Squeezing flow of particles and large molecules suspended in a liquid through nanochannels

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ABSTRACT

The presentation addresses the status of current understanding of the hydrodynamic phenomena accompanied the motion of a nanometer-sized particle through a nanotube.

Keywords: Continuum hydrodynamics, boundary conditions, molecular dynamics simulations.

1 Introduction

Following their discovery, carbon nanotubes have attracted interest not only for their exotic physical properties, but also because their hollow interior can serve as nanometre-sized capillaries, as low as 6-9 nm in diameter. Then it was demonstrated that other techniques could be used for the fabrication of nanochannels. These nano-scale structures provide revolutionary new capabilities for numerous applications, ranging from biological warfare detection to micro chromatography and to proteomics, to interrogate a nanosize object, - a protein, DNA fragment, virus particle, quantum dot, etc. - by imposing external signals. The rapid advances in the fabrication of such systems highlight the need to understand the basic effects of nanoscale confinement on the flow of particles and large molecules and to develop a computational strategy for modeling these phenomena. The ultimate goal of our research is to develop computationally efficient mathematical models and algorithms to provide the predictive power and scaling laws for the intelligent design of novel nanoscale devices. This paper will address the status of presently available theories for the motion of rigid particles and long flexible molecules through a nanochannel. We analyze and scale the results of prior theoretical and experimental studies relevant to the case of channel dimensions comparable to the radius of gyration of a polymer molecule or a particle size.

2 Macroscopic theories

First we consider current macroscopic theories of the viscous motion of particles through channels with near-minimal widths. These are based on the Navier-Stokes equations for the liquid flow at zero Reynolds numbers, ignore thermal fluctuations around an equilibrium state in the liquid, and typically employ the "no-slip" boundary conditions on the particle surface and the channel wall together with a lubrication analysis for the liquid flow in the narrow gap between the particle and the wall. The correction factor for the hydrodynamic force due to slip at the solid boundary was examined only for several simple situations, e.g. a sphere approaching a flat surface.

3 Bridging the molecular to macroscopic scales

We next discuss the static and dynamic properties of liquids confined in very narrow spaces, which have been studied extensively theoretically and experimentally for the last two decades [1]–[5]. It was found that a wall causes liquid molecules to order themselves parallel to the surface in the region within a dozen molecular diameters perpendicular to the wall. In spite of this layering, the Navier-Stokes equations supplemented with "partial slip" boundary conditions at the solid surface provide a reasonable description of the liquid motion outside the near-wall region. However, we show that there exists a lack of understanding of the relation between slip and the surface properties, e.g. roughness and flexibility. Next we address the results of molecular dynamics modeling which operates at the scale of individual atoms or polymer monomers. It has been shown that simulations for simple liquids using a few thousand atoms capture both their microscopic motion and the average behavior given by the continuum equations of elasticity and fluid mechanics. Some pertinent examples include the validity of a lubrication theory at atomic distances, the breakdown of the no-slip boundary conditions at sharp corners, and hysteretic phenomena in wetting due to atomic-scale surface roughness. An important example showing that continuum mechanics works down to surprisingly small length scales is the work of Vergeles et al [2]. They performed molecular dynamics simulations of the motion of a single spherical particle surrounded by a bath of smaller solvent molecules with the aim of determining the length scale down to which Stokes drag works accurately. They found that for a size ratios as small as 3/1 the continuum mechanical expression for drag force worked accurately. Vergeles et al [2] also studied the

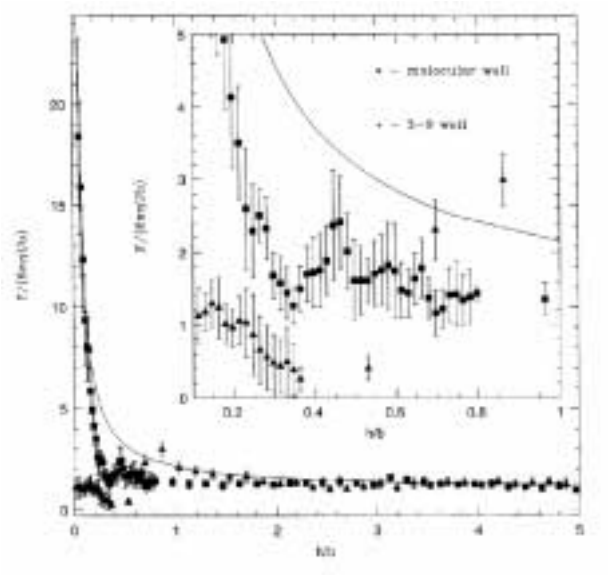

Figure 1: The force of fluid resistance acting on a sphere approaching a solid molecular wall. The solid line represents the theoretical result in the continuum limit.

motion of a particle near a solid wall and, as shown in Figure 1, the continuum expression for the drag force was accurate to within one solvent molecule radius of the wall. However, the fine resolution of molecular dynamics calculations is an unnecessary computational drawback in considering larger systems, e.g. a micrometer-long nanotube.

Summarizing and scaling the results considered above, we then discuss the strategy for developing theoretical models and computational methods to bridge the molecular to macroscopic scales for the transport and interaction of biomolecules and particles through nanochannels [6].

4 Molecular dynamics simulations

As a first step toward understanding the mentioned phenomena, we consider the case of a nanometer size particle flowing through a nonotube by means of molecular dynamics simulations. The motion of such small suspended particles in nano-devices is strongly influenced by the presence of surface forces and by the random molecular motion of the suspending fluid. While the latter is intrinsic to the molecular dynamics approach, we will account for the surface forces through the wall-particle interaction potential, which allow us to model cases in which the particles are attracted to the surface or in which the interaction is purely repulsive. In all cases we shall compare and test the continuum approach with the results of the molecular dynamics simulations, with particular focus in the effects due to the small molecular scale of the particle and the channel. Specifically, the effects of roughness on both the channel walls and the suspended particles, the validity of the "no-slip" boundary condition, the effects of the ordering of the fluid molecules close to the walls and the effects of the random fluctuations due to the molecular character of the fluid.

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