of solid material at which the velocity field in the fluid extrapolates to zero.

In this Letter, we present a new approach to the problem. Onsager's principle of regression of fluctuations [15] is used to compute the time-dependent correlation function of the momentum density for a fluid confined between two parallel solid planes, with BCs given by (1). The results are then compared to correlation functions obtained from *equilibrium* MD simulations with various types of solid walls. This comparison allows us to unambiguously define the "hydrodynamic position" z_0 and the slipping length δ associated with a given fluid-wall interface. The use of equilibrium MD bypasses all the difficulties (high shear rates, temperature control, choice of a particular flow) inherent in nonequilibrium MD simulations. An equilibrium characterization of BCs should also make it possible to attack the problem theoretically using the well established methods of equilibrium statistical mechanics.

We first describe the computation of the phenomenological form of the correlation functions for an infinite slab of fluid confined by two solid walls. At each wall, a BC of type (1) is applied. The "hydrodynamic positions" of the walls are $z=0$ and $z=h$, and the slipping lengths δ_0 and δ_h, respectively. The quantity that will be of central interest in our study is the correlation function of a component of the transverse momentum density $j_a(z,t) = \sum_i \delta(z-z_i) m v_{a,i}$ (m being the mass of an atom, z_i and $v_{a,i}$ its z coordinate and velocity along $\alpha = x,y$, respectively) parallel to the walls:

$$C(z,z',t) = \langle j_a(z,t) j_a(z',0) \rangle . \qquad (2)$$

(The subscript $\alpha = x,y$ has been dropped from the definition of C in order to simplify notations.)

More precisely, we want to study the long-wavelength (i.e., on a scale larger than the structure induced by the walls in the fluid) behavior of this correlation function. In this limit, $C(z,z',t)$ can be obtained from the following assumptions: (i) The density ρ of the fluid is uniform for $0<z<h$. (ii) Momentum fluctuations obey the macroscopic equations for a fluid of viscosity $\eta(\rho)$ *and* verify the BCs at the walls. (iii) The equal-time correlation function is given by its canonical ensemble value, $C(z, z', t=0) = m k_B T \rho \delta(z-z')$. A straightforward calculation yields

$$C(z,z',t) = \frac{2}{h} \rho m k_B T \sum_{n=0}^{+\infty} \Psi_n(z) \Psi_n(z') \exp(-\Gamma_n t) , \qquad (3)$$

where the $\Psi_n(z)$ are a set of orthonormal functions defined over the interval $[0,h]$ by $\Psi_n(z) = \cos(\lambda_n z - \theta_n)$, the λ_n and θ_n being solutions of

$$\begin{aligned} \tan(\lambda_n h) &= \lambda_n(\delta_0 + \delta_h)/(\lambda_n^2 \delta_0 \delta_h - 1) , \\ \cos(\theta_n) &= \lambda_n \delta_0 / [1 + (\lambda_n \delta_0)^2]^{1/2} , \end{aligned} \qquad (4)$$

and $\Gamma_n = \eta \lambda_n^2 / \rho$.

For the purpose of comparison with MD simulations, we finally introduce the Fourier transform

$$\begin{aligned} F(k,t) &= \int dz \int dz' e^{ikz} e^{-ikz'} C(z,z',t) \\ &= \langle \hat{j}_a(k,t) \hat{j}_a(-k,0) \rangle , \end{aligned} \qquad (5)$$

where $\hat{j}_a(k,t) = \sum_i e^{ikz_i} m v_{a,i}$ is a Fourier component of the fluid momentum density. If $C(z,z',t)$ is the phenomenological correlation function defined by Eq. (3), the integration domain in (5) can be restricted to $0<z<h$. The microscopic current $\hat{j}_a(k,t)$, however, involves a summation over all particles, irrespective of the value of their z coordinate. As the system is not invariant by translation along the z direction, $F(k,t)$ contains less information than the original correlation function. This limitation is, however, necessary for practical purposes.

MD simulations were performed for a fluid of "soft spheres" interacting through the potential $v(r) = \epsilon(\sigma/r)^{12}$ (cut off at $r = 2.5\sigma$). The interaction between the walls and the fluids was also taken to be purely repulsive, of the form $v_{wf}(\mathbf{r}) = \epsilon \sigma^{12} [z - z_w(x,y)]^{-12}$. Such a simplistic interaction was chosen in order to test the method, but it is obviously possible to extend it to more realistic models of the "solid walls." The temperature was $T = 1\epsilon/k_B$, and far from the walls the fluid had a uniform density $\rho = 0.64\sigma^{-3}$. The viscosity of the corresponding bulk thermodynamic state was independently determined to be $\eta = 0.60(m\epsilon)^{1/2}\sigma^{-2}$. The simulations were performed at constant energy, with systems of 500 particles and periodic BCs in the x and y directions. Typical runs extended over several thousand microscopic times $\tau = (m\sigma^2/\epsilon)^{1/2}$.

A first set of simulations was performed with two perfectly flat walls $[z_w(x,y) = \text{const}]$ separated by $L = 30\sigma$. Note that L is the physical distance between the two walls, and is not to be confused with the distance h between the phenomenological BC. Such flat surfaces are an interesting benchmark, for it is clear that since no tangential momentum is exchanged between fluid and wall, the BC that should be applied is one of perfect slip, $\delta = \infty$. One difficulty in this case is that the momentum of the fluid parallel to the walls is a strictly conserved quantity, so that the hypothesis (iii) used in the derivation of (3) is no longer valid. The fluctuations in $\hat{j}_a(0,t)$ vanish, while canonical statistics imply $\langle |\hat{j}_a(0,t)|^2 \rangle = N m k_B T$. The corresponding corrections to $C(z,z',0)$ can, however, be computed using methods similar to those presented in [16]. The phenomenological form for $C(z,z',t)$ is still given by (3) and (4) with $\delta = \infty$, but with the term $n=0$ excluded from the summation. The phenomenological and simulated correlation functions $F_a(k,t)$ are compared in Fig. 1 for several values of k. The agreement is seen to be excellent, provided the distance h between the planes at which the perfect-slip BCs are applied is taken to be $h = 26.8\sigma$. The deviations observed at longer times reflect the usual difficulties in obtaining good accuracy when computing time-dependent correlation functions at long times. A study of the density profile perpendicular to the wall indicates that one lay-

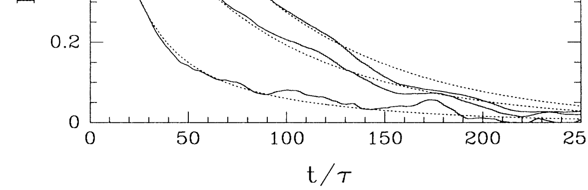

FIG. 1. Normalized correlation functions, $F(k,t)/F(k,0)$, for a fluid confined between two perfectly flat walls. The curves correspond from top to bottom to $k\sigma = 0.033$, 0.167, and 0.267. The solid lines are simulation results. The dashed lines are calculated using Eqs. (3) and (4) with $h = 26.8\sigma$ and $\delta_0 = \delta_h = \infty$.

er of atoms is present on each side between this hydrodynamic boundary and the solid wall.

We now turn our attention to more realistic, but still highly idealized, solid surfaces presenting a "corrugated iron" shape, $z_w(x,y)=\text{const}+u\cos(qx)$. Several values of the corrugation wavelength $2\pi/q$ [in the range $(1\text{-}2)\sigma$] and amplitude u [in the range $(0.005\text{-}0.1)\sigma$], which were identical for the two surfaces, were studied with the following results. Correlations along the y direction are unaffected by the corrugation and still described by the perfect-slip BC and $h=26.8\sigma$. The correlations along the x direction are very well described by Eq. (3), with a distance between hydrodynamic boundaries $h=26.8\sigma$ and a slippage length δ that depends on q and u. For $2\pi/q=1\sigma$ and amplitudes u larger than 0.03σ, the best fit to the simulation results is obtained with $\delta=0$, i.e., a no-slip BC. Similar results have been obtained for other values of q. That such a small corrugation is sufficient to produce a "stick" BC is indeed quite remarkable. For such small values of u, the density profile is practically indistinguishable from that obtained for $u=0$. This probably explains why the same value for h is appropriate in all cases. For smaller amplitudes a finite slipping length must be introduced to fit the simulation results. This is illustrated in Fig. 2 for $u=0.02\sigma$, the value of the slipping length being here 7.2σ. A still larger slipping length, $\delta=40\sigma$, is necessary to account for the results when $u=0.01\sigma$.

An additional simulation was performed with solid walls separated by $L=16.4\sigma$, and a corrugation $u=0.02\sigma$. According to our phenomenological description, the slipping length and the hydrodynamic location of the boundary are intrinsic properties of a given solid-liquid interface. Thus the correlation functions in this situation can be obtained without any further adjustment of parameters. The difference between L and h is the same as for $L=30\sigma$, i.e., $(30-26.8)\sigma=3.2\sigma$, which yields $h=13.2\sigma$. δ also retains its previous value 7.2σ. With these parameters, an excellent agreement with the simulated correlated functions is obtained.

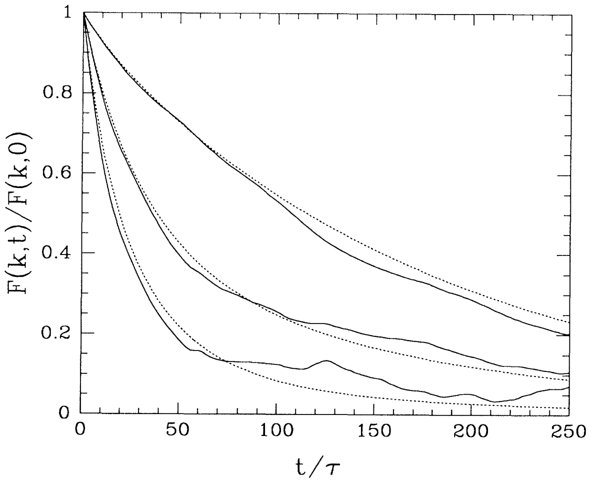

FIG. 2. Same as Fig. 1, but with a corrugated wall characterized by the parameters $u=0.02$, $2\pi q^{-1}=1$, and (from top to bottom) $k\sigma=0$, 0.133, and 0.2. The dashed lines represent the results of Eqs. (3) and (4) with $h=26.8\sigma$ and $\delta_0=\delta_h=7.2\sigma$. Note that in this case the normalization is unnecessary since $F(k,0)=1$.

The suppression of slip by a very small corrugation is not, as it might first seem, in contradiction with the findings of earlier, nonequilibrium simulations [13,17], that concluded in the existence of a small amount of slip for moderately rough solid walls. For the planar Couette flow that was considered in these simulations, a shift in z_0 and a modification of δ have strictly identical consequences. According to our results, such a flow could be described by *slip* BC at $z=0$ and $z=L$, with a slipping length $\delta'=(L-h)/2$, instead of *no-slip* BC at $z=0$ and $z=h$. The former description would qualitatively agree with the findings of [13,17], but would not be appropriate for more complex flow patterns.

Our finding that simulated correlation functions are very well fitted using a phenomenological description calls for several comments. It appears that Onsager's hypothesis, which is usually applied to phenomenological equations of motion, can be extended to boundary conditions. While in the former case the hypothesis can be justified on the basis of a projection operator formalism [18], we are not aware of such a justification for BC problems. One of the main consequences of Onsager's hypothesis is the existence of Kubo formulas relating phenomenological transport coefficients to microscopic correlation functions. No such formulas are known for BCs, and we had to resort to numerical fitting in order to obtain the numerical values of the parameters δ and h. In this respect, the situation is again much less satisfactory than for bulk transport coefficients. A formula that relates the various parameters to a correlation function can nevertheless be obtained by considering the (Poiseuille like) flow of the confined fluid subjected to a uniform force field parallel to the walls. The resulting momentum flux is proportional to the force field with a proportionality constant that can be obtained both from linear response theory and from hydrodynamics. Identifying the results of the two calculations one obtains

$$\int_0^\infty dt\langle \hat{j}_x(0,t)\hat{j}_x(0,0)\rangle = Nm\rho k_B T\frac{h^2}{12\eta}\left[1+3\frac{\delta_0+\delta_h+4\delta_0\delta_h/h}{h+\delta_0+\delta_h}\right]. \qquad (6)$$

Finally, one should recall that the use of the BC (1) in fluctuating hydrodynamics was considered earlier by Wolynes [19]. He concluded that including mode-mode coupling effects would result in a divergence of the slipping length at small wave vector of the form $\delta(k)=\delta+Ak^{-1/2}$, where δ is a "bare" slipping length. This would apparently invalidate our approach. It turns out, however, that the numerical value of the coefficient A in simple liquids is extremely small [19]. If we use as an upper cutoff for k^{-1} the size of the simulation cell (or the distance between the plates) the correction to the "bare" slipping length is much too small to be observable in our simulations.

It is now well established [20] that macroscopic hydrodynamics remains valid down to rather short length scales in bulk liquids. In view of our results, the situation appears to be similar in confined fluids. In the latter case, however, boundary conditions take on much greater importance. The success or failure of hydrodynamics in such systems can be assessed only if the relevant boundary conditions are known. For example, a moderate increase in the *apparent* shear viscosity of a fluid slab as its thickness is reduced can be interpreted as a failure of macroscopic hydrodynamics; if the BC involves a finite slipping length, however, this increase is very naturally interpreted within the framework of hydrodynamics. Another, more microscopic description will be called for only at very small length scales where the exotic behavior (stick-slip, very high viscosities) described in [10,11,21] is observed.

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