Dynamics of He/C_{60} Flow Inside Carbon Nanotubes*

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This draft paper has been submitted to *Nanotechnology* for publication. It is part of the Fourth Foresight Conference on Molecular Nanotechnology. A copy of this paper can be found on the web linked from: http://nano.xerox.com/nanotech/nano4/tuzun Abstract.html.

Abstract

Fluid flow at the molecular scale is likely to be important in future applications of nanotechnology. We have performed several molecular dynamics simulations of a buckyball, C_{60}, cage or idealized atom in a helium fluid flowing axially inside a carbon nanotube. The fluid was started at some initial velocity and both the fluid and buckyball allowed to recycle axially via minumum image boundary conditions. A buckyball introduced into the feedstream (started at zero velocity) usually reached fluid velocity within 5 ps. Leakage rates of helium past the C_{60} depended on the nanotube diameter and fluid velocity. These leakage rates and other important features of the dynamics changed significantly when C_{60} was modelled as an idealized atom or when the nanotube was held rigid, suggesting that simulations of fluid dynamics inside nanomachines should be fully dynamic and atomistic.

*Research sponsored by the Division of Materials Sciences, Office of Basic Energy Sciences, U.S. Department of Energy under contract DE-AC05-84OR21400 with Lockheed Martin Energy Systems Inc.

I. Introduction

Fluid flow at the molecular scale is likely to be important for a range of potential applications of nanotechnology. Whether the use is hydraulic actuators, pistons, and the like; or carrying reactants or products; or the transport of components; or some other application, it is necessary to understand the behavior of such fluid flows at the molecular scale.

One difference in behavior of fluids inside nanomachines and fluids inside and fluids in macroscopic systems is that in nanomachines, both the "walls" and fluids move. Furthermore, the motion of the "walls" may be size-dependent (through normal modes). In macroscopic systems, the "walls", be they reaction vessels or pipes, are usually rigid; they simply contain the fluid and impose appropriate boundary conditions.

Another difference, just as important, is that in macroscopic systems, models of 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. Inside nanomachines, even something as basic as the concept of pressure is more difficult to define, because the motion of the walls may make surface area hard to define. Furthermore, in macroscopic systems viscosity is a property of the fluid alone. Inside nanomachines, one may wish to define an effective viscosity for design purposes. Whatever the definition, any effective viscosity will inevitably contain effects of wall-fluid interactions. Such effects would likely be different in kind in different types of nanomachine components (reaction vessels and pipes, for example).

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. In a previous paper, we began with a very simple system: a fluid, either helium or argon, flowing through a graphite nanotube. We chose 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.

Whereas in the previous paper, we simulated the flow of pure fluids, in this paper, we study the flow of fluids with more than one type of atom. In a macroscopic pipe, for example, a homogeneous non-reacting mixture will stay homogeneous. Inside a nanomachine, different components of the mixture may congregate at the walls, and the motion of the walls may be intimately related to the fluid component masses and therefore to concentration profiles.

The systems studied in this paper are similar to those of the previous paper except that they include either a single idealized buckyball atom or a fully atomistic C_{60} cage flowing with the fluid (helium). The behavior of the C_{60} cage includes vibrational and rotational effects not present in the idealized atom; it is useful to know the effects of such approximations on simulation results. A buckyball was chosen because potential applications involve pistons, and a buckyball could, in a tube of appropriate diameter, act as a piston whose motion could be controlled by changes in fluid pressure.

II. Simulation Methods

Since our MD techniques are well-described elsewhere, we will only describe the potential energy surface and touch on simulation details not stressed elsewhere. Much of this description appears in the previous paper but is included here for the sake of completeness. The expression for potential energy in the previous paper consisted of terms for carbon-carbon bonded interactions and carbon-fluid and fluid-fluid non-bonded interactions. In this paper, we have, in addition, buckyball-atom-carbon and buckyball-atom-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

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

Every non-bonded interaction between the idealized buckyball atom and either fluid or wall is calculated. 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. As shown previously, 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. Potential energy parameters corresponding to bonded interactions are D = 114.3776 kcal/mol, α = 2.1867 A^{-1}, r_e = 1.418 A, E = 67.1383 kcal/mol, and $\cos\theta_o$ = -0.5. Lennard-Jones parameters are σ_{C-He} = 3.191 A, ε_{C-He} = 0.03835 kcal/mol, σ_{He-He} = 2.633 A, and ε_{He-He} = 0.0216 kcal/mol. Lennard-Jones parameters for interactions involving idealized buckyball atoms are σ_{C-B} = 3.573 A, ε_{C-B} = 0.2827 kcal/mol, σ_{He-B} = 3.35 A, and ε_{He-B} = 0.2862 kcal/mol, where B denotes an idealized buckyball atom. The σ values are obtained by adding $2^{-1/6}$ times the buckyball radius. The factor of $2^{-1/6}$ comes from the fact that the Lennard-Jones potential energy minimum falls at $2^{1/6}\sigma$.

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.

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 usually never passes within 3.58 A (the C-He Lennard-Jones well minimum) of any atom in the tube. The lattice parameter is set according to the desired fluid density. Since the initial lattice structure is lost quickly (usually within 0.4 ps), we do not equilibrate the fluid and tube before giving the fluid a z velocity.

In simulations involving an idealized buckyball atom, the buckyball atom is initially located at the middle of the buckytube. The initial fluid lattice does not pass within 7 A in z of the buckyball atom. The idealized buckyball atom can cross the minimum image boundaries in the same manner as the fluid. In most simulations, the buckyball atom starts at zero velocity (this is to simulate a situation in which the buckyball atom is introduced into a feedstream). In some simulations, the buckyball atom is started at the initial fluid velocity.

In simulations involving the C_{60} cage, the cage is initially centered at the middle of the bucktube. Once again, the initial fluid lattice does not pass within 7 A in z of the center of the cage. Atoms in the C_{60} cage cross the minimum image boundary one atom at a time; minimum image boundary conditions are accounted for while dealing with stretch or bend interactions within the cage. The C_{60} cage is started at the initial fluid velocity but was never given any initial rotational or random thermal motion.

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 fluid temperatures 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 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 mimimum 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 ensures that the fluid does not move the entire tube in the z direction. Real nanomachines would necessarily have similarly limited z motion.

III. Results and Discussion

Since every interaction potential term is conservative, the total energy should be conserved subject to changes in the non-bonded interaction neighbor list. Because of the presence of interactions between static atoms in the buckytube and dynamic atoms, angular momentum is not conserved. 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 boundary was crossed), the total energy was not rigorously conserved; the drift in energy was usually a few kcal/mol during the entire simulation. No adverse consequences (sudden large fluid atom diaplacements, for example) appeared to ensue.

Calculations were performed on tubes containing either idealized buckyball atoms or C_{60} cages, 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 leakage of fluid atoms past the buckyball atom or center of mass of the C_{60} cage.

In this discussion we show some or all of the following results for several simulations in Table 1: (a) fluid velocity, (b) buckyball atom or cage center of mass velocity, (c) leakage of fluid atoms past buckyball atom or cage center of mass, (d) distance from buckyball from tube symmetry (z) axis, and (e) buckyball x/y correlation. We first consider simulations involving the idealized buckyball atom. Coordinates of all atoms, and in some cases momenta, are saved every 0.1 ps. Leakage plots are obtained from these coordinates. When a buckyball atom or cage is recycled through the minimum image boundary, the number of leakage atoms is reset to zero. A fluid atom is considered to have leaked if its z coordinate passes that of the buckyball atom or cage center of mass in either direction.

Figure 2 (first entry of Table 1) shows a run in which the tube is static, a behavior which would be most closely approached if the tube were placed under a large stretching tension. After starting at zero velocity, the buckyball atom reaches the fluid velocity within 5 ps (Figures 2a and 2b); after this, the fluid and buckyball velocities are more or less in line. Leakage rates are around 4 atoms/ps in each buckyball atom minimum image cycle. The tube diameter is 15.9 A. In order for a fluid atom to leak, it must pass between the buckyball atom and the tube wall. Because C_{60} has a diameter of about 7 A and the volume within about 2 A of the tube walls is effectively excluded (because of non-bonded interactions), leakage rates are expected to strongly depend on the tube diameter.

Figure 3 (fifth entry of Table 1) shows results similar to those of Figure 2, but with a dynamic tube. The fluid and buckyball clearly slow down more quickly with a dynamic tube (Figures 3a and 3b). 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 buckyball atom starts at zero velocity and reaches its maximum velocity in about 4.5 ps. The buckyball atom velocity actually exceeds the fluid velocity for much of the simulation; after it gets up to speed, the buckyball atom slows down somewhat more slowly than the helium because of its greater inertia. This can be seen in part from the leakage plot (Figure 3c), which shows a leakage rate of about 2.2 atoms/ps after the fluid and buckyball velocities are more or less in line. The buckyball is pushed toward the tube wall (Figure 3d), but there is no evidence of rifling or other correlated behavior (Figure 3e). When designing nanomachine components, approximating the tube as static could predict unrealistically large leakage rates or lead to other errors.

Figure 4 (eighth entry of Table 1) shows results for a with a dynamic tube but with 6 fewer atoms per ring (a diameter of 13.5 A instead of 15.9 A). The maximum buckyball velocity is greater than and is reached sooner than when the tube has a larger diameter. In addition, the leakage rate, approximately 1.2 atoms/ps between 10 and 20 ps, is smaller. In subsequent minimum image cycles, the leakage rate increases, but the fluid is slowed down considerably. In this run the fluid fits more tightly inside the tube than in Figure 2; this would probably be analagous to a feedstream being driven at a higher pressure. Because of the minimum image boundary conditions, however, we do not explicitly test effects of pumping pressures.

Figures 5 and 6 (sixteenth and seventeenth entries of Table

1) show results for simulations involving idealized buckyball atoms in which the buckyball atom begins with the initial fluid velocity. These simulations have dynamic tubes of diameters 15.9 A and 13.5 A respectively, the same as in Figures 3 and 4. As expected, both the fluid and the buckyball in the smaller diameter pipe slow down more quickly; fluid velocities decrease to 20% of their original values in about 40 ps and about 25 ps, respectively. Leakage rates in these two simulations are on the order of 4 and 1 atoms/ps respectively while the fluids have at least 20% of their initial velocity; after this, the leakage rates change from buckyball atom minimum image cycle to cycle.

We now consider simulations involving fully atomistic C_{60} cages. In every such simulation, the C_{60} moves with the fluid velocity. Figure 7 (first entry in cage section of Table 1) shows results for a simulation in which the nanotube has a diameter of 15.9 A and is held frozen. When the nanotube is static, the fluid hardly slows down. The leakage rate is about 7 atoms/ps.

Another noteworthy static nanotube simulation is shown in Figure 10 (eighth entry in cage section of Table 1). Figure 8 shows a C_{60} center of mass x/y correlation plot. The buckyball atom starts at the center of the tube but is rapidly pushed toward the wall. At times, it rifles down the tube clockwise or counterclockwise for a few rotations; at other times, the motion is fairly random. We did not observe rifling in runs for which the tube was dynamic.

Like simulations involving an idealized buckyball atom, simulations involving a fully atomistic cage behave differently if the tube is dynamic. Figure 9 (twelfth entry in cage section of Table 1) shows typical results. Like Figure 7, the Figure 9 simulation involves a buckytube with a diameter of 15.9 A. One way in which the runs are markedly different is that the C_{60} cage is pushed closer to the tube wall; it can distort. However, very little rotation occurs in this or in any other run with fully atomistic buckyball cages. The leakage rate about is 3 atoms/ps after 5 ps. Figure 10 (fifteenth entry in cage section of Table 1) shows results for a simulation identical to that of Figure 9 except for a smaller nanotube diameter, 13.5 A. In this simulation, only three fluid atoms leak before the minimum image cycle that begins at about 14 ps. Runs that are identical except for the length of the tube show similar dynamics and leakage rates. Although Figures 5 and 6 are identical to Figures 9 and 10 except for involving idealized buckyball atoms rather than atomistic buckyball cages, the rates at which fluids slow down and leak around the buckyball are different.

Runs involving an idealized buckyball atom are different from runs with a fully atomistic C_{60} cage in that the cage can vibrate and rotate and in that the center of the buckyball atom is more easily approachable than the center of mass of the buckyball cage (the cage atoms are repulsive centers). We observed very little rotation (for example, the C_{60} cage rolling down the nanotube). In these runs, we tracked angular momentum with respect to the cage center of mass location and momentum. Very little angular momentum developed.

IV. Conclusions

When designing nanomachines or components involving gas flow, one must take into account the motion of both the fluid and the "wall". If the fluid has more than one type of atom, size and mass effects and different interaction ranges or strengths can cause different species to segregate at the walls or to slow down at different rates. In the fluid/buckyball/carbon nanotube system, like the fluid/nanotube systems studied in the previous paper, the motion of the carbon nanotube plays a critical role in fluid flow. In our simulations, the fluid slows down because of buckyball- or 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.

Since assuming the tube to be dynamic or modelling buckyball as a single atom significantly changes simulation results, in nanotechnology/fluid flow applications, it is best to not make any such approximations. Modelling the nanotube as completely static leads to higher leakage rates and to very slow rates of fluid velocity decrease. Modelling the buckyball as a single atom can allow fluid atoms to too closely approach its center.

Leakage rates must be kept low for some applications, and in in particular if the intended application is a piston. The leakage rate of fluid past the buckyball is strongly influenced by the diameter (but not length) of the tube, because the diameter of the buckyball is of the same order of magnitude in this work. Essentially, if there is room for the fluid atoms to leak past the buckyball, some leakage will occur. The leakage rate is also influenced by how rigidly the carbon nanotube is restrained (if it's held under tension, for example) and the pressure at which the fluid is being pumped. Because of the minimum image boundary conditions, pressure effects were not explicitly considered here. Such effects (for example, acoustic waves generated by fluctuations in feed pressure) should be carefully considered during the final stages of design for nanomachines involving fluid flow.

We have considered two types of situations in which a feedstream of helium carries along a buckyball idealized atom or fully atomistic cage: a buckyball moving at the feedstream velocity or with zero velocity. The zero-velocity case could correspond to a buckyball being introduced into the feedstream. The buckyball atom can restrict fluid flow cross section and fluid can immediately slow down, depending on the diameter of the feed tube, and thereby create a back-pressure wave. Design considerations for nanomachines or components in which fluids flow should include the possibility of flow restriction or blockage.

Because of its inertia, the buckyball atom takes time to speed up and may never reach the feed stream velocity. If, for example, a nano-reaction vessel were vented, the buckyball would likely exit the reaction vessel or flow out the vent pipe slower than the rest of the fluid, depending on the sizes of the reaction vessel and vent pipe.

The non-zero-velocity case could correspond to a large feed stream splitting into several smaller streams. Once inside the smaller pipe, the buckyball could flow along the walls and pass the fluid atoms. We have observed this in our simulations, which involve helium. Similar effects might be smaller if much heavier fluid atoms, such as argon, were used.

Many proposed nanomachine components in which fluids would flow would likely be diamondoid. Graphite and diamondoid structures are different in that graphite is less stiff but (because of the presence of terminating atoms on diamondoid structures) has a smoother potential energy surface. The flow characteristics of buckyball carried by helium would likely be strongly influenced by interactions between the buckyball and the terminating atoms on the diamondoid structure and therefore on the geometry of the diamondoid structure.

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

Simulations involving buckyball atom					
n	**n_r**	T_{tu}, K	T_{fl}, K	v_z, A/ps	# fluid atoms
40	61	*	1	10	120
38	61	*	1	10	120
40	61	*	1	4	120
40	61	*	4	4	120
40	61	10	1	10	120
38	61	10	1	10	120
36	61	10	1	10	120
34	61	10	1	10	120
40	61	0	1	4	120
40	61	0	4	4	120
40	61	0	4	10	120
40	81	0	1	10	180
40	81	0	1	4	180
40	81	0	4	10	180
40	81	0	4	4	180
40	61	10	1	10†	120
34	61	10	1	10†	120
40	81	0	1	4†	180
40	81	0	4	4†	180
Simulations involving buckyball cage					

40	61	*	1	10	120
38	61	*	1	10	120
36	61	*	1	10	120
34	61	*	1	10	120
40	61	*	1	4	120
40	61	*	4	4	120
40	61	*	4	10	120
40	81	*	1	10	180
40	81	*	1	4	180
40	81	*	4	10	180
40	81	*	1	10	180
40	61	10	1	10	120
38	61	10	1	10	120
36	61	10	1	10	120
34	61	10	1	10	120
40	61	0	1	4	120
40	61	0	4	4	120
40	61	0	4	10	120
40	81	0	1	10	180
40	81	0	1	4	180
40	81	0	4	10	180
40	81	0	1	10	180

* *Frozen graphite tube. † Buckyball atom started at fluid velocity.

Figure Captions

Figure 1 Schematic of He/C_{60} flowing through a graphite tube. See text for further description of fluid boundary conditions.

Figure 2 (a) Fluid velocity, (b) buckyball velocity, and (c) leakage plot for a static tube simulation (first entry of Table 1). The buckyball is modelled as an atom and starts at zero velocity.

Figure 3 (a) Fluid velocity, (b) buckyball velocity, (c) leakage plot, (d) buckyball distance from symmetry axis, and (e) buckyball x/y correlation plot for a simulation the same as Figure 2 except for a dynamic tube (fifth entry of Table 1).

Figure 4 Same as Figure 3a–c except for a smaller diameter nanotube (eighth entry of Table 1).

Figure 5 Same as Figure 3a–c except for a buckyball atom starting at fluid velocity (sixteenth entry of Table 1).

Figure 6 Same as Figure 4 except for a buckyball atom starting at fluid velocity (seventeenth entry of Table 1).

Figure 7 (a) Fluid velocity, (b) buckyball velocity, and (c) leakage plot for a static tube simulation (first entry in cage section of Table 1). The buckyball is fully atomistic and starts at fluid velocity.

Figure 8 Buckyball rifling motion in a static nanotube simulation (eighth entry in cage section of Table 1).

Figure 9 Same as Figure 7 except for dynamic nanotube (twelfth entry in cage section of Table 1).

Figure 10 Same as Figure 9 except for smaller diameter nanotube (fifteenth entry in cage section of Table 1).