INFLUENCE OF WETTING PROPERTIES ON DIFFUSION IN A CONFINED FLUID

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Abstract

We briefly discuss how the wetting properties of a fluid/solid interface can indirectly influence the diffusion properties of fluid confined between two solid walls. This influence is related to the variability of the hydrodynamic boundary conditions at the interface, which correlates to the wetting properties.

1 The boundary condition at a liquid-solid interface

At a macroscopic level, it is well known that the relative velocity of a fluid with respect to the solid vanishes at a liquid-solid interface. This is the "no-slip" boundary condition, which although very general does not have a microscopic justification. At a microscopic level, it is however necessary to take into account a possible "slip" of the liquid on the solid surface. The amount of slip is quantified by introducing a slipping length in the boundary condition at the solid interface, which in general reads

\[ \frac{\partial v_t}{\partial z}\bigg|_{z=z_w} = -\frac{1}{\delta} v_t\bigg|_{z=z_w}, \]

where \( v_t \) is the tangential velocity at the boundary, and \( z_w \) is the position of the boundary (which is assumed here to be a plane perpendicular to the \( z \) axis). The "slip" length \( \delta \) which appears in this equation can be interpreted as the length one has to extrapolate the velocity field of the fluid into the solid to obtain a vanishing value. Equation (1) can also be interpreted as expressing the continuity of the stress (or momentum flux) at the boundary. At the boundary, the viscous stress \( \eta \frac{\partial v_t}{\partial z} \) in the fluid is then equal to a fluid friction stress between the solid and the liquid, \( \kappa v_t \). \( \delta \) is the ratio of the viscosity \( \eta \) to the friction constant \( \kappa \). The usual "no-slip" boundary condition corresponds to \( \kappa = \infty \), while at a free boundary \( \kappa = 0 \).

In previous work [1, 2] it was shown that even for surfaces which are smooth at the atomic scale, slip is usually a small effect. A small (atomic) corrugation of the wall is enough to produce a "no-slip" boundary condition. This accounts for the findings of experiments performed with the surface force apparatus [3]. However, this result appears to break down when the solid surface is strongly nonwetting for the liquid, i.e. when a liquid drop on this solid substrate has a large contact angle. In that case, it appears [4] that the slip length \( \delta \) can become much larger than the molecular size. Physically, this can be traced back to the fact that the liquid does not "want" to be in contact with the solid. Hence a microscopically thin depletion layer forms between the bulk fluid and the solid, making the momentum transfer much less efficient and effectively decoupling the fluid from the substrate. In the following we discuss how the diffusion of a molecule will be affected when a thin liquid film is confined between two identical parallel plates that are characterized by a "partial slip" boundary condition such as (1). The quantity we focus on is the relative change of the diffusion constant parallel to the plates as a function of the distance \( h \) between the plates,

\[ \Delta = \frac{D_{\parallel}(h) - D_{\text{bulk}}}{D_{\text{bulk}}}. \]

We will be interested in cases where the confinement is moderate (typically \( h \) is larger than 10 molecular sizes), so that the film is still in a clearly fluid state.
2 Confinement effects on diffusion.

2.1 Qualitative discussion.

In this section, we briefly describe, at a qualitative level, how the boundary conditions can influence the diffusion of a molecule confined in a pore. Two complementary points of view are possible, and yield essentially identical results [5]. The first one is a microscopic, "mode-coupling", type of approach. The idea is the following. Very generally, the diffusion constant of a tagged particle can be written as

\[ D = \int_0^\infty dt < \vec{v}(t), \vec{v}(0) > \] (3)

In the bulk, two contributions to the velocity autocorrelation function \(< \vec{v}(t), \vec{v}(0) >\) of the tagged particle can be isolated [5]. A short time part describes the "rattling" motion in the cage formed by the neighbours. A more subtle contribution, which appears for long times, is related to the so called "backflow" effect. The idea is that the initial momentum of the particle is transferred at intermediate times to the long wavelength, hydrodynamic motion of the fluid. According to the Stokes equations, this momentum diffuses away from the tagged particle. However, the properties of the diffusion equation imply that a fraction of this momentum eventually returns to the origin and "pushes" the tagged particle. Let us now consider how this mechanism is modified by confinement. First of all, the "rattling" contribution is not expected to change, since it is governed by the local environment. The hydrodynamic backflow, on the other hand, will be strongly modified. If the confining boundaries correspond to a "no-slip" situation, they will absorb the incoming momentum. In that case the amount of backflow will be reduced, and \(\Delta\) will be negative. On the other hand in a case of perfect slip the momentum will be reflected at the boundary, and the backflow effect will be enhanced. This argument can be made quantitative in both cases [5] and has in fact been used to interpret experimental results on free standing liquid crystal films [6]. However, it turns out that a quantitative calculation for the case of partial slip is difficult.

An alternative, more macroscopic line of thought consists in computing the mobility \(\mu_\parallel(z)\) of a particle at a distance \(z\) from a solid wall, with a boundary condition 1, using macroscopic hydrodynamics. The diffusion constant in a fluid slab is then obtained using the Einstein relation between diffusion and mobility, averaged over the thickness \(h\) of the slab. For the no-slip or perfect slip cases, such a calculation was shown to yield results identical to those obtained within the mode coupling approach. For the general "partial slip" boundary conditions, it offers the advantage of being tractable analytically. The method and results are summarized in the next section.

2.2 Hydrodynamic estimate of the diffusion constant.

Consider a spherical particle of diameter \(R\) moving past a solid boundary characterized by equation [1], with a constant velocity parallel to the boundary. The mobility is obtained by calculating the viscous drag on the particle, which implies solving the Stokes equation for the velocity and pressure fields. This can be achieved using the method of reflections [7]. In this method, the velocity field at zeroth order corresponds to the one obtained for an infinite fluid, and therefore obeys the correct boundary condition on the particle. A first correction term is introduced to obtain the correct boundary condition on the wall, therefore violating the no-slip boundary condition on the particle. A third correction is introduced to correct again the boundary condition on the particle. Assuming convergence of the series, one eventually ends up with a velocity field that has the correct behaviour both at the particle surface and at the solid boundary. The force can then be calculated from the pressure tensor on the particle surface. The details of the calculation are described in [8]. Here we only quote the result, which gives the force on a particle at an altitude \(z\) from the wall, with velocity \(\vec{U}\) as

\[ \vec{F} = \frac{-6 \pi \eta R \vec{U}}{1 - \frac{9}{16} \frac{R}{z} C \left( \frac{R}{z} \right)} \] (4)
where \( C[y] = -\frac{1}{6} y^2 - \frac{1}{2} y - \frac{2}{3} + \left( \frac{1}{6} y^3 + \frac{2}{3} y^2 + \frac{2}{3} y \right) E(y) + \frac{8}{3} y E\left(\frac{y}{2}\right) \) and \( E(y) = e^y \text{Ei}(1, y) \), with \( \text{Ei}(1, y) \) the exponential integral function. The altitude dependent mobility is then averaged over the channel to compute the effective diffusion constant. When applied to the extreme cases of no-slip or perfect slip, this formula yields a relative decrease or increase, respectively, of the diffusion constant, in accordance with the qualitative analysis made in the previous section. The results for \( \Delta \) as a function of \( h/R \) and \( \delta/R \) are summarized in figure 1. An increase in the diffusion constant can be observed as soon as \( \delta \) becomes larger than the pore size.

\[
\frac{\Delta D}{D} = \frac{n}{R} \text{ vs. } \frac{h}{R} \text{ and } \frac{\delta}{R}
\]

**Figure 1:** Reduced diffusion coefficient, \( \Delta = \frac{\Delta D}{D} \) versus \( \frac{h}{R} \) and \( \frac{\delta}{R} \)

### 2.3 Molecular dynamics simulations.

In order to confirm qualitatively the general trend predicted in the above section, we present in figure 2 the results for the diffusion constant in a Lennard Jones fluid confined between two solid walls. The two cases correspond to a wetting situation with a zero slipping length, and to a nonwetting one with a large slipping length. We stress that while varying the pore width \( h \), some care has been taken to keep the density of the fluid at the center of the pore fixed to its “bulk” value, so that variations of the diffusion constant can only originate from confinement contributions.

In the nonwetting case, the increase of the diffusion constant is clearly visible as soon as the pore size becomes smaller than the slip length. Each of these curves corresponds to a constant \( \delta \) cut of the surface in figure 1.

### 3 Conclusion

Both hydrodynamic arguments and microscopic simulations indicate that the diffusion of a tagged molecule in a confined geometry will indirectly be correlated to the wetting properties of the fluid, through the hydrodynamic boundary condition at the interface. In particular, an increase of the diffusion constant with confinement is predicted in the ”nonwetting” case. We emphasize, however,
Figure 2: Diffusion constant (in Lennard Jones units) as a function of the pore width \( h^* = h/\sigma \) for a Lennard Jones fluid confined between two parallel walls. The density in the middle of the pore is 0.92\( \sigma^{-3} \) for panel (a) and 0.86\( \sigma^{-3} \) for panel (b). \( \delta^* = \delta/\sigma \) below the panels indicates the slipping length corresponding to each considered fluid-solid interface (measured independently). The reduced temperature is \( T = 1 \).

that the mechanism discussed in this paper is quite generic, and does not consider the possibility of specific interactions with the substrate. Care should also be taken in measuring the diffusion constant in the bulk and in the confined medium under similar thermodynamic conditions (pressure), in order to make a sensible comparison.

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