Hysteresis, Force Oscillations and Non-Equilibrium Effects in the Adhesion of Nanoparticles to Atomically Smooth Surfaces

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Understanding the transport of suspended nanometer-size particles under molecular scale confinement is crucial for the development of integrated nanofluidic systems. Molecular simulations have provided invaluable insight into the behavior of fluids under nanoconfinement. In our previous work, we used molecular dynamics (MD) simulations to study the transport of nanometer-size particles through a fluid-filled nanochannel, and observed a sharp transition between the steady transport and the spontaneous adsorption of the suspended particles, as a function of the solid-fluid interaction strength. However, we were severely limited in the time scales accessible to simulation to less than 0.1 microseconds, and extrapolation to laboratory time scales is therefore uncertain. Thus, we explore here the free energy and fluid configurational changes associated with the adsorption of nanoparticles, as a first step in developing multiscale simulation techniques which would bridge this gap.

The MD simulations are based on an atomistic description of molecules interacting via Lennard-Jones potentials with a dimensionless parameter A that controls the attraction between the various atomic species and thus determines the wetting properties of the system. The particle and channel wall are made of the same material and their atoms interact via the LJ potential with $A=1$. The fluid atoms also interact among themselves with $A=1$.

In our previous work [1-2], we applied an axial force to the particle, and observed a sudden spontaneous transition from a statistically steady motion parallel to the tube axis to adsorption on the walls, when the strength of the solid-fluid attraction falls below a critical value Ac~0:8 (for both spherical and ellipsoidal particles). Here, we discuss the changes in the Helmholtz free energy F of the system by performing a thermodynamic integration as the sphere approaches the wall in the radial direction and then recedes to its original position at the center of the tube. We show that the average force on the sphere as a function of its radial position exhibits a large hysteresis as $A \rightarrow 1$. On the other hand, we found no hysteresis, even at relatively large approaching velocities, for the $A=0$ case of a completely non-wetting fluid. The observed hysteresis is not due to the drag or other irreversible forces arising from the motion of the sphere, in spite of the relatively large approaching speed. It is important to note, however, that the motion of the sphere in these simulations is very slow compared with the natural time scale of the spontaneous process.

The hysteresis appears to be due to the history dependence of the number of particles in the gap between the sphere and the tube wall, for gap sizes of the order of the diameter of a single fluid molecule. The number of particles in the gap during the desorption branch is smaller, corresponding to a depletion of particles relative to the bulk density. The absence of fluid leads to the dominance of the attractive wall-particle interactions and depletion forces. In addition, the presence of a wall induces both layering as well as in-plane ordering of the fluid, which might lead to the crystallization of the first fluid layer depending on the solid-fluid interactions. Such structural correlations, can contribute to hysteresis if any significant time is required for the structure to reestablish itself after the particle is pulled away. The dependence of hysteresis on the degree of wetting of the fluid may be understood in terms of the relative ease of pushing fluid atoms out of the gap region, which obviously improves as the fluid becomes less wetting.

A notable feature of the force measurements is that the particles leave the gap continuously, without a noticeable effect on the solvation layers known to occur close to solid surfaces. The smoothness of this transition is in agreement with the absence of oscillatory solvation forces in the measurements. This effect results from the ability of the particle to rotate freely as it approaches the wall, and indicates that a freely suspended particle might overcome solvation force barriers, that would otherwise prevent strong adhesion, by adjusting its atomic lattice orientation relative to that of the wall. Results of an alternate simulation where the orientation of the particle is fixed during its slow motion towards the wall, exhibit the familiar oscillations as layers of fluid are successively squeezed out of the gap region. Moreover, the free energy displays substantial hysteresis also in this case and, in addition, it exhibits a shift in the distance of the first peak during the pull-off branch of the measurement, which corresponds to a delay in replenishing fluid in the gap.

The results presented here show some of the issues arising when particle dynamics at the nanoscale is examined in quantitative detail. The results pose some serious challenges for the long-term goal of modifying the continuum description of particle-fluid dynamics to describe phenomena at these length scales, since, for example, there is no single potential of mean force which may be incorporated. One immediate avenue for further study would be to explore the validity of the number of particles in the gap as an order parameter for a multiscale description.

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