Adsorption phenomena in the transport of a colloidal particle through a nanochannel containing a partially wetting fluid

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Abstract

Using molecular dynamics simulations, we study the motion of a closely fitting nanometer-size solid sphere in a fluid-filled cylindrical nanochannel at low Reynolds numbers and for a wide range of fluid-solid interactions corresponding to different wetting situations. For fluids that are not completely wetting we observe an interesting and novel adsorption phenomenon, in which the solid sphere, that was initially moving along the center of the tube, meanders across the channel and suddenly adsorbes onto the wall. Thereafter, the adsorbed sphere either sticks to the wall and remains motionless on average, or separates slightly from the tube wall and then moves parallel to the tube axis, while rotating on average. On the other hand, at short times, i.e. when the solid particle moves with its center close to the middle of the tube, we find surprisingly good agreement between our results and the predictions of the continuum approach in spite of the large thermal fluctuations present in our simulations.

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Recent developments of micro- and nano-fluidic devices for fluid transport have led to revolutionary new capabilities in the transport and process of suspended small particles [1, 2], with the rapid advances in those areas highlighting the crucial importance of understanding the new features that emerge when nanometer size particles move through a fluid-filled nanochannel. But, in contrast to the extensively studied case of the nano-confinement of single fluids which illustrates how their varied hydrodynamic behavior differs drastically from that observed in macro-scale flows, only a few experimental or numerical studies have dealt with the hydrodynamics of nanometer size particles under similar conditions.

Here, we consider the motion at low Reynolds numbers of a solid sphere in a fluid-filled capillary tube when the dimensions of both the particle and the tube approach molecular scales, a typical situation in nano-fluidics (see Fig. 1 for a schematic view of the system under consideration). We present the results of molecular dynamics (MD) simulations, which have already proved very useful in capturing the behavior of single fluids at fluid-solid interfaces. Motivated by a series of recent experimental [3, 4, 5, 6] and numerical [7, 8, 9] studies where the wetting properties of the fluid is shown to play a crucial role at the fluid-solid interface, such as large slip effects for “nonwetting” fluids, we investigate the behavior of the system as the wetting properties of the fluid are varied, from perfect to partial wetting.

The hydrodynamic behavior of single fluids in nanochannels and its dependence on the wetting properties of the liquid, has been reproduced in molecular dynamics (MD) simulations using simple Lennard-Jones liquids, where the wetting properties of the fluid were
modeled by varying the strength of the solid-liquid attraction term in the potential \[8, 9\]. We therefore investigate the motion of a single sphere in a nanochannel in the simplest possible numerical framework, where all molecular interactions are modeled by slightly modified Lennard-Jones potentials. Our main objective is to investigate to what extent the molecular character of the system introduces new features not present when the traditional continuum approach is adopted.

In our MD simulations we consider a tube of inner radius \(R\), which is constructed by deleting a cylindrical region of atoms from an fcc-lattice. The fluid filling the nanochannel has a reduced density \(\rho\sigma^3 = 0.8\), where \(\sigma\) is the size of the repulsive core, \(\sigma \sim O(0.3nm)\), and two fluid atoms, separated a distance \(r\), interact through the Lennard-Jones potential \(V_{LJ}(r) = 4\epsilon[(r/\sigma)^{-12} - (r/\sigma)^{-6}]\), truncated (and shifted to give a continuous force) at \(2.5\sigma\). The simulations are performed at a temperature \(T = 1.0\epsilon/k_B\) (just above the liquid-gas coexistence value for the bulk Lennard-Jones liquid) and with a characteristic time unit \(\tau_0 = \sqrt{m\sigma^2/\epsilon}\) (where \(m\) is the mass of the fluid atoms), \(\tau_0\) being \(O(1ps)\) for typical liquids. The tube wall has the same density as the fluid, and the lattice constant equals \(0.85\sigma\), with the wall atoms having mass \(100m\) and tethered to the fixed lattice sites by a harmonic potential with a large spring constant. Following Ref. [10] (see also Ref. [9] for less dense fluids) the wall-fluid interactions are modeled by means of a modified Lennard-Jones potential \(V_{wf}(r) = 4\epsilon[(r/\sigma)^{-12} - A(r/\sigma)^{-6}]\), where the parameter \(A\) determines the wetting properties of the fluid-wall system, with the partially wetting situation corresponding to values of \(A\) less than 1. Specifically, this molecular model leads to the expression \(\cos \theta \approx -1 + 2A\), for the equilibrium contact angle \(\theta\) at the fluid-solid interface [11]. Let us mention that, slip effects at the solid-fluid interface, being negligible at \(A = 1\), rapidly increase with decreasing \(A\) for this molecular model [9,11]. The solid particle is constructed by extracting a sphere of radius \(a = 5.1\sigma\) from an fcc-lattice having the same lattice constant as the tube wall (\(0.85\sigma, N_A \approx 466\) atoms inside the spherical solid particle and fixed in their lattice sites). The same \(V_{wf}\) and \(V_{LJ}\) potentials are used for the interactions between the atoms of the solid particle and either those of the fluid or those of the tube wall respectively. Also, periodic boundary conditions are imposed in the direction along the tube axis at \(x = L \sim 50\sigma\).

We consider first the situation in which a constant force, directed along the axis of the tube, is applied to the solid particle (a force \(f = 0.1\epsilon/\sigma\) applied to each of its atoms), for a tube radius \(R = 2a\) and various values of the attractive strength \(A\), ranging from 0.1 to
FIG. 2: Radial position of the solid particle as a function of time for 6 independent MD simulations with \( A = 0.1, 0.4 \) and 0.7. The left graph corresponds to cases in which the particle remains motionless on average ("stick"), while on the right graph, for the same values of \( A \), we show cases in which the particle is adsorbed but moves along the tube axis ("rolling").

1. In Fig. 2 we present the radial position of the particle as a function of time, for six different realizations corresponding to \( A = 0.1, 0.4 \) and 0.7. In all cases, the solid particle not only moves along the tube axis, due to the applied external force, but it also meanders in the radial direction due to the thermal fluctuations present in the system. Eventually, the particle reaches a critical radial position after which it suddenly adsorbes onto the wall and thereafter shows two types of behavior: a stick situation in which the solid particle remains motionless on average, and a rolling condition in which the sphere separates slightly from the tube wall and then moves parallel to the tube axis while rotating on average. Moreover, as observed in Fig. 2, the radial position at which the particle suddenly jumps to the tube wall increases with \( A \). It is clear that the potential energy reduction due to the adsorption of a solid particle is proportional to \( 1 - A \), since the solid particle displaces fluid particles which are less attracted to both the solid particle and the wall by a factor \( A \), and hence the smaller the value of \( A \), the larger the adsorption force. In fact, we find that for \( A = 1 \), where all interactions are equal and complete wetting exists, a solid particle initially moving away from the wall does not become adsorbed even after very long times when it has meandered all across the tube. On the other hand, if the solid sphere is initially placed on the tube wall,
with no fluid atoms in the particle-tube gap, the sphere remains adsorbed during the whole duration of the simulation $O(1000\tau_0)$. These results indicate that, for $A = 1$, a solid particle moving in the channel is not able to squeeze out all the fluid atoms and become adsorbed to the tube wall, but, if placed next to the wall, there is no tendency for fluid atoms to infiltrate between the sphere and the wall, so that the solid particle remains adsorbed.

The two different regimes that are observed after the particle has been adsorbed at the wall are also shown in Fig. 2 where, on the left-side, we present cases in which the particle remains motionless on average, but where fluctuations in its radial position can be observed. On the other hand, the right-side of Fig. 2 shows examples where the particle continues to roll after being adsorbed, and exhibits much larger fluctuations in its radial position (e.g. compare the two $A = 0.1$ cases shown in Fig. 2 for times $t > 200\tau_0$). In some cases, we also observe an intermittent behavior between the two regimes, as can be seen in Fig. 3. Figure 4 gives the probability density function (p.d.f) for the radial position of the solid particle once it has been adsorbed to the wall, where the subtle difference between the “stick” and “roll” regimes is evident. It is interesting to note that, when the particle is adsorbed, particularly for low values of $A$ and in the “stick” regime, almost all the fluid atoms have been squeezed out from the particle-wall gap (see Fig. 5), a phenomenon which would have required an infinite force in the continuum limit [12]. The absence of liquid atoms in the particle-wall gap results in a pressure imbalance that causes the particle to remain adsorbed (note that this pressure imbalance plays a particularly important role in the case $A = 1$, in that, with all interactions being alike, it is the only cause of adsorption for a particle placed next to the tube wall). This situation strongly resembles the phenomenon of capillary drying on nanometer length scales observed experimentally [13], in which, when a fluid-filled gap between two hydrophobic surfaces falls below a critical value, the liquid is spontaneously ejected from the gap.

In order to investigate the effects of varying the ratio of the tube radius to that of the sphere, $R/a$, we have also performed MD simulations of the same sphere, initially placed at the center of the tube, moving through the tube for different values of $R$, ranging from $7\sigma$ to $24\sigma$. First, we investigated the case of $A = 1$, where slip effects at the solid-liquid interface have been shown to be negligible even at the molecular level [9], and which also corresponds to complete wetting. In Fig. 6 we show the results thus obtained for the mean particle velocity along the tube axis, $U_x$, as a function of the relative radius, $R/a$, when a
FIG. 3: a) Particle position along the tube as a function of time, for $A = 0.1$ and $R = 2a$. After the particle is adsorbed ($t \sim 400$), alternative "stick" and "roll" situations can be observed. b) Time evolution of the radial position for the same realization shown in a).
FIG. 4: The solid symbols correspond to the probability density function (p.d.f) for the radial position of the solid particle averaged over 6 different realizations for $A = 0.1$. Two peaks, corresponding to “stick” and “roll”, can be observed. The dashed lines refer to the p.d.f’s of the two realizations shown in Fig. 2 for $A = 0.1$, where the particle is either motionless or rolling along the tube wall.

constant force is applied to the sphere ($f = 0.1 \epsilon/\sigma$, as before). The results are for short times, in that the averaging time is too small for the particle to have meandered away from the center of the tube towards the tube wall. For purposes of comparison, we also present the continuum solution for a non-Brownian, perfectly smooth sphere, moving along the center of the tube in the limit of vanishingly small inertia effects [12]. It can be seen that, despite the large thermal fluctuations present in the system and the fact that the Reynolds number in our simulations is not exactly zero ($\text{Re} \lesssim 0.2$), the continuum calculations are in good agreement with the reduction observed in the mobility of the sphere as the tube radius decreases. Moreover, the fact that the continuum solution slightly overestimates the mean velocity along the tube might simply be due to the transverse random motion of the particle in the MD simulations. We have also investigated the effects of the wetting properties of the
FIG. 5: Snapshots of the solid particle adsorbed to the wall for the case $A = 0.7$ shown in Fig. 3. On the left-side snapshot the sphere is motionless whereas on the right-side the particle is rolling along the tube. In both cases, however, the gap between the sphere and the wall is smaller than the size of a single fluid atom.

FIG. 6: Mean particle velocity along a tube at short times, when a constant force is acting on the sphere and for $A = 1$. Points correspond to MD simulations and the solid line corresponds to the continuum results of Bungay and Brenner [12]. The error bars correspond to temporal fluctuations in the instantaneous velocity of the solid particle.
fluid, and find that, although the average sphere velocity increases with decreasing values of $A$, deviations from the continuum results using the no-slip boundary conditions are small even for attraction strengths as small as $A = 0.05$ (the deviations in the average particle velocity from that predicted by continuum hydrodynamics are within 30%). Let us remark that the simulation results are for short times, in that the solid particle remains close to the center of the tube and therefore adsorption effects are absent even for the smallest values of $A$. Similar conclusions concerning the robustness of continuum calculations for a sphere approaching a plane wall were presented in Ref. [14]

In summary, an interesting adsorption phenomenon was identified in the transport of a colloidal particle suspended in a partially wetting fluid though a nanochannel. We also observed “stick” and “roll” regimes for the adsorbed particle, in which the “stick” case apparently corresponds to a particular orientation of the sphere roughness with respect to the molecular roughness of the tube wall. Surprisingly, all fluid atoms are displaced out from the particle-wall gap in both regimes, something which would have required an infinite force in the traditional continuum description. Finally, in view of what has been presented above, it is clear that understanding this wetting-induced adsorption phenomenon is crucial to the successful modeling of the transport of colloidal particles in nanofluidic devices.

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