


Enhancement of the water flow velocity through carbon nanotubes resulting from the radius dependence of the friction due to electron excitations

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Secchi *et al.* [*Nature (London)* **537**, 210 (2016)] observed a large enhancement of the permeability and slip length in carbon nanotubes when the tube radius is of the order of 15 nm, but not in boron nitride nanotubes. It will be pointed out that none of the parameters that appear in the usual molecular dynamics treatments of water flow in carbon nanotubes have a length scale comparable to 15 nm, which could account for the observed flow velocity enhancement. It will be demonstrated here, however, that if the friction force between the water and the tube walls in carbon nanotubes is dominated by friction due to electron excitations in the tube walls, the enhanced flow can be accounted for by a reduction in the contribution to the friction due to electron excitations in the wall, resulting from the dependence of the electron energy band gap on the tube radius.

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I. INTRODUCTION

It has been observed that water is able to flow through carbon nanotubes with radii of the order of nanometers with very large slip length, signifying low friction between the water and the tube walls [1–3]. Recently Secchi *et al.* [4,5] have presented measurements of water flow through individual carbon and boron nitride nanotubes, which show that the resistance to water flow in carbon nanotubes decreases rapidly as the tube radius is reduced, as has been found in molecular dynamics simulations by Thomas *et al.* [6]. Water flow through carbon nanotubes is of great interest because it has been demonstrated by both computer simulations and measurements that water can flow more rapidly through these tubes than salt ions can [7], opening the possibility of using them in water filtration using reverse osmosis. The strong dependence of the slip length on tube radius found for carbon nanotubes, however, is not found for boron nitride nanotubes, even though boron nitride nanotubes have the same crystal structure as carbon nanotubes. The slip length L_s is defined by

$$\lambda v_s = \eta(\nabla v)_s \approx \eta v_s / L_s, \quad (1)$$

where λ is the friction coefficient, η is the water viscosity, v_s is the tangential component of the water velocity at the wall, and $(\nabla v)_s$ is the normal component of the gradient of the water velocity at the wall. It is essentially the distance outside the tube at which the water velocity extrapolates to zero. Although Tocci *et al.* [8], have demonstrated via computer simulations that, despite the fact that boron nitride and carbon have nearly equal contact angles, the rate of water flow above a flat sheet of graphene is three times the rate of flow above a sheet of boron nitride, this does not explain the fact that the flow rate dependence on nanotube radius observed for carbon nanotubes appears to be completely absent for boron nitride nanotubes. Falk *et al.* [9], have shown that the lattice wall periodicity when projected onto the layer of water nearest to the wall becomes smaller as the tube radius decreases. They show that since the calculated friction experienced by the flowing water decreases

as the wall periodicity seen by the water decreases, this effect is able to explain the observed dependence of the water flow rate in carbon nanotubes on the tube radius. They did not, however, provide an explanation for the absence of a radius dependence of the water flow rate in boron nitride nanotubes. It should be pointed out, however, that although this mechanism gives a slip length, which increases as the radius decreases, it only works for carbon nanotubes with radii of a few nanometers, whereas the large radius dependence of the slip length and permeability of carbon nanotubes and its absence in boron nitride nanotubes observed by Secchi *et al.* [4], occurs at a radius comparable to 15 nm, which is much larger than the distance of the center of a first hydration shell oxygen from the tube wall of about 0.32 nm. Therefore, the radius dependence that they observe must involve a length scale R_0 much larger than atomic length scales. This means that the slip length has the functional form $L_s = f(R/R_0)$, where R_0 is much larger than atomic dimensions. The possibility that there could be one mechanism for the water flow enhancement in nanotubes at the nanometer scale and a different mechanism operating at the scale of tens of nanometers is consistent with previous experimental results, which show large enhancement at a radius of tens of nanometers and still larger enhancement at a radius of the order of a nanometer [2,3,9,10]. Molecular dynamics calculations on shorter [11] and narrower nanotubes [12] show much different behavior than that observed in the longer and wider nanotubes studied experimentally in Ref. [4].

II. WHY THE USUAL THEORETICAL TREATMENT OF WATER FLOW IS NOT EXPECTED TO EXPLAIN EXPERIMENT

The solution of the Navier-Stokes equation with a slip velocity v_s at the walls of a tube of radius R is

$$v = -\frac{(R^2 - r^2)}{4\eta} \frac{dP}{dz} + v_s, \quad (2)$$

where r is the distance from the center of the tube and dP/dz is the pressure gradient. From Eq. (2) and the definition of L_s in Eq. (1), we obtain $L_s dv/dr|_s = (dP/dz)L_s R/(2\eta) = v_s$. The slip velocity can also be written as

$$v_s = qF = \frac{q}{n_L} \frac{dP}{dz}, \quad (3)$$

where q is the mobility of water molecules at the surface and n_L is the number density of water molecules at the wall, using the expression in Ruckstein and Rajora's [13–15] for the force F acting on a water molecule at the wall. Combining Eq. (3) with the expression for v_s above Eq. (3), we obtain

$$L_s = \frac{2\eta q}{R n_L} = \frac{2\eta q \varepsilon_0 \delta}{R W_A}, \quad (4)$$

where η is the viscosity for the water, n_L is the number of water molecules per unit volume at the surface, W_A is the work of adhesion between the water and the wall per unit area, δ is the thickness of the first hydration shell, and ε_0 is the energy scale for the van der Waal's interaction between a first hydration shell water molecule and the wall. Here, we have used the fact that $W_A \sim \varepsilon_0 n_L \delta$ [16]. Neither W_A nor q is expected to vary by a significant amount over distances of the order of 15 nm, since R is much larger than interatomic spacings in the walls and interwater molecule spacings. Basically, the water at the walls will see the walls as nearly flat. Large flow enhancement might be expected to first occur when R becomes comparable to L_s , which takes place when

$$\frac{L_s}{R} = \frac{R_0^2}{R^2} \sim 1, \quad (5)$$

where

$$R_0 = \left(\frac{2\eta q \varepsilon_0 \delta}{W_A} \right)^{1/2}. \quad (6)$$

Thus, R_0 plays the role of a radius length scale for the onset of flow enhancement in nanotubes. From Eq. (5), using the fact that $L_s = 300$ nm when $R = 15$ nm, we find that $R_0 = 67.1$ nm. The value of W_A for boron nitride is only a little smaller than that for carbon [17]. Therefore, in order to explain the large difference in radius dependence of the flow rates observed for boron nitride and carbon nanotubes on the basis of the arguments of Refs. [13–15], we must postulate that q is much larger for carbon than for boron nitride, which is likely to be true because of the larger spatial variation in the wall potential in boron nitride than in carbon nanotubes [8]. Solving Eq. (5) for q using the values of the above parameters in Ref. [13], namely $\eta_w = 10^{-3}$ Ns/m², $\varepsilon_0 \approx 25k_B T = 10^{-19}$ J, $\delta = 0.3 \times 10^{-9}$ m and $W_A = 0.150$ J/m², we obtain $q = 1.13 \times 10^{16}$ m/Ns, if $R_0 = 67.1$ nm. This is much larger than the value of q used in Refs. [13–15], which assumes thermally activated hopping with a diffusion constant $D_s = 2 \times 10^{-9}$ m²/s, obtained from molecular dynamics simulations of water flowing along a graphene sheet [13–15], namely

$$q = \frac{D_s}{k_B T} = 5 \times 10^{11} \text{ m/Ns}. \quad (7)$$

Since the circumference of the nanotubes $2\pi R = 94.2$ nm, which is much larger than both the water molecule size and a

lattice constant of the nanotube walls (which are both less than a nanometer), one would expect that q would be nearly equal to the value it would have for a flat surface, and be independent of R to a good approximation. Therefore, in order to explain the large radius dependence of the slip length observed for a carbon nanotube when its radius drops below 15 nm, we must find a length scale of this magnitude.

III. EXAMINATION OF THE CONTRIBUTION OF ELECTRONIC FRICTION

Consider the possibility that the dominant contribution to the friction between the water and the carbon nanotube walls is due to the contribution to the friction from the creation of excitations of the electrons in the conduction band of the carbon nanotube. If the nanotubes in the work of Secchi *et al.* [4], were semiconducting, the energy gap in the band structure becomes comparable to the product of Boltzmann's constant and the temperature, $k_B T$, when R is close to 15 nm, and becomes larger than $k_B T$ for smaller values of R [18,19]. Thus the number of conduction electrons decreases rapidly as R decreases, resulting in a rapid reduction in the number of conduction electrons available to be excited. In contrast, the band gap in boron nitride nanotubes is larger and does not become comparable to $k_B T$ for R in the vicinity of 15 nm, and hence, there are no conduction electrons to contribute to the friction. The interaction of the water with the tube wall should be sufficiently weak to treat it by time-dependent perturbation theory (e.g., the Kubo formula [20]). The contribution to the force of friction due to excitation of the electronic states of the nanotube resulting from a single water molecule can be found using Fermi golden rule perturbation theory [21–24],

$$f v = \frac{dE}{dt} = (2\pi/\hbar) \sum_{\vec{k}_i, \vec{k}_f, \alpha} |M_{\vec{k}_i, \vec{k}_f, \alpha}|^2 (\varepsilon_\alpha(\vec{k}_f) - \varepsilon_\alpha(\vec{k}_i)) \times \left[\exp\left(\frac{\mu - \varepsilon_\alpha(\vec{k}_i)}{k_B T}\right) - \exp\left(\frac{\mu - \varepsilon_\alpha(\vec{k}_f)}{k_B T}\right) \right] \times \delta(\varepsilon_\alpha(\vec{k}_f) - \varepsilon_\alpha(\vec{k}_i) - \hbar \vec{v} \cdot (\vec{k}_f - \vec{k}_i)), \quad (8)$$

where $M_{\vec{k}_f, \vec{k}_i, \alpha}$ is the matrix element of the interaction potential between the water molecule and the electrons in the conduction band of the tube wall, f is the force of friction acting on a water molecule, \vec{v} is the mean flow velocity of the water, μ is the electron chemical potential, $\varepsilon_\alpha(\vec{k})$ is the energy of an electron in the α^{th} conduction band, and \vec{k}_i and \vec{k}_f are the electron wave vectors before and after scattering, respectively. There is also a similar expression for the friction due to excitation of holes in the valence band. If the innermost tube of the multiwalled tubes studied in Ref. [4] is semiconducting (most nanotubes are semiconducting), the gap energy in eV is given by g_1/R [18], where g_1 is a constant. When $R = 15$ nm, the gap is comparable to $k_B T$, where k_B is Boltzmann's constant, for T equal to room temperature. As R decreases, the band gap increases to values above $k_B T$, and hence, the number of electrons in the conduction band drops off rapidly. Consequently, the force of friction due to excitation of conduction electrons drops off rapidly, resulting in a rapid increase in the slip length given by $L_s = \eta/\lambda$, where $\lambda = (\pi R^2 L)(2\pi R L)^{-1} \rho f/v = (R/2)\rho f/v$,

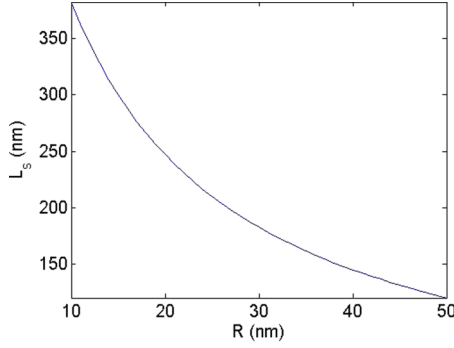


FIG. 1. A plot of L_s versus R based on Eq. (9) with L_{s0} chosen so that $L_s = 300$ nm when $R = 15$ nm.

where ρ is the number of water molecules per unit volume. A similar argument holds for holes in the valence band. An approximate model calculation of the slip length is given in the Appendix. It gives a slip length of the form [19]

$$L_s = \eta/\lambda = (L_{s0}/x) \left[\frac{(1/3) \exp(-x/3) + (2/3) \exp(x/3)}{[1 - \exp(-x)]^2} + \frac{\exp(-x/3) + \exp(x/3)}{1 - \exp(-x)} \right]^{-1}, \quad (9)$$

where $x = g_0/(2k_B T)$, where g_0 is the main gap in the energy bands of the electrons in the wall. [See Eq. (A17) in the Appendix for details.] Equation (9) is plotted with L_{s0} chosen so that $L_s = 300$ nm for $R = 15$ nm in Fig. 1, which exhibits an increase of L_s from about 120 nm at $R = 50$ nm to 300 nm at $R = 15$ nm. Although in Secchi *et al.*'s paper [4] L_s drops to about 17 nm at $R = 50$ nm, if one takes into account impurity scattering of the electrons, it is easy to account for this apparent discrepancy by the fact that at $R = 50$ nm, even for a mean free path ℓ as large of 50 nm, the width of the electron states $\Delta E = \hbar/\tau = \hbar v_F/\ell = 10^{-2}$ eV resulting from impurity scattering is larger than the band gap. Thus, at $R = 50$ nm there is no longer a band gap, and hence, λ is expected to be much larger than it would be if there were a nonzero gap. This will lead to a much smaller slip length than would occur with a nonzero gap. It is easy to show that in the experiments reported in Ref. [4], $\hbar v G$, where G is the magnitude of a primitive reciprocal lattice vector of the wall or 2π divided by a graphene lattice constant, is much smaller than the gap energy for the smaller values of R , and hence, there will be little contribution to the friction from excitations of electrons across the band gap.

IV. CONCLUSION

In summary, the large radius dependence of the slip length and permeability of water flowing in a carbon nanotube found by Secchi *et al.*, at values of R between 15 nm and 20 nm is difficult to understand without postulating that the friction between the water and the tube wall becomes much smaller than the values obtained from molecular dynamics performed on a flat graphene surface [8] at a radius of 15 nm, which is much larger than the molecular spacing in the water and the tube wall. If the inner walls of tubes are semiconductors (i.e., zig-zag nanotubes), however, it is possible to explain the rapid drop in the friction for such large radii, if the friction in

carbon nanotubes is dominated by friction due to electronic excitations. The reason for this is that as the tube radius drops below 15 nm, the electronic energy band gap becomes larger than $k_B T$, resulting in a rapid reduction in the number of electrons in the conduction band, whose excitation produces the electronic contribution to the friction. In contrast, since boron nitride nanotubes are insulating, and hence they do not have a contribution to the friction due to the excitation of conduction electrons, this does not occur.

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APPENDIX

The perturbing potential due to one water molecule is the potential energy of a conduction (or valence) band electron in the potential due to the water molecule dipole, which is in MKS units

$$v(\vec{r}) = k_e \frac{e\vec{p} \cdot (\vec{r} - \vec{r}_0)}{|\vec{r} - \vec{r}_0|^3}, \quad (A1)$$

where k_e is the proportionality constant in Coulomb's law, $(4\pi\epsilon_0)^{-1}$, e is the electron charge, \vec{p} is the water dipole moment, and \vec{r}_0 is the location of the water molecule under consideration. It can be written in terms of its Fourier transform,

$$\begin{aligned} \bar{v}(\vec{k}) &= V^{-1} k_e \int \frac{e\vec{p} \cdot (\vec{r} - \vec{r}_0)}{|\vec{r} - \vec{r}_0|^3} e^{i\vec{k} \cdot \vec{r}} d^3r \\ &= k_e \frac{4\pi e\vec{p} \cdot \vec{k}}{V k^2} \exp(-i\vec{k} \cdot \vec{r}_0), \end{aligned} \quad (A2)$$

where V is the volume of space, as

$$v(\vec{r}) = \frac{4\pi e}{(2\pi)^3} k_e \int d^3k \exp[i\vec{k} \cdot (\vec{r} - \vec{r}_0)] \frac{\vec{p} \cdot \vec{k}}{k^2}. \quad (A3)$$

Since the radius of curvature of the tube is much larger than the interatomic spacing of the wall and the mean spacing between water molecules and the electrons in the wall can to a first approximation be treated as a two-dimensional electron gas, the matrix element of the above perturbing potential between the electron wave functions inside the wall is given by

$$\begin{aligned} M_{\vec{k}_f, \vec{k}_i, \alpha} &= \frac{4\pi e}{(2\pi)^3} k_e \int d^3k \exp(-i\vec{k} \cdot \vec{r}_0) \frac{\vec{p} \cdot \vec{k}}{k^2} \int \exp(i\vec{k} \cdot \vec{r}) \\ &\quad \times \exp(-i\vec{K} \cdot \vec{r}) u_{\vec{k}_f, \alpha}^*(\vec{r}) u_{\vec{k}_i, \alpha}(\vec{r}) d^2r, \end{aligned} \quad (A4)$$

(where z is the distance of the water molecule from the tube wall), where $\vec{K} = \vec{k}_f - \vec{k}_i$, where \vec{k}_i is the wave vector before the electron is scattered, and \vec{k}_f is the wave vector of the electron after it is scattered by the water molecule. The electron states [19] are Bloch functions, with a wave vector along the tube axis (taken to be the x axis), of the form $\exp(kx)u(\vec{r})$, where $u(\vec{r})$ is a periodic function of repeat distance in the x direction and the circumference in the y direction, and hence can be written in the following Fourier series: $u(x, y) = (LC)^{-1/2} \sum A_{G, \vec{G}} \exp[i(Gx + \vec{G}y)]$, where L and C are the tube length and circumference, G is a reciprocal lattice vector along the tube axis, and \vec{G} is an integer multiple

of $2\pi/C$. Since the Bloch functions in graphene sheets and nanotubes are often treated in the tight binding approximation, the Fourier coefficients $A_{G,\bar{G},\alpha}$ are proportional to Fourier transforms of the carbon atomic functions. Then, Eq. (A4) becomes,

$$M_{\vec{k}_f,\vec{k}_i,\alpha} = \frac{4\pi e}{(2\pi)^3} k_e \int d^3k \exp(-i\vec{k} \cdot \vec{r}_0) \frac{\vec{p} \cdot \vec{k}}{k^2} \int \exp(i\vec{k} \cdot \vec{r}) \exp(-i\vec{K} \cdot r) \sum_{\vec{G}_f,\vec{G}_i} A_{\vec{G}_f}^* A_{\vec{G}_i} \exp[-i(\vec{G}_f - \vec{G}_i) \cdot \vec{r}] d^2r, \quad (\text{A5})$$

where $\vec{G}_{f,i} = G_{f,i}\hat{x} + \bar{G}_{f,i}\hat{y}$, where \hat{x} and \hat{y} are unit vectors in the x and y directions, respectively, \vec{G}_i is the reciprocal lattice vector for the electron wave function before scattering, and \vec{G}_f is the reciprocal lattice vector of the electron wave function after scattering by the water molecule. Since $\vec{r}_0 = r_0\hat{z}$, where the z direction is along the radius of the tube, this integral becomes

$$\begin{aligned} M_{\vec{k}_f,\vec{k}_i,\alpha} &= \frac{e}{2\pi^2} k_e \int \frac{dk_z}{LC} \exp(-ik_z r_0) \sum A_{G_f,\bar{G}_f,\alpha}^* A_{G_i,\bar{G}_i,\alpha} \left(\frac{(Q_x p_x + Q_y p_y + k_z p_z)}{Q_x^2 + Q_y^2 + k_z^2} \right) \\ &= \frac{e}{2\pi^2 LC} k_e \sum A_{G_f,\bar{G}_f,\alpha}^* A_{G_i,\bar{G}_i,\alpha} (p_x Q_x + p_y Q_y - i Q p_z) \frac{\exp(-Q r_0)}{Q}, \end{aligned} \quad (\text{A6})$$

where $\vec{Q} = (K + G)\hat{x} + \bar{G}\hat{y}$, where $G = G_f - G_i$ and $\bar{G} = \bar{G}_f - \bar{G}_i$ after doing the integral over k_z . There is also a small form factor to account for the finite thickness of the walls, which is not included here, since it does not have a significant effect on the results. Then, averaging the square of the absolute value of $M_{\vec{k}_f,\vec{k}_i}$ over all directions of \vec{p} , we obtain

$$\begin{aligned} |M_{\vec{k}_f,\vec{k}_i,\alpha}|_{av}^2 &= \frac{e^2 p^2}{12\pi^4 L^2 C^2} k_e^2 \sum_{\vec{Q}} |A_{\bar{G}_f,\alpha}|^2 |A_{\bar{G}_i,\alpha}|^2 \left(\frac{Q_x^2 + Q_y^2 + Q^2}{Q^2} \right) \exp[-2Q r_0] \\ &= \frac{e^2 p^2}{6\pi^4 L^2 C^2} k_e^2 \sum_{\vec{Q}} |A_{\bar{G}_f,\alpha}|^2 |A_{\bar{G}_i,\alpha}|^2 \exp[-2Q r_0], \end{aligned} \quad (\text{A7})$$

since $Q^2 = Q_x^2 + Q_y^2$. The band structure at the bottom of the conduction band in a carbon nanotube wall can be approximated by an effective mass approximation $\varepsilon_\alpha(\vec{k}) \approx g_\alpha + \hbar^2 k^2 / (2m_\alpha)$, where m_α is the effective mass and g_α is the band gap between the α^{th} and the $(\alpha + 1)^{\text{st}}$ band.

Then, Eq. (7) in the text becomes

$$\begin{aligned} f v &= \frac{2\pi}{\hbar} (4\pi)^2 k_e^2 \sum_{\vec{k}_f,\vec{k}_i} \frac{e^2 p^2}{6\pi^4 L^2 C^2} \sum_{\vec{G}_i,\vec{G}_f,\alpha} |A_{\bar{G}_f,\alpha}|^2 |A_{\bar{G}_i,\alpha}|^2 \exp[-(2Q)r_0] \int dk_i dk_f \hbar^2 / (2m_\alpha) (k_f^2 - k_i^2) \\ &\quad \times \delta[(\hbar^2/2m_\alpha)(k_f^2 - k_i^2) \mp \hbar v Q_x] \left[\exp\left(\frac{\mu - g_\alpha - \hbar^2 k_i^2 / 2m_\alpha}{k_B T}\right) - \exp\left(\frac{\mu - g_\alpha - \hbar^2 |\vec{k}_i + \vec{K}|^2 / 2m_\alpha}{k_B T}\right) \right], \end{aligned} \quad (\text{A8})$$

where f is the force exerted on the tube by the water molecule and v is the water molecule's velocity. The index α labels the various sub-bands that arise from the rolling of a graphene sheet into the nanotube and g_α is the energy difference between the center of the $\alpha = 0$ gap and the bottom of the α^{th} sub-band. The summation over is over all \vec{k}_i and \vec{k}_f within the each band and μ is the chemical potential. Then, converting the summations to integrals in the standard way, this expression becomes

$$\begin{aligned} f v &= \frac{2\pi}{\hbar} \frac{(4\pi)^2}{(2\pi)^2} k_e^2 \iint dk_i dk_f \frac{e^2 p^2}{6\pi^4 C^2} \sum_{\vec{G}_i,\vec{G}_f,\alpha} |A_{\bar{G}_i,\alpha}|^2 |A_{\bar{G}_f,\alpha}|^2 \exp[-(2Q)r_0] \\ &\quad \times (\hbar^2/2m_\alpha)(k_f^2 - k_i^2) \delta[(\hbar^2/2m_\alpha)(k_f^2 - k_i^2) \mp \hbar v Q_x] \frac{(\hbar^2/2m_\alpha)(k_f^2 - k_i^2)}{k_B T} \exp\left(\frac{\mu - g_\alpha - \hbar^2 k_i^2 / 2m_\alpha}{k_B T}\right). \end{aligned} \quad (\text{A9})$$

We may change integration variables in the integral over \vec{k}_f to an integral over K giving

$$\begin{aligned} f v &= \frac{2\pi}{\hbar} \frac{(4\pi)^2}{(2\pi)^2} k_e^2 \iint dk_i dK \frac{e^2 p^2}{6\pi^4 C^2} \sum_{\vec{G}_i,\vec{G}_f,\alpha} |A_{\bar{G}_i,\alpha}|^2 |A_{\bar{G}_f,\alpha}|^2 \exp[-2Q r_0] \\ &\quad \times \delta[(\hbar^2/2m_\alpha)((k_i + K)^2 - k_i^2) \mp \hbar v Q_x] \frac{\hbar^2 V^2 Q_x^2}{k_B T} \exp\left(\frac{\mu - g_\alpha - \hbar^2 k_i^2 / 2m_\alpha}{k_B T}\right). \end{aligned} \quad (\text{A10})$$

Integrating over K , we obtain

$$\begin{aligned} f v &= \hbar^{-1} \int dk_i \frac{2e^2 p^2}{3\pi^3 C^2} k_e^2 \sum_{\vec{G}_i,\vec{G}_f,\alpha} |A_{G_i,\alpha}|^2 |A_{\bar{G}_f,\alpha}|^2 \exp[-2Q r_0] \\ &\quad \times \frac{2m_\alpha}{\hbar^2 [(k_i - m_\alpha v / \hbar)^2 + 2m_\alpha v G / \hbar]^{1/2}} \frac{\hbar^2 v^2 Q_x^2}{k_B T} \exp\left(\frac{\mu - g_\alpha - \hbar^2 k_i^2 / 2m_\alpha}{k_B T}\right). \end{aligned} \quad (\text{A11})$$

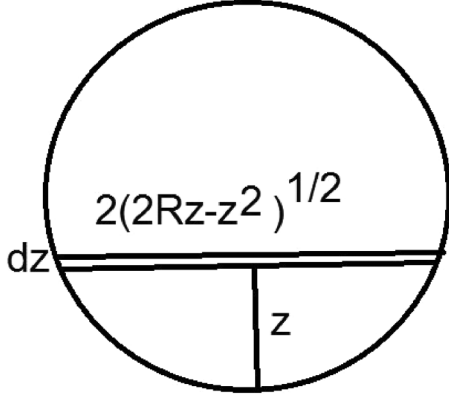


FIG. 2. An illustration of the calculation in Eq. (A12).

For a semiconducting nanotube, $\mu = (1/2)g$. We can replace $\exp[-2Qr_0] \approx \exp[-Gr_0]$, where G is a reciprocal lattice vector (which is of the order of 10^{10} m^{-1}), by its average over the cross-sectional area of the tube, illustrated in Fig. 2 given by

$$\begin{aligned} \langle \exp[-Gr_0] \rangle &= (\pi R^2)^{-1} 2 \int_0^{2R} dz [R^2 - (R-z)^2]^{1/2} \\ &\quad \times \exp(-Gz) = \frac{4}{\pi GR}. \end{aligned} \quad (\text{A12})$$

In the summations in Eq. (A11), we may neglect the dependence on K of all of the quantities in Eq. (A11), which depend on the components of the Q vectors in Eq. (A11) since $|K|$ is much smaller than the smallest reciprocal lattice vector, and hence the integral over k_i is to a good approximation given by

$$\begin{aligned} I &= 2 \int_0^\infty dk_i \frac{\exp(-\hbar^2 k_i^2 / 2m_\alpha k_B T)}{[(k_i - m_\alpha v / \hbar)^2 + 2m_\alpha v G / \hbar]^{1/2}} \\ &= \int_0^\infty \frac{\exp[-m_\alpha v^2 x^2 / 2k_B T] dx}{[(x-1)^2 + 2\hbar G / m_\alpha v]^{1/2}} \\ &= \int_{-\infty}^\infty dy \frac{\exp(-y^2)}{[(y-b)^2 + a]^{1/2}}, \end{aligned} \quad (\text{A13})$$

where $x = \hbar k_i / m_\alpha v$, $y = (m v^2 / 2k_B T)^{1/2} x$, $a = (\hbar v G / k_B T) \approx 10^{-1}$, and $(m v^2 / 2k_B T)^{1/2} \approx 10^{-11}$. When I is evaluated with these parameters, it is about equal to 24. All of the functions of the components of the Q vectors in Eq. (A11) can to a good approximation be considered constants.

In Ref. [19], it is shown that $m_\alpha = (\alpha \pm 1/3)m_0$ and $g_\alpha = (\alpha \pm 1/3)g_0$, where α is an integer that runs from 0 to ∞ , $g_0 = (2/3)\hbar v_F / R$ and $m_0 = \hbar / (v_F R)$, where v_F is the graphene Fermi velocity. Then, the friction coefficient for a single water molecule,

$$\begin{aligned} \lambda &= f/v \approx \frac{4}{3\pi^3 \hbar} \frac{e^2 p^2 G^2}{C^2} k_e^2 \sum_\alpha \frac{m_\alpha}{k_B T} I \sum_{\vec{G}_i, \vec{G}_f, \alpha} |A_{\vec{G}_i, \alpha}|^2 |A_{\vec{G}_f, \alpha}|^2 \\ &\quad \times \langle \exp[-2Qr_0] \rangle \exp(-g_\alpha / 2k_B T) \\ &= \frac{8}{3\pi^3 \hbar} \frac{e^2 p^2}{C^2} k_e^2 \frac{4G}{\pi R} \frac{I}{k_B T} \sum_\alpha m_\alpha \exp(-g_\alpha / 2k_B T). \end{aligned} \quad (\text{A14})$$

In order to get the friction coefficient per unit area for the total force of friction acting on the tube, we must multiply this by

$$(1/2)\rho\pi R^2 L / (2\pi RL) = (1/2)\rho R, \quad (\text{A15})$$

where ρ is the number of water molecules per unit volume and L is the length of the nanotube. Performing the summation over α , neglecting the dependence of the sums over the $A_{\vec{G}_i, \alpha}$ coefficients, we find that the friction coefficient has the form

$$\begin{aligned} \lambda_{\text{tot}} &= \lambda_0 x \sum_{\alpha, \pm} (\alpha \pm 1/3) \exp[-(\alpha \pm 1/3)x] \\ &= \lambda_0 x \left[\frac{(1/3) \exp(-x/3) + (2/3) \exp(x/3)}{[1 - \exp(-x)]^2} \right. \\ &\quad \left. + \frac{\exp(-x/3) + \exp(x/3)}{1 - \exp(-x)} \right], \end{aligned} \quad (\text{A16})$$

where

$$\lambda_0 = \frac{16}{3\pi^4} k_e^2 e^2 p^2 m_0 \rho I C^{-2} \sum_{\vec{G}_i, \vec{G}_f} |A_{\vec{G}_i, \alpha}|^2 |A_{\vec{G}_f, \alpha}|^2 \frac{G}{k_B T},$$

where $G = G_{fx} - G_{ix}$, is treated as a constant (i.e., the α dependence is neglected) and $x = g_0 / (2k_B T)$. With $G \sim 10^{10} \text{ m}^{-1}$ and $m_0 = 1.25 \times 10^{-32} \text{ kg}$ and $C = 94.2 \times 10^{-9} \text{ m}$, their values for $R = 15 \text{ nm}$, and $\rho = 0.334 \times 10^{29} \text{ m}^{-3}$, and we assume that $\sum_{\vec{G}_i, \vec{G}_f} |A_{\vec{G}_i, \alpha}|^2 |A_{\vec{G}_f, \alpha}|^2 \sim 1$, we obtain a value for λ_0 of the order of $1.34 \times 10^{12} \text{ N s/m}^3$. While for this value of λ_0 , $L_{s0} = \eta / \lambda_0 = 0.746 \times 10^{-15} \text{ m}$, meaning that λ_0 is too large to give a slip length of 300 nm, the above calculation does not include dielectric screening of the interaction of the water with the electrons in the tube walls and we do not know the electron wave functions well enough to calculate $\sum_{\vec{G}_i, \vec{G}_f} |A_{\vec{G}_i, \alpha}|^2 |A_{\vec{G}_f, \alpha}|^2$ correctly. The product of C^{-2} and the summation over \vec{G}_i and \vec{G}_f is nearly independent of C , if the tight binding approximation accurately describes the wave functions because, as was stated earlier, the Fourier coefficients of the wave functions, $A_{\vec{G}_i, \alpha}$ are proportional to Fourier transforms of carbon atomic wave functions evaluated at wave vector $\vec{G}_{f,i}$. Therefore, the summation over the y components of $\vec{G}_{f,i}$ is restricted to a limited range of magnitudes by this function (because it falls off with increasing values of $\vec{G}_{f,i}$) and the spacing of successive values of $\vec{G}_{f,i}$ is equal to $2\pi/C$. Then the slip length

$$\begin{aligned} L_s &= \eta / \lambda = (L_{s0}/x) \left[\frac{(1/3) \exp(-x/3) + (2/3) \exp(x/3)}{[1 - \exp(-x)]^2} \right. \\ &\quad \left. + \frac{\exp(-x/3) + \exp(x/3)}{1 - \exp(-x)} \right]^{-1}, \end{aligned} \quad (\text{A17})$$

where L_{s0} is treated as a constant to be chosen so as to best reproduce the data (since we do not know the precise values of the Fourier coefficients of the wave functions, $A_{\vec{G}, \alpha}$ and η is the water viscosity. It is easy to show from the results of Ref. [19] that both m_0 and g_0 are inversely proportional to R and $g_0 R / (k_B T) = 8.26 \text{ nm}$. If we choose the value of L_{s0} , which gives $L_s = 300 \text{ nm}$ for $R = 15 \text{ nm}$, we get Fig. 1 in

the text, which exhibits an increase of L_s from about 120 nm at $R = 50$ nm to 300 nm. In Secchi *et al.*'s paper (Ref. [4]), however, L_s drops to about 17 nm at $R = 50$ nm. If one takes into account impurity scattering of the electrons, it is easy to account for this apparent discrepancy by the fact that at $R = 50$ nm, even for a mean free path as large of 50 nm, the width of the electron states resulting from impurity scattering is larger than the bandwidth. Thus, there is no longer a band gap, and hence λ is expected to be much larger than it would be if there were a nonzero gap. This will lead to a much smaller

slip length than would occur with a nonzero gap. Although the numerical value of L_{s0} determined from the parameters in Eqs. (A14) and (A15) is too small (it should be of the order of a nanometer), this is not unexpected, since we do not have precise information about the expansion of the conduction electron wave functions in a Fourier series. The use of Eq. (1) in the text, despite the fact that we are using the average value of the water velocity, rather than its value at the wall, is valid when L_s is large compared to R because for large L_s the average value of v is nearly equal to its value at the tube wall.

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- [1] G. Hummer, J. C. Rasaiah, and J. P. Noworyta, *Nature (London)* **414**, 188 (2001).
- [2] M. Majumder, N. Chopra, N. Andrews, R. Andrews, and B. J. Hinds, *Nature (London)* **438**, 44 (2005).
- [3] J. K. Holt, H. G. Park, Y. Wang, M. Stadermann, A. B. Artyukhin, and C. P. Grigorop, *Science* **312**, 1034 (2006).
- [4] E. Secchi, S. Marbach, A. Nigues, D. Stein, A. Siria, and L. Bocquet, *Nature (London)* **537**, 210 (2016).
- [5] A. Michaelides, *Nature (London)* **537**, 171 (2016).
- [6] J. A. Thomas and A. J. H. Mc. Gaughey, *Nano Lett.* **8**, 2788 (2008).
- [7] H. G. Park and Y. Jung, *Chem. Soc. Rev.* **43**, 565 (2014).
- [8] G. Tocci, L. Joly, and A. Michaelides, *Nano Lett.* **14**, 6872 (2014).
- [9] K. Falk, F. Sedlmeier, L. Joly, R. R. Netz, and L. Bocquet, *Nano Lett.* **10**, 4067 (2010).
- [10] M. Whitby, L. Cagnon, M. Thanou, and N. Quirke, *Nano Lett.* **8**, 2632 (2008).
- [11] C. Y. Won and N. R. Aluru, *J. Am. Chem. Soc.* **129**, 2748 (2007).
- [12] M. E. Suk, A. V. Raghunathan, and N. R. Aluru, *Appl. Phys. Lett.* **92**, 133120 (2008).
- [13] E. Ruckenstein and P. Rajora, *J. Colloid Interface Sci.* **96**, 488 (1983).
- [14] F. Calabro, K. P. Lee, and D. Mattia, *Appl. Math. Lett.* **26**, 991 (2013).
- [15] D. Mattia and F. Calabro, *Microfluid. Nanofluid.* **13**, 125 (2012).
- [16] J. N. Israelachvili, *Intermolecular and Surface Forces* (Academic Press, Burlington, 2011).
- [17] H. Li and X. C. Zeng, *ACS Nano* **6**, 2401 (2012).
- [18] P. G. Collins and P. Avouris, The electronic properties of carbon nanotubes, in *Carbon Nanotubes*, edited by A. Zettl and S. Sato (Elsevier, Amsterdam, 2008).
- [19] J.-C. Charlier, X. Blasé, and S. Roche, *Rev. Mod. Phys.* **79**, 677 (2007).
- [20] L. Bocquet and J.-L. Barrat, *Phys. Rev. E* **49**, 3079 (1994).
- [21] B. N. J. Persson, *J. Chem. Phys.* **98**, 1695 (1993); *Phys. Rev. B* **44**, 3277 (1991); *Surf. Sci.* **269-270**, 103 (1992).
- [22] R. G. Tobin, *Phys. Rev. B* **48**, 15468 (1993).
- [23] B. N. J. Persson, *Phys. Rev. B* **48**, 15471 (1993).
- [24] J. B. Sokoloff, *Phys. Rev. B* **52**, 5318 (1995).