

# Multiscale modeling of nanoflows

G. Drazer\*, A. Acrivos\*, B. Khusid\*\*, and J. Koplik\*\*\*

\*The Benjamin Levich Institute, City College of The City University of New York, New York, NY 10031, [drazer@mailaps.org](mailto:drazer@mailaps.org), [acrivos@sci.ccny.cuny.edu](mailto:acrivos@sci.ccny.cuny.edu)

\*\*Department of Mechanical Engineering, New Jersey Institute of Technology, University Heights, Newark, NJ 07102; [khusid@adm.njit.edu](mailto:khusid@adm.njit.edu)

\*\*\*The Benjamin Levich Institute and Department of Physics, City College of The City University of New York, New York, NY 10031, [koplik@sci.ccny.cuny.edu](mailto:koplik@sci.ccny.cuny.edu)

## ABSTRACT

We consider the possibility of using a quasi-equilibrium approximation for multi-scale simulations of the transport of a closely fitting nanometer-size solid sphere through a fluid-filled cylindrical nanochannel (*Phys. Rev. Lett.* **89**, 244501, 2002). To this end, by means of molecular dynamics simulations, we compute the force acting on the sphere slowly approaching the wall and then receding to its original position at the center of the tube. We find that the effective free-energy of the system exhibits substantial hysteresis as a function of the radial position of the particle. This clearly indicates that the multiscale description of the system should include an additional *order parameter* or *reaction coordinate*. For example, the number of fluid molecules inside the gap, which shows hysteretic behavior similar to that of the effective free-energy, may perhaps be used as such a parameter.

**Keywords:** nanoflow, adsorption, nanochannel, hysteresis, multiscale.

## 1 INTRODUCTION

The rapid development of micro- and nano-fluidic devices and their potential applications in a variety of fields, particularly those associated with the so-called lab-on-a-chip devices or  $\mu$ -TAS, have led to a renewed interest in the problem of transport phenomena under microscopic confinement. Since the flow of suspended particles in nanochannels involves characteristic length scales far below the range of applicability of the continuum fluid mechanics, it becomes necessary to make use of a molecular description in order to obtain a proper understanding of the relevant flow phenomena. In this context, molecular simulations provide a powerful tool to study the rich dynamics of fluids under nano-confinement, which drastically differs from the hydrodynamics of bulk fluids. In our previous work [1-4], we employed molecular dynamics simulations to investigate the transport of a nanometer-sized spheroidal particle in a fluid-filled capillary tube of similar dimensions and identified a new adsorption phenomenon in which, for poorly wetting fluids, a suspended particle, initially moving along the center of the nanochannel, is adsorbed onto the tube wall while

displacing all the fluid molecules from the particle-wall gap. The particles also exhibited stick-slip motion following their adsorption on the tube wall. We also found that, a sharp adsorption/no-adsorption transition occurs as the wetting properties vary from nonwetting to complete wetting, independent of the particle shape.

On the other hand, direct molecular simulations are typically limited to time-scales less than microseconds and it is thus crucial to develop multiscale simulation techniques to incorporate micro-scale information into macroscopic calculations.

## 2 TOWARDS A MULTISCALE DESCRIPTION

The thermodynamic variables of a macroscopic system incorporate the behavior of its constituents, so a natural first step is to compute the free energy as a function of the obvious coordinate, the particle's radial position.

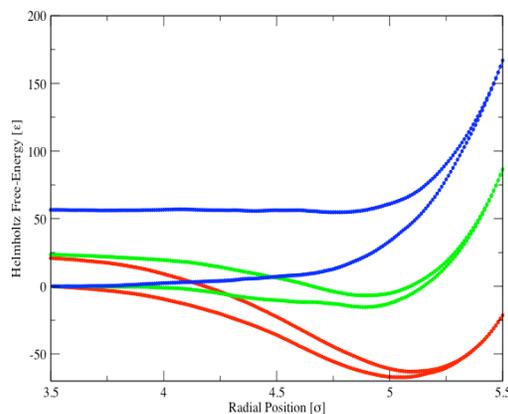


Figure 1: Change in the Helmholtz free-energy of the system as a function of the radial position of the suspended particle inside the tube. Different colors correspond to different wetting conditions. (Blue circles correspond to  $A=1.0$ , green circles correspond to  $A=0.8$  and the red circles correspond to  $A=0.6$ , where  $A$  is the coefficient of the attractive  $1/r^6$  term in the Lennard Jones potential.)

Using molecular dynamics methods, we simulate an adsorption/desorption cycle by very slowly displacing the particle from the center of the tube, to the wall, and back to the center. We measure the radial force exerted by the fluid on the particle, and compute the work required for the process, which in this case equals the change in the Helmholtz free energy of the (particle+fluid+wall) system. The result in Fig. 1 shows that the free energy is distinctly hysteretic, although the potential energy, shown in Fig. 2, is not. The hysteresis is evidently associated with the entropy of the system, and in fact can be correlated with the history dependence of the number of fluid atoms in the gap between the particle and the tube wall: there are fewer on the receding part of the cycle than in the approach part, and thus more force is needed to separate the particle from the wall than to move it towards it.

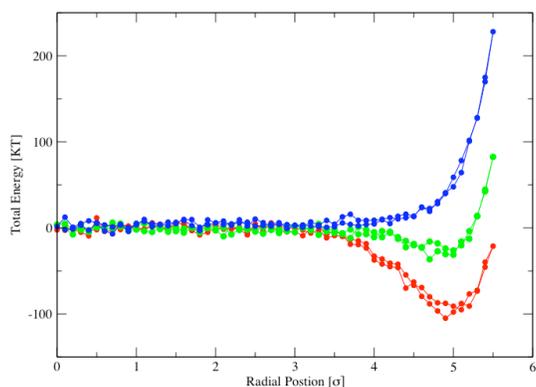


Figure 2: Total energy of the system as a function of the particle position in the tube (colors as in Fig. 1).

The presence of hysteresis clearly indicates that a multiscale description of the transport of particles through the channel cannot be based solely on a single free energy function, but should include an *order parameter* or *reaction coordinate* in addition to the radial position of the particle. For example, the number of fluid molecules inside the gap, which shows hysteretic behavior similar to that of the effective free-energy, is an obvious candidate for such a parameter.

Finally, it is instructive to compare these quasi-equilibrium results to the previously-studied situation [1,2] in which an external force parallel to the channel axis is applied to the spheroidal particle. In that case, the sphere displays intermittent stick-slip motion after adsorption, and also exhibits spontaneous desorption events (Fig. 3). In contrast we do not observe spontaneous desorption in the present case, because of the free energy barrier apparent in Fig. 1. We observed in the forced case that the stick-slip motion of a sphere along the channel correlates with large fluctuations in the number of fluid molecules in the sphere-

wall gap. This again suggests that the number of fluid molecules may be an appropriate variable to describe the *state* of this system in a future multi-scale calculation.

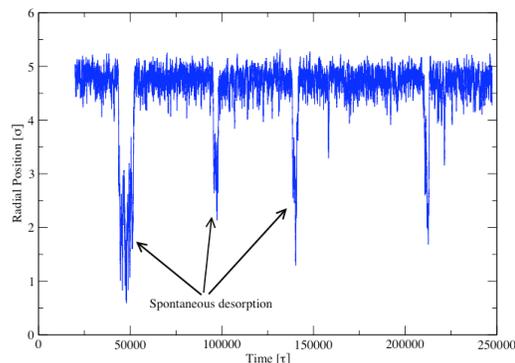


Figure 3: Radial position of an adsorbed sphere vs. time in the presence of axial forcing. The dips indicate spontaneous desorption and readsorption events.

A.A. and G.D. were partially supported by the Engineering Research Program, Office of Basic Energy Sciences, U.S. Department of Energy under Grant No. DE-FG02-90ER14139 and by the NSF-CTS-0307099 grant; J.K. was supported by NASA's Office of Biological and Physical Research; B.K. was partially supported by a grant through the joint NSF/Sandia program; and G.D. was partially supported by CONICET Argentina.

## REFERENCES

- [1] "Adsorption Phenomena in the Transport of a Colloidal Particle through a Nanochannel Containing a Partially Wetting Fluid", G. Drazer, J. Koplik, B. Khusid and A. Acrivos, Phys. Rev. Lett. 89, 244501 (2002).
- [2] "Wetting and particle adsorption in nanoflows", G. Drazer, B. Khusid, J. Koplik and A. Acrivos, Phys. Fluids 17, 017102 (2005).
- [3] "Squeezing flow of particles and large molecules suspended in a liquid through nanochannels", A. Acrivos, B. Khusid, J. Koplik and G. Drazer, Technical Proceedings of the Second International Conference on Computational Nanoscience and Nanotechnology, pp. 97-98, Computational Publications, 2002; and Technical Proceedings of the Fifth International Conference on Modeling and Simulation of Microsystems, pp. 66-67, Computational Publications 2002.
- [4] "Adsorption phenomena in particle transport through a fluid-filled nanochannel", G. Drazer, B. Khusid, J. Koplik and A. Acrivos, Technical Proceedings of the 2003 Nanotechnology Conference, pp. 142-143, Computational Publications, 2003.