Adsorption phenomena in particle transport through a fluid-filled nanochannel

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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, for a wide range of fluid-solid interactions corresponding to different wetting situations. For fluids that are not completely wetting we observe a novel adsorption phenomenon in which the solid sphere is adsorbed onto the wall, and thereafter executes an intermittent *stick-slip* motion, while the gap between the sphere and the wall remains smaller than the size of a fluid atom.

The rapid advances in the development of micro- and nano-fluidic devices shows that crucial new features emerge when nanometer-sized particles move through a fluid-filled nanochannel [1]. However, few experimental or numerical studies have dealt with the hydrodynamics of nanometer size particles in confined motion. Here we consider the low Reynolds number motion of a solid sphere in a fluid-filled capillary tube when the dimensions of both the particle and the tube approach molecular scales. We present the results of molecular dynamics (MD) simulations, which already proved very successful in capturing the behavior of single fluids at fluid-solid interfaces. In particular, recent MD studies show that the wetting properties of the fluid play a crucial role at the fluid-solid interface, such as producing large slip effects for "nonwetting" fluids [2]. Motivated by these results, we investigate the behavior of the system as the wetting properties of the fluid are varied from perfect to partial wetting. We observe, for poorly wetting fluids, a novel phenomenon in which the solid sphere is eventually adsorbed onto the tube wall [3].

The hydrodynamic behavior of single fluids in nanochannels, and in particular the dependence on the wetting properties of the liquid, has been reproduced in 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 [2]. We therefore investigate the motion of a single sphere in a nanochannel in the same numerical framework. The MD simulations are based on the generalized Lennard-Jones potential $V(r) = 4\epsilon[(r/\sigma)^{-12} - A(r/\sigma)^{-6}]$ acting between any two atoms separated a distance r. σ is roughly the size of the repulsive core, $\sigma \sim O(0.3nm)$, the characteristic time unit is $\tau_0 = \sqrt{m\sigma^2/\epsilon}$ where m is the mass of the fluid atoms, $m \sim 40u$ for liquid argon, and $\tau_0 = O(1ps)$ for typical liquids. The potential is truncated at 2.5σ and shifted by a linear term to give a continuous force. The fluid filling the nanochannel has an $A = 1$ interaction and density $\rho\sigma^3 = 0.8$, and occupies a tube of (variable) inner radius R and length $L \approx 50\sigma$, constructed by deleting a cylindrical region of atoms from an fcc lattice. 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. The tube wall has the same density as the fluid, a lattice constant of 0.85σ, and its atoms have mass $100m$ and are tethered to fixed lattice sites by a stiff harmonic potential. Following Ref. [2, 4], the wall-fluid interactions are varied by adjusting the constant A in the potential which controls the wetting properties of the fluid-wall system. The partially wetting situation corresponding to values of A less than 1; in this molecular model the equilibrium contact angle θ at the fluid-solid interface is given approximately by $\cos\theta \approx -1 + 2A$ [5]. The solid particle is constructed by extracting a sphere of radius $a = 5.1\sigma$ with $N_A \simeq 466$ atoms from an fcc-lattice having the same lattice constant as the tube wall, and fixing the atoms' relative positions. The solid particle atoms interact with the fluid with the same value of A as the wall atoms, and interact with the wall atoms with $A = 1$. Periodic boundary conditions are imposed in the direction parallel to the tube axis. We have also performed numerical simulations for an *amorphous* case, which is constructed as before except that a random perturbation is added to the position of each atom of the solid sphere and tube wall (with uniform distribution in the range $[0, 0.34\sigma]$ in each direction).

We consider the case of a constant force applied to the solid particle directed along the tube axis (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 1. 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 and is suddenly adsorbed onto the wall, and thereafter shows an intermittent *stick-slip* motion parallel to the tube axis. It is interesting to note that in both the stick and slip modes of its motion, the particle stays in direct contact with the wall since the gap separating them is smaller than the size

of a fluid atom. The critical 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 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 (the factor $1 - A$ plays a similar role to that of the Hamaker constant in continuum studies of the Van der Walls attraction between a solid sphere and a solid wall [6]) In fact, we see in Fig. 1 that for values of $A \gtrsim 0.8$, 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, whereas for $A \lesssim 0.7$ the particle is eventually adsorbed. Completely analogous behavior is obtained for the amorphous case, in that the transition form adsorption to no-adsorption is also observed at $A \sim 0.75$. Therefore, this phenomenon seems robust in that it does not require perfect matching between the underlaying solid lattices of the particle and the tube wall, and implies the possibility of wetting-controlled separation of colloidal particles flowing through a capillary tube.

On the other hand, if the solid sphere is initially placed on the tube wall, with no fluid atoms in the particle-wall gap, the sphere remains adsorbed for the duration of the simulation, $O(1000\tau_0)$, even for $A = 1$. These results indicate that for A close to 1 the configuration has a qualitative stability – a solid particle will not squeeze out the fluid atoms and become adsorbed to the tube wall, and conversely if it is placed next to the wall, there is no tendency for fluid atoms to infiltrate between the sphere and the wall. The stick-slip motion observed for sufficiently low A differs drastically from that predicted by a continuum model that accounts for the Van der Waals and double-layer forces acting on a closely-fitting sphere traveling along a fluid-filled tube. Specifically, the balance of these forces in the direction normal to the tube axis was found to lead to a stable radial position of the sphere, without adsorption and squeezing out of the fluid atoms, as it travels along the tube [6].

The probability density function (p.d.f) for the radial position of the solid particle once it has been adsorbed to the wall, shows a subtle difference between the "stick" and "slip" situations, in that slipping spheres are slightly separated from the tube wall. On the other hand, when the particle is adsorbed, all the fluid atoms are squeezed out of the particle-wall gap, a phenomenon which would required an infinite force in the continuum limit [7]. The depletion of liquid atoms in the particle-wall gap results in a pressure imbalance that gives rise to an attractive depletion force between the particle and the wall, leading to the adsorption of the solid sphere [8]. (Note that this depletion force plays a particularly important role in the case $A = 1$, since when all the interactions are identical it is the only cause of adsorption for a particle placed
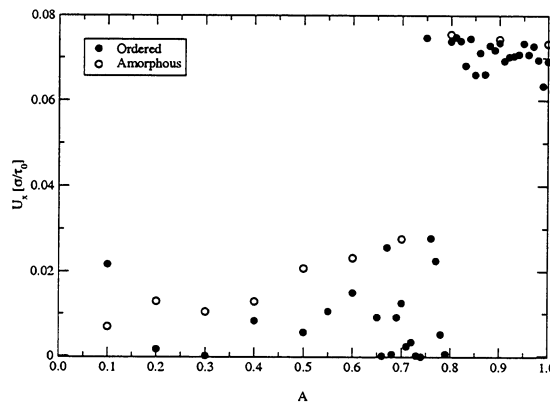

FIG. 1: Mean particle velocity along a tube for long simulation runs, $O(10^4\tau_0)$ (the mean velocity of eventually adsorbed particles is computed after adsorption has occurred). For values of $A \lesssim 0.7$ all particles get eventually adsorbed, whereas for $A \gtrsim 0.8$ no adsorbed particles are observed, in both *ordered* and *amorphous* cases. The observed fluctuations in the average velocities for $A \lesssim 0.7$, particularly in the ordered case, are a consequence of the described "stick-slip" phenomenon.

next to the tube wall). This situation strongly resembles the phenomenon of capillary drying on nanometer length scales [9], in which liquid is spontaneously ejected from the gap between two hydrophobic surfaces when the width falls below a critical value.

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