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The role of activation energy and reduced viscosity on the enhancement of water flow through carbon nanotubes

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Molecular dynamics simulations are carried out to study the pressure driven fluid flow of water through single walled carbon nanotubes. A method for the calculation of viscosity of the confined fluid based on the Eyring theory of reaction rates is proposed. The method involves the calculation of the activation energy directly from the molecular dynamics trajectory information. Computations are performed using this method to study the effect of surface curvature on the confined fluid viscosity. The results indicate that the viscosity varies nonlinearly with the carbon nanotube diameter. It is concluded that the reason behind the observed enhancement in the rate of fluid flow through carbon nanotubes could be the nonlinear variation of viscosity. © *2011 American Institute of Physics*. [doi:10.1063/1.3592532]

I. INTRODUCTION

Nanofluidics is an emerging branch of science which deals with the behavior of fluids flowing in and around nano-sized objects.[1] Recent advances such as improved fabrication and characterization facilities have opened up new possibilities for the design and development of nanofluidic devices.

Carbon nanotubes (CNTs) are one of the most commonly used nanoscale engineering materials. CNTs can be considered as an atomic structure formed of carbon atoms linked as a molecule into a hollow cylinder. They are expected to play an important part in nanofluidic applications like gas storage,[2,3] membrane separation,[4,5] nanopipes for the precise delivery of gases and liquids,[6,7] etc. The design of carbon nanotube based nanofluidic devices depends on understanding and controlling the interactions between the nanotubes and the confined fluid. The study of CNT based nanofluidic devices will serve as a platform for fundamental studies in nanofluidics.[8] For example, the study of fluid flow through CNT will also help in understanding the transport mechanisms in biological pores. But due to confinement related changes in the fluid flow process, the continuum approximation will be invalid in systems of such dimensions. Nowadays, atomistic modeling techniques like molecular dynamics (MD) have emerged as a competent tool for studying the nano-sized domain where fluid transport is governed by the liquid structure and collective molecular motion.

Even though the CNT surface is hydrophobic, previous studies on CNTs (Refs. 8–13) have provided evidence for the flow of water through CNTs. Many studies have reported a higher than expected flow rate, when compared to the predictions of classical Hagen Poiseuille (HP) equation, for water flowing through CNT. Hummer *et al.*[10] had done MD computations to study the water conduction through a CNT and they pointed out that the inherent smoothness of the CNT, the tight hydrogen bonding, and the lower chemical potential were responsible for the pulse like transmission of water through the nanotube. Also Noy *et al.*[8] have pointed out that the unique combination of extremely high aspect ratio with small dimensions makes CNTs an attractive option for transport applications. MD simulations performed by Joseph and Aluru[12] have claimed that this enhancement in flow may be due to the existence of a hydrogen bond depleted area near the tube wall. Experiments were conducted by Majumder *et al.*[13] and Holt *et al.*[9] using CNT membranes and the measured water flow rates were orders of magnitude higher than that predicted by the no slip HP equation. Recently, Goldsmith and Martens[11] had performed MD computation of pressure induced flow of water through CNTs and have reported that the calculated flux of water was several times larger than that predicted using continuum theory. Myers[14] has explained the enhanced flow in CNTs using a continuum model that includes a depletion layer with reduced viscosity near the wall. But the validity of the model was limited to CNTs with diameters greater than ten times the molecular diameter of the confined fluid.

The observed enhancement in water flow rate through CNTs can be investigated by studying the effect on the viscosity of the confined water. Such an investigation would help us to check if there is nonlinearity in viscosity in the nanoscale regime and also to understand the limit up to which the continuum definitions are valid.

Chen *et al.*[15] observed that the viscosity of water molecules confined in CNTs decreases rapidly not only when the tube radius is reduced but also when faster flow rate is maintained. They have observed that the shearing stress between the nanotube wall and the water molecules is the key parameter in the determination of the nanofluidic properties. Liu *et al.*[16] had performed MD simulations to study the effects of CNT diameter, density of water and temperature on the molecular distribution and transport behavior of water confined in CNTs. They had used Green Kubo[17] equation to find the viscosity of the confined water and found

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that the shear viscosity was larger than that of the bulk and also that it increases sharply as the diameter of the CNT decreases. But this result disagreed with the findings of Thomas and McGaughey.[18] They had studied the pressure driven water flow through CNTs and found out that the viscosity was less than that of the bulk and decreases with decreasing CNT diameter. This discrepancy may be due to the fact that Liu *et al.*[16] had performed the simulation at a fixed water density inside the nanotube which was much higher than the density obtained when the water molecules were allowed to freely enter the CNT from an external bath. As a result of this the mobility of the water molecules in the CNT was reduced in the former case.[19] Thomas and McGaughey[18] had also observed that their results on flow rate obtained from MD were similar to those obtained from continuum theory for CNTs with diameters more than ten times the molecular diameter of water. But the limitation of these two works was that, while calculating the viscosity of the confined fluid, the fluid was assumed to be in the linear response regime. The nonlinearity that may arise in the fluid behavior has not been dealt with.

To overcome this, Zhangh *et al.*[20] have developed a semi-empirical formula for calculating the confined fluid viscosity on the basis of Eyring theory of reaction rates[21] and MD simulations. This method was also advantageous from the computational point of view and comparatively more accurate. In the present study we propose a new method for the calculation of viscosity based on the Eyring theory of reaction rates.[21] Based on the Eyring theory we have derived a relation for calculating the viscosity of water confined in small diameter CNTs. The details of the MD methodology for the prediction of activation energy and flow rate of water through CNT are described. The significant results obtained from our study and major conclusions are presented.

II. EYRING METHOD

It was Eyring[21] who gave an explanation for transport mechanisms in fluids in terms of the statistical mechanical theory of absolute reaction rates. According to this theory, we can consider viscous flow as a chemical reaction in which the elementary process is the activated jumping of a single molecule from one equilibrium position to another.[22,23] For example, consider the liquid to have a quasilattice structure as shown in Fig. 1(a).[24] For the molecule at position 1 to move to the next equilibrium position 2 it has to overcome a potential barrier created by its neighbors or in other words it has to pass through an activated state. This concept is clearer from Fig. 1(b) where we can observe a peak in the potential energy between the two equilibrium positions 1 and 2. The additional energy required by the molecules to overcome this barrier is the activation energy. Powel *et al.*[25] have defined activation energy as the potential required by an individual molecule to overcome the potential barrier created by its neighbors and squeeze past them into the next equilibrium position. Hence, for the flow to occur the molecules should possess the necessary activation energy to overcome the potential barrier. Also, it is assumed that this additional energy is partially distributed among the new neighbors, so that the energy possessed by the molecule at the new equilibrium position is insufficient for the return of the molecule to the previous equilibrium position.

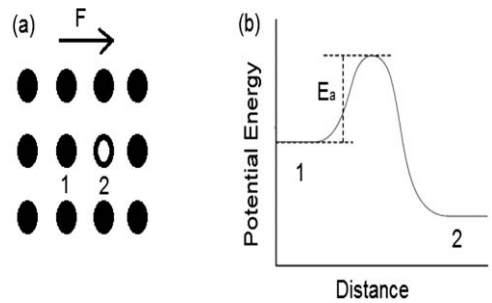

FIG. 1. (a) Liquid lattice structure. (b) Potential energy as a function of distance between the molecules.

In order to derive the equations for the confined fluid viscosity let us consider the fluid to possess a lattice structure as shown in Fig. 1(a).[26] Let the distance between the lattice site be a, the distance between adjacent planes be δ, the number of molecules per unit volume be n, and the external force acting per unit area be F. The Eyring equation for the specific rate constant for the viscous flow process is

$$k' = \frac{k_B T}{h} \exp\left(\frac{-E_a}{RT}\right), \tag{1}$$

where k_B is the Boltzmann's constant, h is the Planck's constant, E_a is the activation energy, R is the gas constant, and T is the temperature. If we take k_f' and k_r' as the frequencies of the forward and reverse processes, then the net velocity of flow of the fluid with respect to the lattice sites in the direction of the applied force is given by

$$v_0 = a(k_f' - k_r'). \tag{2}$$

If we assume the activated state to be midway between the two lattice sites, then the work done in moving the molecule a distance $\left(\frac{a}{2}\right)$ into the activated state is $\left(\frac{aF}{2n\delta}\right)$. The external force helps in the forward motion of the molecule by providing additional energy to overcome the energy barrier, but hinders the motion of the molecule in the reverse direction. Hence, the frequencies k_f' and k_r' can be expressed as

$$k_f' = k' \exp\left(\frac{+aF}{2\delta n k_B T}\right), \tag{3}$$

$$k_r' = k' \exp\left(\frac{-aF}{2\delta n k_B T}\right). \tag{4}$$

Then the net velocity of flow is

$$v_0 = a(k_f' - k_r') = 2ak' \sinh\left(\frac{aF}{2\delta n k_B T}\right). \tag{5}$$

Using the definition of coefficient of viscosity, we obtain

$$\eta = \frac{F\delta}{v_0} = \frac{F\delta}{2ak' \sinh(aF/2\delta n k_B T)}. \tag{6}$$

But for ordinary liquids and reasonably small external forces

$$\frac{aF}{2\delta n k_B T} \ll 1.$$

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Hence,

$$\sinh\left(\frac{aF}{2\delta n k_B T}\right) \cong \frac{aF}{2\delta n k_B T}. \tag{7}$$

From Eqs. (6) and (7) we obtain

$$\eta = \left(\frac{\delta}{a}\right)^2 \frac{n k_B T}{k'} = \left(\frac{\delta}{a}\right)^2 nh \exp\left(\frac{E_a}{RT}\right).$$

Assuming $\left(\frac{\delta}{a}\right) \cong 1$, we get

$$\eta = \frac{Nh}{V} \exp\left(\frac{E_a}{RT}\right), \tag{8}$$

where η is the shear viscosity of the fluid, N is the Avogadro's number, and V is the molar volume.

But from our computations we observed that in the case of fluid flow through small nanotubes the flow occurs only in the direction of the externally applied force. Hence the net velocity of flow of the fluid with respect to the lattice sites in the direction of the applied force can be written as

$$v_0 = ak'_f = ak' \exp\left(\frac{+aF}{2\delta n k_B T}\right). \tag{9}$$

Hence the equation for coefficient of viscosity becomes

$$\eta = \frac{Fh\delta}{ak_B T} \exp\left(\frac{E_a}{RT} - \frac{aF}{2\delta n k_B T}\right). \tag{10}$$

The major obstacle in using this method is the determination of the activation energy of the flow process. One major method that has been extensively used is to relate the activation energy to the energy of vaporization; this is based on the assumption that the bonds which are broken are same as those that would be broken in the process of vaporization.[25] Zhangh *et al.*[20] have derived an expression for activation energy based on the assumption that the probability distribution of water potential energy obeys the Gaussian distribution. Subsequently they have performed a set of numerical experiments on bulk water to study the dependence of activation energy on temperature and potential energy. Based on this an empirical relation for activation energy was derived and this was used to predict the activation energy in the case of confined fluids.

In the present work we have applied the actual definition of activation energy to formulate a methodology for obtaining the viscosity of fluids confined in nanosized domains. To the best of our knowledge such an attempt has not been reported elsewhere. As mentioned earlier, activation energy in a flow process is defined as the minimum energy required by the molecules to overcome its intermolecular interactions and move to the next equilibrium position. Hence activation energy can be calculated as the difference in the potential energy possessed by the molecule when it switches between its activated and equilibrium states. This can be calculated by assuming the potential barrier to be situated just halfway between the initial and final equilibrium states.[25] The detailed methodology will be presented in Sec. III.

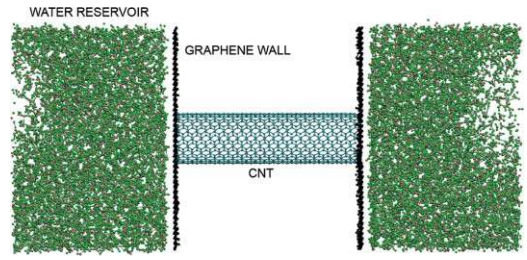

FIG. 2. MD simulation domain for the pressure-induced water flow inside a CNT. The length of the CNT is 47.95 Å, dimension of the graphene wall is 40 × 40 Å and the total length of the simulation domain in the flow direction is 130 Å.

III. METHODOLOGY

The MD simulation technique[27,28] has been used to study the pressure driven water flow through CNT. MD has been implemented using LAMMPS package[29] and visualization of the MD trajectory is done using VMD open source software.[30] The simulation system consists of two water reservoirs connected by a single walled carbon nanotube (SWCNT). The water reservoirs are bounded by a graphene wall on one side as shown in Fig. 2. The water reservoirs are maintained at different pressures. The CNT and graphene wall were treated as a rigid body. For studying the effect of surface curvature of the CNT on the flow properties, computations were performed with nanotube diameters ranging from 8.136 Å to 54.2 Å. In order to maintain translational symmetry of the nanotubes, the length of the nanotubes was chosen corresponding to ten translational unit cells. The CNT length used in the present simulation is comparable to those employed by Goldsmith and Martens[11] in their published work on pressure driven water flow through carbon nanotubes. The initial number of water molecules in the reservoirs is calculated based on the bulk water density of 1 g/cm^3.

The TIP3P water model[31] is employed for water intermolecular interaction. Lennard-Jones 12-6 potential is employed for the water-CNT, water-graphene, carbon-carbon, and graphene-graphene intermolecular interaction. The interaction parameters were similar to those used by Hummer *et al.*[10] The AMBER force field parameters[19,32] were used for the intramolecular stretching, angular and dihedral interactions. The Verlet integration scheme is employed for time integration with a 1 fs time step and periodic boundary conditions are applied in all the three directions. Initially the two ends of the SWCNT are closed with the graphene wall and the two reservoirs are equilibrated in NVT ensemble at 298 K for 50 ps. Langevin dynamics has been employed with a damping coefficient of 100 time units. Then the atoms of the graphene wall in the vicinity of the CNT are removed so that the two ends of the nanotube are now open. The system is allowed to equilibrate for 200 ps, with the two reservoirs at 298 K and no temperature rescaling for the water molecules inside the CNT. During this period the oxygen atoms of the water molecules in one of the reservoirs, situated far away from the entrance region of the nanotube, are given an additional force in the z direction for creating a pressure difference between the two reservoirs. Finally the system is run for additional 500 ps for property evaluation. Simulations were performed

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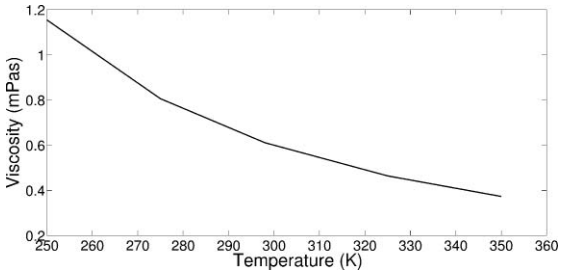

FIG. 3. Variation of viscosity of bulk water with temperature calculated using Eyring theory of reaction rates.

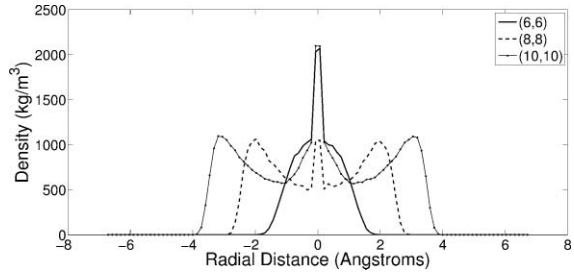

FIG. 5. Density profiles of (6, 6), (8, 8), and (10, 10) nanotubes.

at very high pressure drops mainly due to the computational limitations; smaller pressure drop would mean longer it will take for the flow to establish. In all the computations the pressure difference between the two reservoirs is maintained at 50 MPa, which is comparable to that employed in many studies reported earlier.[11,18]

The flow rate is determined by calculating the number of water molecules that pass through a region defined inside the carbon nanotube for a fixed time interval. The flow rate through the CNT is constantly monitored during the study and the property evaluation is performed only when a steady flow rate was observed. The results of the MD simulation help to obtain the different equilibrium positions taken by the water molecules during the flow process at each time step. Based on this we can calculate the potential energy, E_b, experienced by a molecule when it is situated at the midpoint of two equilibrium positions. If E is the potential energy of the fluid molecules at their equilibrium position, then we can express activation energy E_a as

$$E_a = E_b - E. \tag{11}$$

The activation energy required by a single molecule for each of its molecular jump from one equilibrium position to the next during its travel from one end of the nanotube to the other can be calculated and an average value can be obtained. This procedure is repeated for all the water molecules inside the nanotube and the average of this is taken as the activation energy. Viscosity is calculated using Eq. (10) for smaller nanotubes and Eq. (8) for larger nanotubes with diameters more than ten times the molecular diameter of water, where the flow becomes more or less disordered like bulk liquid flow.

Since we are considering the intermolecular interaction experienced by the target molecule due to both water molecules and the CNT, this method will help us to directly involve the carbon atoms of the CNT into the viscosity calculation. The fact that the density and distribution of water molecules inside the CNT will have an influence on the activation energy is also taken into account in this method. The changes in the water-water interaction due to the presence of the carbon molecules are also considered. Only minimum computation is required as the activation energy calculation is performed by the postprocessing of the MD output data. To validate the proposed methodology, the variation of viscosity of bulk water with temperature has been performed and the results are given in Sec. IV.

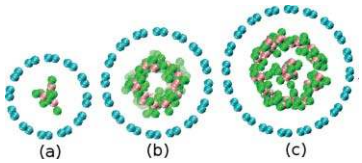

FIG. 4. Distribution of water molecules inside (a) (6, 6), (b) (8, 8), and (c) (10, 10) nanotubes.

IV. RESULTS AND DISCUSSIONS

In this section we discuss the results obtained from our MD simulation studies on water flow through CNTs. The uncertainty in the data has been calculated by performing five independent simulations for each case and it was found to be <5% in all the computations. Figure 3 shows the variation of viscosity of bulk water with temperature calculated using the methodology proposed in the present work. The viscosity value of 0.611 mPas at 298 K is found to be in good comparison with the value 0.66 mPas obtained by Zhangh *et al.*[20]

The results obtained from the MD computation of pressure driven water flow through SWCNT of various diameters are presented next. Figures 4(a)–4(c) show the distribution of water molecules inside the (6, 6), (8, 8), and (10, 10) nanotubes, respectively. It clearly shows that only single file transport of water molecules is possible inside a (6, 6) nanotube, but as the diameter is increased we get a concentric tube of water molecules in (8, 8), a concentric tube of water molecules with a single file inside that in (10, 10) nanotube and so on. This distribution is also evident from the radial density profile of water molecules inside the CNTs obtained from the present study. This is presented in Fig. 5. The reason behind the formation of such structures inside the nanotubes is the space confinement inside the nanotube and also the interaction between the nanotube and the water molecules. The

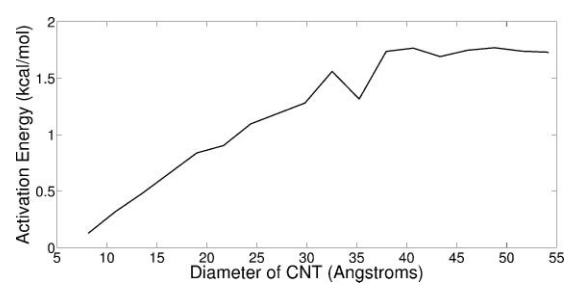

FIG. 6. Variation of activation energy with CNT diameter.

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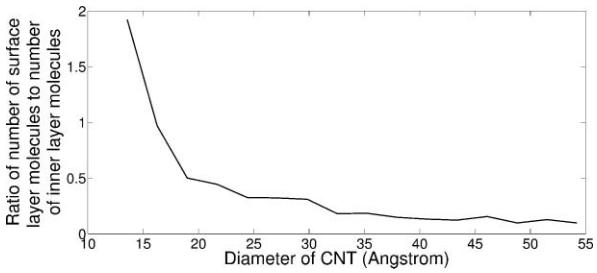

FIG. 7. Variation of the ratio of number of water molecules situated in the layer adjacent to the wall (surface layer molecules) to the number of molecules in the inner layers with CNT diameter.

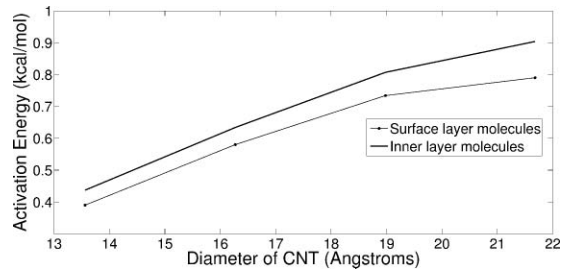

FIG. 9. Variation of activation energy along the nanotube cross section for various nanotube diameters.

formation of ordered structures inside the nanotube validates our basic assumption that the liquid molecules arrange themselves in a quasilattice structure.

Figure 6 shows the variation of activation energy with the nanotube diameter. The activation energy values are found to be very small for water confined in small diameter CNTs. This could be due to the reduction in the number of neighboring molecules and the weak interaction with the CNT wall atoms. Also, in the case of water confined in CNTs, the number of hydrogen bonds is less compared to that of bulk water.[10] It is evident from the figure that the activation energy increases with the nanotube diameter. This could be attributed to the increase in the number of neighboring molecules leading to a larger interaction and hence more energy. As the diameter of the CNT is increasing, the ratio of number of molecules situated in the first liquid layer adjacent to the wall (surface layer molecules) to the number of molecules in the inner layers is decreasing as shown in Fig. 7. The well defined layered structure of confined molecules is slowly replaced by the disordered bulk fluid arrangement and the water-water interaction begins to dominate. The reduction in activation energy of the confined molecules due to the presence of the CNT becomes insignificant compared to the contribution from the neighboring water molecules in larger nanotubes. Hence, the activation energy tends to be a constant for the larger diameter CNTs. From Fig. 6 we can see that there exists a drop in activation energy around the range of diameters 30 to 40 Å. This might be due to the drop observed in the ratio of confined water molecules to the number of carbon atoms in the CNT in the same diameter range, as shown in Fig. 8. This variation will influence the interaction between water and carbon atoms and subsequently a decrease in activation energy.

The influence of carbon atoms on the confined water properties is clearer from our result (see Fig. 9). The variation of activation energy along the CNT cross section, i.e., the difference between the activation energy of the surface layer molecules and that of the inner layer molecules, is presented. It can be seen that there is a slight reduction in the activation energy for the surface layer molecules implying that the water-carbon interaction is weaker than the water-water interaction.

Viscosity is defined as an internal friction; it operates in any liquid or gas whenever one part flows past another.[33] So when we consider the smaller (6, 6) or (8, 8) nanotube, there is only a single file or a single layer of molecule flowing through it and hence, we can say that the definition of viscosity is not valid for such small nanotubes. Therefore, we have calculated the viscosity only from the (10, 10) nanotube wherein we have two layers of molecules flowing through the nanotube. Figure 10 shows the variation of viscosity with diameter. Similar to the activation energy, the viscosity is found to increase with the diameter, but it is found to be smaller than that for bulk water. For the smaller diameter nanotubes the weak carbon-water interaction and the layered structure of water is seen to influence the behavior of the confined fluid leading to a monotonous increase in the viscosity. For CNTs with diameters >30Å, the strong water-water interaction dominates due to a sudden increase in the number of confined water molecules as shown in Fig. 8, leading to a non-monotonous increase in the viscosity value. For larger diameter nanotubes the carbon atoms in the CNT is found to have negligible influence on the confined fluid behavior and hence the viscosity values tend to achieve a constant value. Zhangh *et al.*[20] had also reported that the viscosity of confined water is found to increase with the diameter; but the difference from our calculation may be due to the difference in the approach to

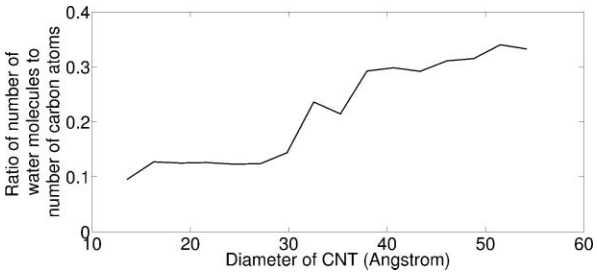

FIG. 8. Variation of the ratio of number of confined water molecules to the number of carbon atoms with CNT diameter.

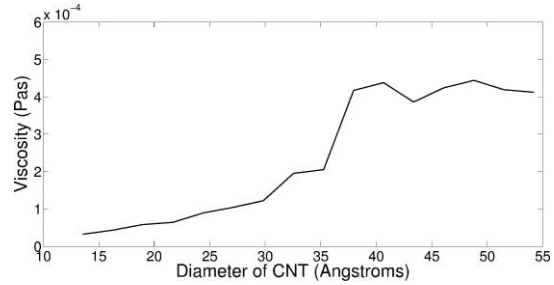

FIG. 10. Variation of viscosity with nanotube diameter.

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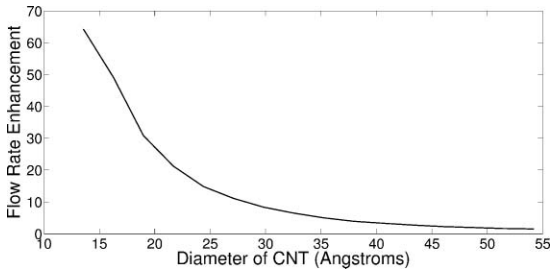

FIG. 11. Variation of flow enhancement with nanotube diameter.

calculate viscosity and also the high pressure gradient applied in our computation.

A high water flow rate is observed through CNTs which can be attributed to the low activation energy required by the confined water molecules to jump from one equilibrium position to the next. Figure 11 shows the enhancement in the flow rate computed by the MD simulation when compared to the no-slip HP equation. The enhancement in flow rate is defined as the ratio of the actual flow rate obtained from MD computation to the flow rate predicted by the no-slip HP equation. The enhancement in flow rate observed is similar to that reported in literature.[11,12] But the HP equation employs the bulk viscosity of water without considering the changes occurring to the viscosity at smaller scales. It considers only the diameter as a variable if we keep the pressure difference as constant. But we argue that in the case of smaller diameter nanotubes where the viscosity values depend on the nanotube surface curvature, the viscosity should also be considered as a scale dependent variable. As mentioned previously, many studies[9,11] have also reported enhancements in the fluid flow rate through CNTs, but all these comparisons were performed with the predictions from the no-slip HP equation using bulk viscosity. Hence the reported enhancement in flow rate, based on no-slip HP equation, of liquid through smaller diameter pores needs a careful analysis as the changes in viscosity due to nanoconfinement were not considered. Figure 12 compares the flow rates predicted by the HP equation, using the viscosity values obtained from MD computation, with the flow rates obtained from MD computation. We can see that the predictions from the HP equations with size affected viscosity values differ from the MD predictions for smaller diameter nanotubes. This may indicate the failure of HP equation in accurately describing the fluid flow phenomenon through smaller diameter nanotubes.

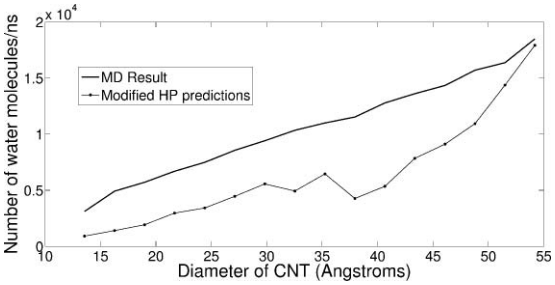

FIG. 12. Comparison of flow rate predicted by no-slip HP equation using the size affected viscosity values with results from MD computation.

V. CONCLUSIONS

In this paper a new methodology has been presented for the calculation of viscosity for fluids confined in CNTs based on the Eying theory of reaction rates. The methodology involving the calculation of activation energy is more accurate because we are able to directly include the influence of the carbon atoms on the transport of water molecules through the nanotube. The methodology developed was applied to study the pressure driven flow through SWCNTs. The effect of surface curvature of nanotubes on viscosity was studied by varying the diameter of nanotubes. Simulations were done for nanotube diameters varying from 8.136 Å to 54.2 Å. It is found that the definition of viscosity fails for very small diameter nanotubes since they have only single file transport of water molecules through them. Activation energy and thereby, viscosity was found to increase nonlinearly with CNT diameter, with very small values reported for smaller diameter nanotubes. The results are found to be in good agreement with the available computational results. Enhancement in the fluid flow through CNTs on the basis of a comparison with the continuum predictions was observed, but the suitability of the no-slip HP equation for comparing the fluid flow rate through small nanotubes is questionable since the HP equation does not consider the variation of viscosity occurring at this nanosized domain. The high rate of flow through smaller nanotubes could be attributed to the very low activation energy required for the flow process; the viscosity values are almost negligible in this domain when compared with the bulk values.

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