Dynamics of Fluid Flow Inside Carbon Nanotubes*

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Abstract

The dynamics of fluid flow through nanomachines is different from other systems in that the flow is granular (no continuum assumption) and that the "walls" move. We have performed molecular dynamics simulations of the flow of helium and argon through several sizes of carbon (graphite) nanotube. The fluid was started at some initial velocity; fluid particles were allowed to recycle axially through the tube via minimum image boundary conditions. Argon slowed down more quickly than helium. In addition, the behavior of the fluid strongly depended on the rigidity of the tube; a dynamic tube slowed down the fluid far more quickly than one in which the tube was held frozen. It also depended on the fluid density and tube diameter. It did not, however, depend on the tube length, because fluid flow tended to prevent the development of strong longitudinal modes, whose behavior are length-dependent.

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I. Introduction

Gases or liquids that flow through pipes or are confined to small volumes are likely to find a wide variety of applications in nanotechnology. For example, they could serve as hydraulic fluids in mechanical actuators or pistons or carry reactant molecules into reaction chambers.

The behavior of fluids in nanomachines is expected to be fundamentally different from fluid behavior in other systems. Consider, for example, a liquid flowing through a macroscopic pipe. Models of the fluid behavior usually begin with the continuum hypothesis, where one ignores the atomic structure of the fluid and instead characterizes it by viscosity, density, etc [1]. If the flow is laminar, one can calculate the velocity-radius profile. Problems to be solved in this size regime include, for example, calculating power requirements for pumping the fluid through the pipe. The behavior of the pipe itself is usually ignored except to provide boundary conditions. One common boundary condition is the no-slip condition (zero fluid velocity) at the walls. The fluid velocity isn't necessarily zero at the walls; it is simply negligibly small compared to bulk fluid velocities. Although one can explain the validity of the no-slip condition in terms of the behavior of the fluid and pipe at the atomic scale, only the no-slip condition itself, and not the physics behind it, is required for the purpose of engineering design.

At smaller size scales, diffusion is an important consideration. A common example of this is the design of chemical processes involving catalysts deposited in a porous solid [2]. The overall reaction rate depends on (a) the fluid mechanics outside the porous catalyst, (b) diffusion of reactant molecules to the pore surface, (c) reaction kinetics at active catalyst sites, and (d) diffusion of product molecules away from the pores. Pores are usually considered to be rigid. Behavior of the catalyst site at the atomic level (poisoning of these sites, for example) is approximated as kinetic parameters.

Modelling fluid behavior inside nanomachines or components introduces another level of complexity: both the "walls" and fluid can move. Furthermore, the movement of the "walls" is sometimes strongly size-dependent (through normal modes) [3]. Design considerations for nanomachines or components in which fluids flow will therefore include both fluid and "wall" effects *and their interplay*. Such concepts as viscosity and pressure may sometimes have a narrow range of application and must be applied carefully. For example, one could calculate a pressure from force and surface area. This area may not always be well-defined. For example, buckytubes, which are one atom thick, could develop kinks. Although the overall shapes of diamondoid structures are more rigid, the terminating atoms (hydrogen, for example) have more freedom of movement. Since the most important interactions involve fluid-terminating atoms, once again the effective surface area of interaction may be hard to define. The behavior of fluids in nanotechnology applications is not a well-developed area of research and is amenable to analysis by molecular dynamics (MD) techniques.

To this end, we begin with a very simple system: a fluid, either helium or argon, flowing through a graphite nanotube. We choose this system in part because this will be a common nanotechnological application and in part because we have extensively studied the dynamics of carbon nanotubes.

II. Simulation Methods

Since our MD techniques are well-described elsewhere [4-7], we will only describe the potential energy surface and touch on simulation details not stressed elsewhere. The expression for potential energy consists of terms for carbon-carbon bonded interactions and carbon-fluid and fluid-fluid non-bonded interactions. The carbon-carbon terms consist of terms for stretch and bend interactions. The stretch interactions are of the Morse functional form

$$V(r) = D\,[\,1 - \exp(-\alpha(r - r_e))]^2 \tag{1}$$

where D, α, and r_e are constants and the bend interactions are quadratic in $\cos\theta$

$$V(\cos\theta) = E\,(\cos\theta - \cos\theta_o)^2 \tag{2}$$

where E and $\cos\theta_o$ are constants. Non-bonded interactions are of the Lennard-Jones functional form

$$V_{LJ}(r) = 4\varepsilon\,[(\sigma/r)^{12} - (\sigma/r)^6] \tag{3}$$

In order to reduce computational effort, we calculate non-bonded forces and energies only if the distance between the two atoms involved is less than 20 A. Beyond this distance, the interactions are negligibly small. The Lennard-Jones functional form is convenient in that both energies and forces can be evaluated very economically, without the need for evaluating square roots [8]. When calculating Lennard-Jones interactions between two particles at (x_1, y_1, z_1) and (x_2, y_2, z_2), the energy can be written

$$V_{LJ}(w) = 4\varepsilon\,w^3\,(w^3 - 1) \tag{4}$$

where $w = \sigma^2/r^2$. The x force acting on particle 1 is

$$F_{x,1} = h(w)\,(x_2 - x_1) \tag{5}$$

where

$$h(w) = w^4\,[(24\varepsilon/\sigma^2) - (48\varepsilon/\sigma^2)\,w^3] \tag{6}$$

Similar expressions hold for y and z, and for particle 2. Potential energy parameters corresponding to bonded interactions are D = 114.3776 kcal/mol (794.7168 maJ), α = 2.1867 A^{-1}, r_e = 1.418 A, E = 67.1383 kcal/mol (466.4894 maJ), and $\cos\theta_o$ = -0.5 [9]. Lennard-Jones parameters are σ_{C-He} = 3.191 A, ε_{C-He} = 0.03835 kcal/mol (0.26646 maJ), σ_{He-He} = 2.633 A, ε_{He-He} = 0.0216 kcal/mol (0.15008 maJ), σ_{C-Ar} = 3.573 A, ε_{C-Ar} = 0.2827 kcal/mol (1.9643 maJ), σ_{Ar-Ar} = 3.35 A, ε_{Ar-Ar} = 0.2862 kcal/mol (1.9886 maJ) [10,11].

Hamilton's equations were solved with a fourth-order symplectic integrator with alternating q,p, then p,q, propagation and with analytic fifth-order conservation of energy and angular momentum [12].

Figure 1 shows the fluid and tube at the beginning of a simulation. The graphite tube rotational axis is denoted the z axis. The number of atoms per ring and number of rings for the tube are denoted n and n_r, respectively. Bond distances and bend angles are initially approximately at their equilibrium values. The fluid begins in a cubic lattice inside the tube; this initial lattice never passes within 2.5 A of any atom in the tube. The lattice parameter is set according to the desired fluid density. In some cases it may be necessary to allow the fluid and tube to equilibrate before giving the fluid a velocity because an initial lattice structure would be unrealistic; in this study, this was unnecessary because the lattice structure was almost always lost within 0.2 or 0.4 ps, a small fraction of the simulation times.

The liquid densities of He and Ar correspond to cubic lattice parameters of 3.76 A and 3.58 A respectively [13]. We used higher densities so as to be able to perform enough simulations in a reasonable length of time. Simulations at liquid densities or below would have taken far longer to perform. The liquid density simulations we did perform showed the same trends as we will illustrate in the next section but took longer to develop.

Tube and fluid atoms are assigned random momenta. Initial temperatures are shown in Table 1; however, runs with no initial fluid velocity and with frozen tubes built up a temperature of up to about 80 K. In every simulation, the first 10 and last 10 rings of the tube (each about 25 A in length) are frozen. The length of the rest of the tube is about 100 A for most of the simulations; others are 50 A longer. The middle rings are either frozen or allowed to move. In addition to random thermal motion, each atom in the fluid is given an initial z velocity. Minimum image boundary conditions [4] are imposed on the fluid in the z direction; the fluid does not occupy the space of the first or last five rings of the tube. Thus, the minimum image boundaries are made to occur in the static end regions of the tube. This ensures smoother fluid motion. If the minimum image boundaries occurred in the dynamic region, as an atom passed through the boundary it could appear close to the tube on the other side. This could cause sudden energy jumps that would invalidate the simulation. Freezing the first and last rings of the tube also ensures that the fluid does not move the tube in the z direction. Real nanomachine components would necessarily have similarly limited overall motion.

III. Results and Discussion

The systems studied here consist of dynamic fluid atoms, sometimes dynamic rings in the tube, interacting with each other and with frozen rings of the tube. Since the interaction potentials between the dynamic and static atoms are conservative, the total energy should be conserved, subject to changes in the neighbor list (angular momenta should not) and changes in distances upon crossing either mimimum image boundary. The kinetic energy of ordered motion of the fluid atoms goes into random thermal motion of the fluid and dynamic rings of the tube. Since the dynamic rings of the tube, if any, are attached to frozen rings at both ends, no appreciable center of mass or rotational motion is introduced into the tube.

All calculations were performed in double precision using the methods discussed in Section II on an IBM SP2. Because of the changing neighbor list (especially when the minimum image boundaries were crossed), the total energy was not rigorously conserved; each run exhibited a small positive drift. This did not appear to seriously affect the dynamics.

Calculations were performed on tubes containing either helium or argon atoms, as shown in Table 1. If the middle rings of the tube were dynamic, the initial temperature of the tube is indicated. In every run, careful track was kept of the average z fluid velocity and the number of fluid atoms that crossed z = 0, the middle of the tube. From the second quantity in adjacent time steps, the flux (number of atoms per ps) was calculated. In many simulations, fluid atoms crossed the z = 0 boundary several times.

It is immediately obvious that a dynamic carbon nanotube slows down fluids faster than a static one. Figures 2a and 2b compare runs which are identical (initial velocity 20.4 A/ps) except that one has a static and the other a dynamic tube. Figure 2a shows fluid velocities for the first and third entries in the helium section of Table 1. When the tube is static it takes about 42 ps for the fluid to slow down to 2.5% of its initial velocity (0.51 A/ps); for the dynamic tube, by contrast, the time required to slow down to this same velocity is 15 ps. When the tube moves, it perturbs the motion of the nearest fluid atoms. This causes the fluid motion to randomize faster, leading to hard collisions with the tube. Since the tube, on the average, does not move in the z direction, tube-fluid collisions tend to slow the fluid down. The fluid velocities are essentially zero at 40 ps and 80 ps, respectively, for the dynamic and static cases.

Figure 2b is similar to Figure 2a except that the initial fluid temperatures and velocities (102.2 A/ps) are higher; data comes from the second and fourth entries in the helium section of

Table 1. From Figure 2b, when the tube is static, the fluid does not appreciably slow down until after about 25 ps; after this, it slows down rapidly and essentially stops flowing at around 60 ps. When the tube is dynamic, on the other hand, the fluid slows down steadily until it essentially stops flowing at around 20 ps. In runs involving dynamic tubes, the faster the initial velocity, the less time it takes for the fluid to slow down. For the fifth and sixth runs in the helium section, for example, these times are 30 and 10 ps, respectively.

Similar trends as above hold for simulations involving argon. For argon, however, the trends in velocity damping are even more pronounced. One interesting set of runs is shown in Figure 3a (from the fifth and sixth entries of the argon section of Table 1). In both of these runs, the fluid essentially stops flowing within 2 ps. Since Ar is 10 times more massive than He, it excites larger amplitude vibrations in the tube; as a result, fluid motion is randomized faster. At high fluid velocities, this is true even when the fluid initially has no random thermal energy, only uniform z motion (Figure 3b).

Figure 4 shows several simulations involving Ar in which the tube is static. Despite the fact that the fluid velocities are up to 10 times larger than simulations involving dynamic tubes, it takes between 10 and 15 ps for the fluid velocity to die down. Since fluid-fluid interactions are stronger for Ar than for He and because of the greater mass of Ar, it takes less time for Ar to stop flowing than He.

In addition to keeping track of fluxes and fluid velocities, we have made movies of several simulations and obtained detailed velocity profiles (coordinates and momenta of every atom saved every 0.1 ps). Although the tube radius was too small and the flow too granular to ever develop nearly constant density-radius or velocity-radius profiles, we observed that at low fluid velocities, the density profiles tended to shift toward the tube (individual atoms, however, moved throughout the entire radius of the tube).

If two carbon nanotubes are clamped at the ends and then allowed to vibrate freely, the longer one will develop larger amplitude vibrations (longitudinal modes, for example). One might therefore expect that the longer tube, having larger amplitude longitudinal vibrations, would slow down the fluid faster. We found no such effect, however. Figure 5 shows two sets of runs involving helium which are identical except for the length of the tube (the number of atoms of fluid are different but the densities are the same). In most of our runs, the tube is about 150 A long, including the end static regions which have a total length of 50 A. The longer tubes are 200 A long. Figure 5a compares runs with static tubes, 5b dynamic. At appreciable fluid velocities, the fluid tends to straighten the tube if longitudinal motion begins to develop. This would probably not occur at very low fluid densities.

We find that the higher the fluid density, the faster it slows down. Figure 6 shows fluid velocities for simulations involving helium that are identical except for their densities, which differ by a factor of about 1.75. Figure 6a compares runs with static tubes, 6b dynamic. In Figure 6a, we show the first 12 ps of simulation. It takes the denser fluid about 12 ps to lose 6% of its initial velocity; the less dense fluid takes twice as long. When the tube is dynamic (Figure 6b), the fluids slow down faster, but the effect of density is somewhat less pronounced. Having a dynamic tube enhances hard collision fequencies (and consequent velocity randomization) more than changing the density.

In this study, we have concentrated on trends in fluid and wall behavior. We do not calculate viscosities from our data, nor is it clear how best to define an effective viscosity. For example, to calculate a shear viscosity one might establish a steady state average velocity flow and attempt to find a steady state radial velocity profile. From such a profile one could estimate the viscosity. We have found, however, that since the diffusion length scale is of the order of magnitude of the diameter, an appreciable radial velocity gradient may not develop. Other methods for determining viscosity depend on certain types of periodic boundary conditions and are not applicable here (in many of our simulations, the "simulation box" moves and is affected by the fluid). Any effective viscosity will contain information about fluid-wall interactions; any value for effective viscosity must be carefully considered in the context of the system being studied.

IV. Conclusions

When designing nanomachines or components involving gas flow, one must take into account the motion of both the fluid and the "wall". Because of mass effects on fluid-wall collisions, which fluid flows through a machine or component greatly affects its performance.

In a fluid/carbon nanotube system, the motion of the carbon nanotube plays a critical role in fluid flow. In our simulations, the fluid slows down because of fluid-carbon nanotube collisions. If the tube is static, the collisions are more elastic than if the tube is dynamic. In addition, as the tube moves, it jostles the fluid atoms nearest it, causing the fluid motion to randomize more quickly.

At equivalent volumetric flow rates and number densities (which can be reasonably approximated from initial fluid atom lattice spacing), a He fluid flows through a carbon nanotube more easily than Ar. This is because Ar is 10 times more massive than He and induces larger amplitude vibrations in the carbon nanotube.

The length of the carbon nanotube does not appear to appreciably affect the behavior of the fluid. The longer a carbon nanotube, the larger amplitude some of its vibrations (longitudinal modes, for example) would be. A fluid flowing through the tube tends to straighten out the tube as it flexes.

Thus, modes which include longitudinal motion never get a chance to develop. Since the tube is clamped at both ends, stretch modes do not develop, either.

Whether the tube is static or dynamic, the more dense a fluid is, the faster it slows down. This is a straightforward consequence of increased collision frequency. At very low densities, the fluid would not interfere with the development of longitudinal motion in the carbon nanotube, and the length of the tube would likely have some effect on the fluid behavior.

The behavior of a fluid inside a nanocomponent strongly depends on the rigidity of that component. We have found that both helium and argon flow far easier through a static carbon nanotube than one which is dynamic. In a real nanosystem, this behavior would most likely be approached if, for example, the carbon nanotube were placed under a stretching tension. We have found that as longitudinal modes begin to excite, fluid motion tends to straighten the nanotube. Because a nanotube under a large enough stretching tension would be far stiffer, such modes could not begin to develop. The rigidity of a nanotube under tension and with fluid flow would likely be intermediate between the static and dynamic cases considered here.

Many proposed nanomachine components in which fluids would flow would likely be diamondoid. Whether fluids would flow more easily through diamondoid or graphite tubes depends on at least two factors. On one hand, our simulations of individual diamondoid tubes show that they are stiffer than carbon nanotubes (have little overall distortion); they would not change in shape and perturb the fluid. On the other hand, graphite has a smoother potential energy surface than hydrogen terminated diamondoid structures. The terminating atoms on the diamondoid structure (hydrogen, for example) would move fairly freely and would probably perturb the fluid more than a static graphite tube. Because the diamondoid structures have little overall distortion, we would expect to be able to find trends in the fluid flow in accordance with the model of a well-defined surface area based on the non-terminating bond network atoms. Since the surface dynamics of diamondoid and carbon nanotubes are fundamentally different, we would expect effective viscosities and other fluid mechanical quantities to have different values for these systems.

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Table 1. Carbon nanotube sizes and temperatures and initial fluid temperatures and velocities.

Simulations involving helium					
n	**n_r**	T_{tu}, K	T_{fl}, K	v_z, A/ps	# fluid atoms
40	61	*	11	20.4	533
40	61	*	167	51.1	533
40	61	349	11	20.4	533
40	61	349	167	51.1	533
40	61	349	11	102.2	533
40	61	349	11	51.1	533
40	61	*	11	102.2	533
80	61	*	11	20.4	3649
80	61	351	11	51.1	3649
40	81	*	11	20.4	767
40	81	352	11	20.4	767
40	81	*	10	20.4	441
40	81	*	10	51.1	441
40	81	352	10	20.4	441
n	**n_r**	T_{tu}, K	T_{fl}, K	v_z, A/ps	# fluid atoms
40	81	352	10	51.1	441
Simulations involving argon					
40	61	*	105	20.4	533
40	61	*	105	51.1	533
40	61	*	1676	20.4	533

40	61	*	1676	51.1	533
40	61	349	1	2.0	533
40	61	349	1	10.2	533
40	61	*	105	102.2	533
40	61	349	0.3	10.2	533
40	61	349	0.04	10.2	533
40	61	349	0	10.2	533
80	61	351	1	51.1	3649
80	61	*	1	51.1	3649
40	81	*	105	20.4	441
40	81	*	105	51.1	441
n	$\mathbf{n_r}$	T_{tu}, K	T_{fl}, K	v_z, A/ps	# fluid atoms
40	81	352	105	20.4	441
40	81	352	105	51.1	441

*Frozen graphite tube.

Figure Captions

Figure 1 Schematic of a fluid flowing through a graphite tube. See text for further description of fluid boundary conditions.

Figure 2 (a) Fluid velocities from first and third simulations involving helium from Table 1. (b) Same as (a) except for higher initial velocities (second and fourth simulations involving helium).

Figure 3 (a) Fluid velocities for simulations of argon flowing inside a dynamic tube (fifth and sixth simulations involving argon). (b) Effects of initial random thermal energy of fluid (eighth, ninth, and tenth argon simulations).

Figure 4 Same as Figure 3a except for static tube (first, second, and seventh argon simulations).

Figure 5 Effects of length of carbon nanotube: (a) static tube (first and tenth helium simulations) (b) dynamic tube (second and eleventh helium simulations).

Figure 6 Effects of fluid density: (a) static tube (tenth and twelfth helium simulations), (b) dynamic tube (eleventh and fourteenth helium simulations).