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Fast water flow through graphene nanocapillaries: a continuum model approach involving the microscopic structure of confined water

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Water inside a nanocapillary becomes ordered, resulting in unconventional behavior. A profound enhancement of water flow inside nanometer thin capillaries made of *graphene* has been observed [B. Radha et.al., Nature (London) **538**, 222 (2016)]. Here we explain this enhancement as due to the large density and the extraordinary viscosity of water inside the graphene nanocapillaries. Using the Hagen-Poiseuille theory with slippage-boundary condition and incorporating disjoining pressure term in combination with results from molecular dynamics (MD) simulations, we present an analytical theory that elucidates the origin of the enhancement of water flow inside hydrophobic nanocapillaries. Our work reveals a distinctive dependence of water flow in a nanocapillary on the structural properties of nanoconfined water in agreement with experiment, which opens a new avenue in nanofluidics.

Water flow through nanoscale channels, and the determination of the slip length, have been the subject of intensive studies^{1–19}. In a recent study Radha *et al.*²⁰ fabricated atomically flat 2D-capillaries and was able to control the water flux through the channel size. In Ref. [17], an unexpectedly fast flow (up to 1 m/s) of water through flat nanochannels was reported²⁰. In addition to the large slip length, this unexpected phenomena might be due to the high disjoining pressures²¹ inside the nanochannel. The disjoining pressure is added to the well-known capillary pressure that causes oscillation in the meniscus pressure which for channels thinner than $H=8\text{\AA}$, was found to be in the order of 1 kbar^{22,23}.

In the continuum limit, transport of water through a capillary is described by the Hagen-Poiseuille equation (HPE), however, for nanofluidics several modifications (beyond the no slip-boundary conditions) should be made^{20–28}. There have been several studies on the ordering of water inside a hydrophobic nanocapillary^{29–31,33,34}. Particularly monolayer/bilayer ice confined within a hydrophobic nanochannel has been studied using MD simulations^{30,31,33,35,36} and using density functional theory calculations³⁷. Such an ordering of water molecules can change significantly the density^{8,38,39} and its viscosity³¹ inside the channel. Using molecular dynamics simulations the pressure-driven water flow through carbon nanotubes (CNTs) with diameters ranging from 0.83 to 1.66 nm were studied by Thomas et. al.⁴⁰, where a transition from continuum to subcontinuum flow with decreasing CNT diameter was found. While the standard linear relationship in Darcy law is violated, they modified the Darcy (continuum) equation in order to explain their molecular dynamics simulations results.⁴⁰

Here we will demonstrate the profound influence of the density and viscosity of water inside graphene nanocapil-

laries on the water flow rate. Our calculations are based on the well-known continuum model formalism but taking into account the ordering of the water molecules. We propose an analytical model to describe experimental results of Ref. [17], i.e. fast water flow in graphene nanocapillaries, employing aforementioned microscopic structure of confined water. It is entropically unfavorable for a hydrophobic surface to bind water molecules via ionic or hydrogen bonds resulting in low friction of water inside graphene capillaries. The water-solid wall slip length (at molecular scale) is much larger than the capillary size which results in different boundary conditions as compared to bulk water in macroscopic channels. It is well-known that the slip dynamics appears through three different length scales: i) individual molecular, ii) beyond-few molecules, i.e. actual slip at a liquid-solid boundary, and iii) apparent slip due to the motion over complex boundaries. Using a slip length of about 600Å, and a contact angle close to 90°, our analytical results agree very well with recent experiments on water flow through graphene nanochannels²⁰.

The model. The Poiseuille flow solution using no-slip boundary condition for a channel with height H , which is subjected to a pressure difference (ΔP) along the length of the channel, is quadratic in velocity. For water flow through n equal nanochannels when the effect due to the slip velocity ($\frac{\lambda du_x}{dz}$) is taken into account, the volumetric flow rate is given by⁷

$$Q = \rho \frac{|\Delta P|}{12\eta} H^3 \left(1 + \frac{6\lambda}{H}\right) \frac{nw}{L}, \quad (1)$$

where λ is the slip length, ρ is the density, η is the viscosity, and L is the length of each channel having a width w . Notice that in Eq. (1) the slip term is dominant for $\lambda \gg H$. For water inside a nanochannel the density $\rho(H)$ and viscosity $\eta(H)$ vary with the capillary size^{41–43}.

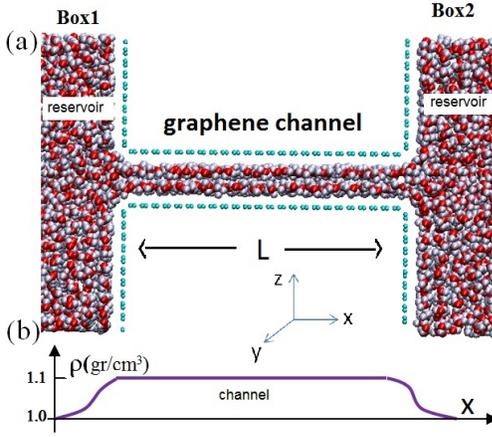


FIG. 1. (color online) Side view of a snapshot of water molecules between two graphene sheets separated by $H=10 \text{ \AA}$ taken from our MD setup. Red (gray) balls are oxygen (hydrogen). (b) A schematic view of the variation of water density inside the reservoirs and the channel.

The density increases due to the fact that the accessible volume for water molecules in a nanochannel is smaller than the geometrical volume – because of excluded volume effect near the confining walls. Furthermore, the interaction within the layers and with the hydrophobic confining walls induces structuring in water which significantly enhances the viscosity^{31,39,44}. Such changes in the density and viscosity are expected to be pronounced for nanochannel with height $H \lesssim 12 \text{ \AA}$. We take $\rho(H) = \rho_0 f(z)$ and $\eta(H) = \eta_0 g(z')$ where $\rho_0 \cong 1 \text{ gcm}^{-3}$ and $\eta_0 \cong 0.89 \text{ mPa.s}$ are the bulk values for density and viscosity, respectively. Here $z = H/\delta$ and $z' = H/\delta'$ are exponential decay lengths for density and viscosity inside the channel where the two parameters δ and δ' are determined from MD simulations. The two functions should approach $f(z) \rightarrow 1$, $g(z') \rightarrow 1$ when $H \gg \delta$, δ' . We propose the following functions fulfilling these boundary conditions

$$f(z) = 1 + ae^{-z}, \quad g(z') = 1 + be^{-z'}, \quad (2)$$

where a , b , δ , and δ' will be obtained by fitting to results from our MD simulations.

By assuming that the hydrostatic pressure is many orders of magnitude smaller than: i) the Laplace pressure^{23,28} which corresponds to the traditional capillary pressure $\Delta P_c = \frac{\gamma}{H} = \frac{2\sigma \cos(\Phi)}{H}$ (here $\sigma \simeq 70 \text{ mN/m}$ is the interfacial tension⁴⁵ and Φ is the contact angle between water and graphite/graphene. The latter has been measured, however the results vary widely which can be traced back to functional groups on the surface, i.e. $\Phi \in [55^\circ - 127^\circ]$ ^{2,46-49}). ii) The disjoining pressure (DP) $\Delta P_d = -\frac{1}{A} \left(\frac{\partial G}{\partial H} \right)_{T,V,A}$ ⁵⁰ which is due to the ordered structure of water inside the nanochannel^{29,31,33} and the interaction of water with the channel wall. The DP can be one to three orders of magnitude larger than the capillary pressure and is a consequence of van der Waals

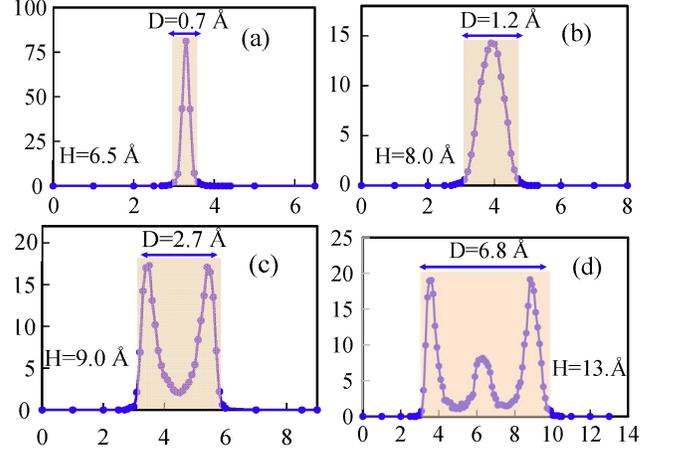


FIG. 2. (color online) Density profile perpendicular to the channel for four typical channel heights. The colored regions show the accessible volume for water which defines the effective height D .

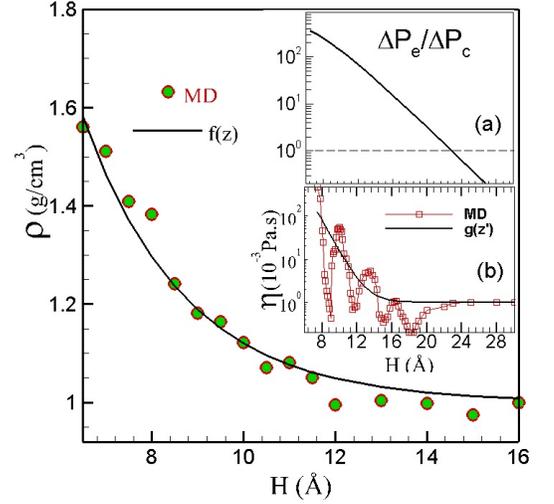


FIG. 3. (color online) The density of water inside the nanochannel as function of the channel height H . The symbols are MD simulation results using the definition for the accessible volume for water molecules (see Fig. 2). The solid curve is a fit with Eq. (2) ($f(z)$). In the inset (a), we show the variation of the ratio between entropic and capillary pressures ($\frac{\Delta P_e}{\Delta P_c}$) with channel size. The inset (b) shows the MD simulation results for viscosity (symbols) and corresponding $g(z')$ function (solid curve) according to Eq. (2).

(vdW) and entropic components²². Substituting aforementioned pressures in Eq. (1), and by including both the density and viscosity functions, we find

$$Q = A \frac{f(z)}{g(z')} (H^2 + 6H\lambda) [\gamma + H\Delta P_d]. \quad (3)$$

The parameter $A = \frac{nw\rho_0}{12\eta_0 L}$ is taken as a scaling factor in our model (using experimental numbers $w = 1300 \text{ \AA}$ and $L = 10^4 \text{ \AA}$ for one channel, is about $1.2172 \times 10^{-4} \text{ s \AA}^{-2}$

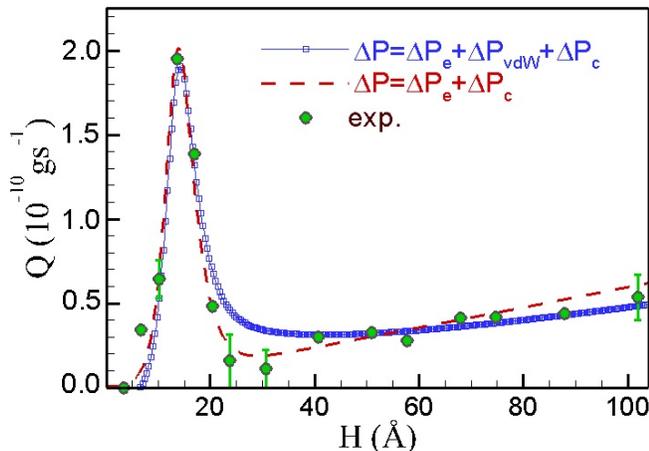


FIG. 4. (color online) Water flow rate - Q - as function of channel height. The experimental data and corresponding error bars are shown by green-dots²⁰. The red-dash curve is the theoretical result including capillary and entropic pressure when $\lambda=600$ Å. The blue-dotted curve is water flow rate when also the vdW pressure is included, see Eq. (4).

which is very close to our obtained number from a fitting on the experimental data, i.e. $1.2174 \times 10^{-4} \text{ sÅ}^{-2}$. By measuring the chemical potential difference inside the capillary and the reservoirs, the entropic pressure is given by⁸ $\Delta P_e = \frac{RT}{V_m} \ln(f(z))$ where $RT=2494.2 \text{ J/mol}$, and $V_m=18 \text{ cm}^3/\text{mol}$.

Computer simulations and experiments confirmed the existence of an ordered structure for confined water inside capillaries with $H \leq 12$ Å.^{29,31,33,35,37}. The distance $d_{OO} = 2.8$ Å in semi-squared lattice structure of confined water results in a water density of about 1.36 gcm^{-3} .

We performed extensive MD simulations using TIP3P force field⁵¹ to find the density and the structure of water inside nanochannels. Our simulation setup consists of three elements, i.e. a graphene nanochannel elongated in the x-direction having height $H \in [6.5 \text{ Å to } 16 \text{ Å}]$, length $L = 50$ Å, and width $w = 20$ Å which connects two water reservoirs on both sides of the channel, see Fig. 1. The simulations are performed using LAMMPS package and we employed an NVT ensemble. The long-range electrostatic interactions were computed with the particle-particle particle-mesh (PPPM) method with a cutoff distance of 12 Å. The non-bonding interactions were modeled by using the Lennard-Jones(LJ) potential. In Fig. 1(a) we show a side view of confined water and the two reservoirs for a channel with height $H=10$ Å.

First we calculate the density profile across the channels (i.e. perpendicular to the graphene layers, i.e. along the z-axis). These profiles were calculated by counting the number of water molecules in the yz-plane (across the channel) and averaging along the channel, i.e. $\overline{N(z)} = \int \int n(x,y,z) dy dx / Lw$ where $n(x,y,z)$ is the number of molecules at point (x,y,z) inside the channel. Four typical density profiles are shown in Fig. 2. We found that e.g. for $H=6.5$ Å, and 8 Å $\overline{N(z)}$ are Gaussian functions with

decreasing width for decreasing H . For other H 's, $\overline{N(z)}$ is divided into two or more distinctive peaks. The middle peak (see Fig. 2(d)) disappears by increasing H and only two peaks remained close to the edges³⁸. Note that beyond $H=11.0$ Å the number of layers and D (where distance ‘ D ’ is effective height of the channel with geometrical height H) becomes larger. For $H=13$ Å the middle layer is smaller than those on both sides which plays an important role in the fast water flow. These results indicate that the accessible volume for water inside the nanochannels (grayed rectangles in Fig. 2) is smaller than the geometrical volume. Therefore, the accessible volume for water inside the channels is proportional to $\frac{N(H)}{D}$ instead of $\frac{N(H)}{H}$. Here $N(H) = \int \overline{N(z)} dz$ is the total number of water molecules per surface area inside the channel with size H . In most of the cases, regions of about 3.0 Å from both sides of the graphene walls are inaccessible for the water molecules³⁸ (independent of H). They form an excluded volume due to the graphene wall-water interaction. Obviously, for larger H , the accessible volume approaches the geometrical volume, i.e. the relative difference $(1 - \frac{D}{H}) \rightarrow 0$.

Henceforth, the problem of determining the density is reduced to determining ‘ D ’ and the corresponding volume. D is taken such that 98% of water molecules are confined in the middle of the channels (i.e. within the colored rectangles shown in Fig. 2). We found $H-D$ is almost the same for $H \geq 12$ Å and the corresponding density is close to bulk water. For the smallest H i.e. $H=6.5$ Å, we obtain almost planar and square-rhombic lattice structure at room temperature and lateral pressure of about 0.9GPa with $d_{OO} = 2.8 \pm 0.05$ Å, from which we determine a maximum density around 1.4 gcm^{-3} . This can be found only if we use $D \approx 1.0 \pm 0.3$ Å. Alternatively one may use the vdW radius of O and C atoms to define the effective height^{39,52}. These led us to conclude that the density of confined water is larger than the bulk density which is in agreement with previous reports^{38,39}. The circle symbols in Fig. 3 are the densities found from our MD simulations using the aforementioned D values. The corresponding $f(z)$ function using the best fit of the MD data is shown by the solid line in Fig. 3 with $a=10.9$ and $\delta=2.2$ Å. The profile shown in Fig. 1(b) schematically shows the variation of the density inside and outside the channel with $H=10$ Å.

Our approach is general and can also be used to describe fast water flow in CNTs. Using an array of field effect transistors defined on individual CNTs, Qin *et al.*⁸ measured the water flow rate through individual CNTs and found a rate enhancement of ~ 882 for CNTs with diameter of 8.1 Å. The water density in the CNT can be described by the same function $f(z) = 1 + 25.e^{-z}$ where $z = \frac{r}{2.5}$ and r is the diameter in units of Angstrom.

The dependence of the viscosity on H was reported in our previous work³¹. In general viscosity is direction dependent in confined systems where the major contribution of the viscosity is due to its xy-component, see Ref. [20]. The large viscosity (in $H < 13$ Å) is due to the

layered/ordered structure of water. The MD simulation results are shown in Fig. 3(b). A typical fit $g(z')$ (which satisfies the above mentioned boundary requirements) on our MD data is shown by the solid curve in Fig. 3(b) with parameters $b=6.23 \times 10^4$ and $\delta' = 1.19 \text{ \AA}$.

Using the obtained $f(z)$ and $g(z')$, we first use $\Delta P_d = \Delta P_e$ (neglecting the vdW pressure). The scaling parameter A is the only fitting parameter and our theoretical results for Q are shown in Fig. 4 (red dashed curve) where the slip length was set to be $\lambda = 600 \text{ \AA}$ and $\gamma = 0.1 \text{ mN/m}$ which results in a contact angle of 89.96° by using $\sigma = 70 \text{ mN/m}$. The symbols in Fig. 4 are the experimental data²⁰ (the green error bars indicate the experimental detection limit) and dash-red curve is the calculated water flow rate. Our results are in very good agreement with the experimental results. In the inset of Fig. 3(a), we depict the ratio between ΔP_e and the capillary pressure which is larger than 40 for $H < 13 \text{ \AA}$. The capillary pressure is larger than the entropic pressure only for $H > 22 \text{ \AA}$.

Finally, it is worthwhile to investigate the effect of vdW pressure.²² To that end, we add the vdW pressure to the DP as

$$\Delta P_d = \frac{A_H}{6\pi H^3} + \Delta P_e, \quad (4)$$

where $A_H \simeq 35zJ^{53}$ is the Hamaker constant for intercalated graphite with water. Using the previous $f(z)$ and $g(z')$ and $\lambda = 600 \text{ \AA}$ we obtain the blue-dotted curve in Fig. 4. It is seen that, including vdW pressure significantly improves the results for large H ($H > 80 \text{ \AA}$) while the results for $H = 23$ and 30 \AA are slightly overestimated. Therefore disjoining pressure causes a substantial enhancement of the water flux for channel heights around 13 \AA . Notice that previous MD simulations (see Fig. 3 in Ref. [20]) found peak in the water-flow rate that are located in the $[17-23] \text{ \AA}$ range which deviates from the experiment where the peak is around 13 \AA .

Notice that, we found that for large channel heights ($H > 30 \text{ \AA}$), the well-known contribution of capillary pressure dominates in Eq. (3) where $f(z) \cong 1$ and $g(z') \cong 1$, which yields a linear dependence $Q \propto H$. Moreover in order to provide an independent check on the chosen slip length in our study, we can roughly estimate the slip length as follows. The Navier slip length is defined as $\lambda = \frac{\eta}{\xi}$ where ξ is the water-solid interfacial friction coefficient. We calculated ξ using the method introduced in Ref. [54], and for $H > 10 \text{ \AA}$ found it almost independent of H , i.e. $\xi = 3 \times 10^4 \text{ Nsm}^{-3}$. Using the obtained number for ξ and those we already found for η , the slip length is in the range $[500-700] \text{ \AA}$. All numbers in this range give a reasonable peak for Q around $H = 13 \text{ \AA}$ and give different Q with only 1% difference. Therefore the

value $\lambda = 600 \text{ \AA}$ as a mean value used in our analysis is reasonable.

Our modelling highlights the unique role of confinement on water flow for channel size $H \approx 13 \text{ \AA}$ and we found our results in very good agreement with the experiment of Ref. [20]. Below $H = 13 \text{ \AA}$, the molecular regime dominates i.e. two layers of water are weakly bound to the walls of the channel and the available cross sectional flow area that remains between these two layers is much smaller than the molecular size of water leading to negligible flow. Around 13 \AA , as shown in Fig. 2(d), a third layer of water appears between the two water layers which assemble into a two-dimensional structure for which neither the slip length nor the effective viscosity is well defined. Water molecules in the middle layer are interacting weakly with the other layers and the walls, and their density is slightly smaller than the one of bulk water. However, the total density of water inside the channel is larger than the bulk density. The water molecules in the middle layer diffuse freely. For larger H , although the two side layers of water are still present, the water molecules in the middle layer (having bulk density) randomly diffuse in the remaining space which results in a resistance against water flow and consequently a decrease in the flow rate. Note that the large viscosity and density we introduced in our analytical model is for water inside the whole of the channel. If we subtract the contribution of the two water layers adjacent to the walls, both density and viscosity are only slightly smaller than the one of bulk for channels of size around 13 \AA and approach the bulk values for larger H . Notice that as shown in Fig. 3, both density and viscosity for the sub-continuum regime ($H \approx 13 \text{ \AA}$) and the continuum regime ($H > 13 \text{ \AA}$) are about the bulk values. This clearly indicates that for $H < 13 \text{ \AA}$ the effect of the two layers adjacent to the walls are important and they are effectively included by having a large density and viscosity for $H < 13 \text{ \AA}$. Therefore, the peak at $H = 12-14 \text{ \AA}$ arises from the rapidly rising disjoining pressure which is due to the crystal structure of the formed two water layers close to the walls and their induced larger density ρ .

We explained the observed fast water flow through graphene nanochannels, which has been reported in a recent experiment²⁰, which finds its origin in the large density and the large viscosity of water inside nanochannels. Our MD simulations confirm the ordered structure and the large density and viscosity of confined water between graphene channels.

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