

Effects of electronic friction from the walls on water flow in carbon nanotubes and on water desalination

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A mechanism for removal of salt from salt water is discussed, which results from friction due to Ohm's law heating, resulting from motion of an electron charge induced in the tube walls by the water molecules' dipoles and the ions' charges. The desalination occurs because this friction is larger for salt ions than for water molecules. Friction due to Ohm's law heating might also provide an explanation for the observation by Secchi *et al.* [[Nature](#) **537**, 210 (2016)] that the flow velocity of water in carbon nanotubes for a given pressure gradient increases rapidly as the tube radius decreases from 50 to 15 nm, which does not occur for boron nitride nanotubes, which are insulators. This friction can have the right magnitude to produce the slip lengths reported by Secchi *et al.* One possibility is that the nanotubes in this experiment were metallic, and their conductivity becomes large as their radius decreases, due to ballistic conduction. Another possibility is that when the tube circumference drops below the electron mean-free path, the wall switches from behaving as a two-dimensional conductor to behaving as a one-dimensional conductor for which the electrons are more strongly localized. When the conductivity is sufficiently small, small displacements of the localized electron states can provide the dominant contribution to the motion of the induced charge, rather than current flow, thus reducing the friction due to Ohm's law heating.

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I. INTRODUCTION

It has been predicted by molecular-dynamics simulations and observed experimentally that water flow velocity in carbon nanotubes is much larger than what is predicted by the usual treatment of liquid flow in confined geometries [1–11]. In Refs. [12–18], it was shown that molecules having a charge distribution, moving near an electrically conducting solid, experience a force of friction due to its interaction with the electrons in the solid. Two mechanisms have been proposed for the interaction of such molecules with an electrically conducting solid. In one mechanism, the moving molecule creates excitations of the electrons [12–15]. This mechanism was proposed [19] as a possible way to explain the rapid increase in the slip length observed for water flowing through carbon nanotubes by Secchi *et al.* [20]. It is based on the assumption that because carbon nanotubes are hydrophobic and atomically quite smooth, whatever roughness that exists in their walls might be avoided by the flowing water, allowing friction due to interaction between the water and the electrons in the tube walls to be the dominant mechanism for friction between the water and the tube walls. In the mechanism discussed in Ref. [19], the friction is due to excitation of the conduction electrons. In the mechanism to be discussed here due to Ohm's law heating, a moving molecule induces a charge distribution on the surface of the solid, which moves along with the moving molecule. For a conducting solid, the motion of this charge distribution occurs via local electric currents, which results in energy loss due to Ohm's law heating. If the solid were insulating but polarizable, the induced charge distribution moves by local polarization of the electronic charge, due to local displacements of the charges in the solid. One possible way to explain the results reported in Ref. [20] that will be discussed

is that as the nanotube radius decreases, the tube can switch from behaving as a two-dimensional to a one-dimensional conductor, leading to a much higher degree of localization. This can result in a rapid drop in friction due to this mechanism, which could possibly explain the observations of Secchi *et al.* [20], if this friction mechanism dominates over the mechanism discussed in Ref. [19]. The mechanism proposed in Ref. [19] might not explain these experiments because the mechanism for electronic friction discussed there might not be large enough and the gaps in the electron energy bands of the wall might be too small to explain the rapid increase in the slip length when the tube radius is near 15 nm. This is discussed in more detail in Appendix A. Since the mechanism for friction due to Ohm's law heating discussed in Refs. [16–18] was derived for a three-dimensional solid, whereas at least for single-walled carbon nanotubes, the current flow occurs in a single molecule thick wall, it will be derived here for a conductor that is only one atom thick.

Section II will discuss the Boyer or Ohm's law mechanism for electronic friction, and how it might be used to explain the results reported in Ref. [20]. Section III will discuss how the Boyer mechanism for electronic friction can be used to filter salt out of salt water.

II. BOYER OR OHM'S LAW FRICTION

The mechanism for Ohm's law friction proposed by Boyer [16], which was described above, was derived for a three-dimensional conductor. It will be derived here for a two-dimensional material such as graphene. Carbon nanotubes consist of a sheet of graphene rolled into a tube, and for water molecules which are sufficiently close to the tube wall, the wall can be treated as a sheet of graphene to a

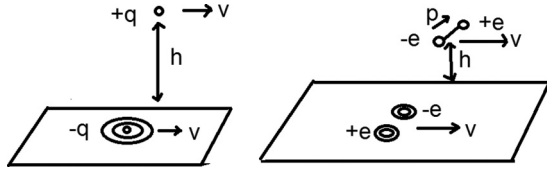


FIG. 1. The moving charge distribution induced in a conducting sheet is illustrated for (a) a moving positive point charge and (b) a moving dipole moving above the conducting sheet.

good approximation. We begin by describing the physics. A point charge moving parallel to and a distance h above a flat, conducting two-dimensional solid will induce an equal and opposite charge in the solid, given by the usual image charge argument [21], as illustrated in Fig. 1.

As the point charge moves, the image charge moves along with it, resulting in a local current that dissipates energy by Ohm’s law heating. In the case of a dipole moving over the solid, the positive and negative charges of the dipole will induce a negative and positive charge density in the solid, respectively, both of which move together with the velocity of the moving dipole.

The current density in the surface (i.e., current per unit length normal to the flow direction) is given by

$$j = v\sigma(\vec{r}), \quad (1)$$

where v is the charge or dipole velocity and $\sigma(\vec{r})$ is the induced charge density. Thus, the moving dipole results in two local induced currents, one (due to the negative charge of the dipole) flowing in the direction of motion of the dipole and the other (due to the positive charge of the dipole) moving in the opposite direction. Then the rate of dissipation is given by

$$P = \sigma_{2d}^{-1} v^2 \int d^2r \sigma(\vec{r})^2 = f v, \quad (2)$$

where σ_{2d} is the conductivity of the two-dimensional conductor and f is the resulting force of friction. The induced charge density for the point-charge case is [21]

$$\sigma(\vec{r}) = \frac{-qh}{2\pi[(x-vt)^2 + y^2 + h^2]^{3/2}}. \quad (3)$$

Performing the integral over the surface, we obtain

$$\begin{aligned} f &= vq^2 h^2 (4\pi^2 \sigma_{2d})^{-1} \int \frac{dxdy}{[(x-vt)^2 + y^2 + h^2]^3} \\ &= vq^2 h^2 (4\pi)^{-1} \sigma_{2d}^{-1} \int \frac{rdr}{[r^2 + h^2]^3} = \frac{vq^2}{8\pi \sigma_{2d} h^2}. \end{aligned} \quad (4)$$

This calculation is a factor of 2 too large, because it includes both the electric field due to the point charge and its image.

The above use of the method of electrical images is not totally consistent, because it assumes that the point charge lies precisely over its image charge, and hence, exactly above the center of the induced charge distribution in the wall. This would imply that there is no net friction force on the point charge, but there must be a friction force because work must be done to drag the induced charge distribution along with it. Therefore, the point charge must always be a small distance

Δx ahead of the center of the induced charge distribution in the wall, and hence, a distance $2\Delta x$ ahead of its image charge. The details of this calculation are given in Appendix B. [See Eq. (B18)]. The resulting expression for the average force on the water molecule is

$$\langle f_x \rangle = \frac{\langle p^2 \rangle v}{12\pi \sigma_{2d} h^4} \quad (5)$$

Then, the force on the nanotube due to the water molecules F_w is given by

$$F_w = \frac{1}{12\pi} \frac{\langle p^2 \rangle v \rho_w L}{\sigma_{2d}} \int_0^{R-a} \frac{2\pi r dr}{(R-r)^4}, \quad (6)$$

where R is the tube radius, L is its length, ρ_w is the number density of water molecules, r is the distance from the tube center, and a is the minimum distance of the molecule from the tube wall (i.e., the radius of the molecule). We are assuming here (as we have earlier) that molecules making the largest contribution are close enough to the wall compared to the tube radius so that the above expression, which was derived for a flat wall, is valid to a good approximation. The integral is equal to

$$2\pi \left(\frac{1}{6R^2} + \frac{2R-3a}{6a^3} \right) \approx \frac{2\pi R}{3a^3} \quad (7)$$

for $R \gg a$. Then,

$$F_w = \frac{1}{36} \frac{\langle p^2 \rangle v \rho_w L R}{\sigma_{2d} a^3}, \quad (8)$$

and hence, the friction coefficient is given by

$$\lambda = \frac{F_w}{2\pi R L v} = \frac{p^2 \rho_w}{36\pi \sigma_{2d} a^3} = 10.1 \text{ N s/m}^3 \quad (9)$$

if we substitute $p = ed$, where $d = 0.38 \times 10^{-10} \text{ m}$, $\rho_w = 0.334 \times 10^{29} \text{ m}^{-3}$, $\sigma_{2d} = 0.4 \times 10^{-4} \text{ } \Omega^{-1}$, and $a = 3 \times 10^{-10} \text{ m}$. This gives a slip length of $\eta/\lambda = 1.32 \times 10^{-4} \text{ m} = 1.32 \times 10^5 \text{ nm}$, where η is the water viscosity. If the conductivity were smaller by a factor of 440 and the numerical factor in my expression for the force on a dipole was really larger than what I assumed it to be, or if a were smaller than the value given above, we could get the observed slip length of 300 nm at $R = 15 \text{ nm}$, observed by Secchi *et al.* [20]. It is known that the viscosity of water is smaller than the bulk value near the tube wall [22]. This could also reduce the size of the slip length. The Ohm’s law heating mechanism predicts a friction force inversely proportional to the conductivity. If the motion of the electrons in the tube wall is ballistic [23], as occurs as the tube radius decreases, there is no back scattering, due to impurities in the nanotube. Hence, there will be no Ohm’s law friction. Ballistic motion, however, will likely only come into play for tubes with much smaller radii.

There is another possible way to explain the observed increase in the slip length (i.e., decrease in the water-wall friction) with decreasing radius for water flowing through carbon nanotubes. When the tube radius is small enough, the electron wave function can be coherent around the tube circumference, and hence, the wave functions are standing waves around the circumference and propagating waves along

the tube axis. Thus, the tube is a one-dimensional conductor, and hence all of the electron wave functions are localized [24,25]. Under these circumstances, the Ohm's law heating friction mechanism that was described above will not give rise to friction because the charges on the water molecules are not able to pull charges in the tube wall along the tube as they flow. If, in contrast, the water flows through a tube of circumference larger than the mean-free path, however, since the electron wave functions will no longer be coherent around the tube's circumference, the electrons will not be able to distinguish the wall from a two-dimensional sheet of graphene, and hence the wall will no longer behave as a one-dimensional conductor but rather as a two-dimensional conductor. The electron wave functions in two-dimensional solids are not as strongly localized [26]. This means that friction due to Ohm's law heating will act on the water molecules, resulting in a smaller slip length. In fact, it is shown in Ref. [27] that the mobility for multiwalled nanotubes is about 220 cm²/Vs, from which, if one uses the free-electron mass for the electron effective mass, one gets a mean-free path of 110 nm. The tube circumference for a radius of 15 nm is 94 nm, whereas for 30 nm it is 188 nm. (On the other hand, the effective mass for a nanotube of these radii is much smaller than the free-electron value, but the mobility for graphene is much larger than the above.)

The above suggested mechanism for the observed increase in the slip length as the tube radius decreases will only work if the conductivity becomes completely zero when the tube behaves as a one-dimensional conductor. For most one-dimensional conductors, however, there is thermally activated hopping conductivity at any nonzero temperature. Therefore, the electrical conduction will not vanish, even if the tube behaves as a one-dimensional conductor at sufficiently small radius. This would be the case if the motion of the induced polarization charge is a result of electric current flow into the region of the wall that is under the moving water molecule or ion. The motion of induced charge can also result from local displacements of electrons occupying nearby localized states, however, rather than current flow. Since the amount of energy dissipated by this mechanism is likely much smaller than that due to current flow, the friction due to Ohm's law heating could become much smaller as the motion of the polarization charge switches from being dominated by electrical conduction to being dominated by local charge displacement. Let us examine this mechanism. The charge induced in the wall as a result of local displacement of the electronic charge in the wall is given by [21]

$$q_{\text{pol}} = -\frac{q}{2\pi} \frac{\varepsilon - \varepsilon_0}{\varepsilon + \varepsilon_0} h \int_0^\infty \frac{2\pi r dr}{(h^2 + r^2)^{3/2}} = -q \left(\frac{\varepsilon - \varepsilon_0}{\varepsilon + \varepsilon_0} \right). \quad (10)$$

Thus if the wall has a large dielectric constant, we would have $q_{\text{pol}} \approx -q$. The electric-field component parallel to the wall when the polarization is complete is given by

$$E_x = (4\pi\varepsilon_0)^{-1} \left[\frac{qx}{[r^2 + (z-h)^2]^{3/2}} + \frac{q_{\text{pol}}x}{[r^2 + (z+h)^2]^{3/2}} \right]_{z=0} \\ = \frac{q}{2\pi\varepsilon_0} \left(\frac{\varepsilon_0}{\varepsilon + \varepsilon_0} \right) \frac{x}{(r^2 + h^2)^{3/2}}, \quad (11)$$

and E_y is given by the above expression with x replaced by y , which can be small if $\varepsilon \gg \varepsilon_0$. Hence, the magnitude of the field in the plane of the wall is given by

$$E = (E_x^2 + E_y^2)^{1/2} = \frac{q}{2\pi\varepsilon_0} \left(\frac{\varepsilon_0}{\varepsilon + \varepsilon_0} \right) \frac{r}{(r^2 + h^2)^{3/2}}, \quad (12)$$

which is maximum when $r = 2^{-1/2}h$. Then, the rate of flow of electrons into the region in the wall opposite the molecule or ion under consideration is given by

$$\frac{dq_{\text{pol}}}{dt} = 2\pi r j_{\parallel} |_{r=2^{-1/2}h} \\ = 2\pi\sigma_{2d} \frac{q}{2\pi\varepsilon_0} \left(\frac{\varepsilon_0}{\varepsilon + \varepsilon_0} \right) \frac{r}{(r^2 + h^2)^{3/2}} |_{r=2^{-1/2}h} \\ = \left(\frac{2}{9} \right)^{3/2} \frac{\sigma_{2d}q}{(\varepsilon + \varepsilon_0)h}. \quad (13)$$

The timescale for displacement of the charge is the inverse of a vibrational frequency for the localized electrons, which is of the order of

$$\left(\frac{V_{\text{imp}}}{m\ell^2} \right)^{1/2}, \quad (14)$$

where V_{imp} is the mean impurity potential causing the localization, m is the electron mass, and ℓ is the localization length. Then, the condition for charge displacement to dominate over charge flow is

$$\left(\frac{2}{9} \right)^{3/2} \frac{\sigma_{2d}q}{(\varepsilon + \varepsilon_0)h} \ll q \left(\frac{V_{\text{imp}}}{m\ell^2} \right)^{1/2}. \quad (15)$$

Then,

$$\sigma_{2d} \ll \left(\frac{9}{2} \right)^{3/2} (\varepsilon + \varepsilon_0)h \left(\frac{V_{\text{imp}}}{m\ell^2} \right)^{1/2}. \quad (16a)$$

For $V_{\text{imp}} \approx 1$ eV, $\ell \approx 10^{-8}$ m, and $\varepsilon \gg \varepsilon_0$, we obtain

$$\sigma_{2d} \ll 0.339 \times 10^{-4} \Omega^{-1} \left(\frac{\varepsilon}{\varepsilon_0} \right). \quad (16b)$$

If $\varepsilon/\varepsilon_0$ and V_{imp} are large enough and/or if ℓ is small enough, the inequality in Eq. (16) will be satisfied, and hence, the motion of the polarization charge will result from local displacement of electrons occupying the localized states, rather than current flow. This means that the Ohm's law heating mechanism for friction does not operate. If the localization length is very long (as in weak localization) [25], the localized states occupied by the electrons will extend over a long distance along the tube. Therefore, the contribution to the polarization from a localized state due to an applied electric field along the tube E is given by

$$\Delta P \propto \sum_{n>1} [\varepsilon_1 - \varepsilon_n]^{-1} \left| \int dx \psi_n^* (x) x \psi_1 \right|^2 E, \quad (17)$$

where $\psi_1(x)$ is the lowest localized state that the electron under consideration can occupy, ψ_n denotes an excited state, and ε_1 and ε_n denote the energies of these states. Because of the large spatial extent of the localized states, the matrix

element can be large compared to atomic distances, leading to a large value of the permittivity ϵ . From the arguments given in Eqs. (10)–(16), the motion of the charge distribution induced in the wall due to the ion charges and water dipoles is likely to be dominated by local displacement of the electron charge as described above.

If the above is the correct mechanism for the observed increase of the slip length with decreasing tube radius, one prediction is that the radii at which this effect occurs should change if the degree of disorder in the tube is changed.

III. FILTRATION OF SALT WATER

Regarding the possibility of using this mechanism to filter out salt ions, since the friction force on a charged ion is given by

$$F \approx \frac{q^2 v}{16\pi \sigma_{2d} h^2}, \quad (18)$$

the total friction force acting on the ions is

$$F_i = \frac{1}{16\pi} \frac{q^2 v \rho_i L}{\sigma_{2d}} \int_0^{R-a} \frac{2\pi r dr}{(R-r)^2}, \quad (19)$$

where ρ_i is the number of ions per unit volume, giving

$$F_i = \frac{1}{16\pi} \frac{q^2 v \rho_i L}{\sigma_{2d}} \left[\frac{R}{a} - \ln\left(\frac{R}{a}\right) - 1 \right] \approx \frac{1}{16\pi} \frac{q^2 v \rho_i LR}{\sigma_{2d} a}. \quad (20)$$

For sea water, for example, there are about 35 g of salt per liter of water, or 35 000 g per cubic meter. Then there are $(35\,000/58)(6.02 \times 10^{23}) = 3.63 \times 10^{26} \text{ m}^{-3}$ salt molecules, and hence, $\rho_i = 7.26 \times 10^{26} \text{ m}^{-3}$. Using Eqs. (8) and (20), the rate at which work is done pushing the ions out of solution is given by

$$\begin{aligned} (F_i - F_w)v &= \rho_i \left(\frac{1}{16\pi} \frac{q^2 v LR}{\sigma_{2d} a} - \frac{1}{18} \frac{\langle p^2 \rangle v LR}{\sigma_{2d} a^3} \right) v \\ &= \frac{1}{16\pi} \frac{q^2 v^2 \rho_i LR}{\sigma_{2d} a} \left[1 - 3.32 \left(\frac{d}{a} \right)^2 \right], \end{aligned} \quad (21)$$

since $F_i - F_w$ is the amount that the friction force on the ions exceeds the friction force on the water molecules that they replaced when they were dissolved. In order to separate the ions from the water, this quantity must exceed the rate of doing work per unit area against the osmotic pressure, which is given by

$$\pi R^2 P_{\text{osm}} v = \pi R^2 \rho_i k_B T v, \quad (22)$$

where P_{osm} is the osmotic pressure due to the ions.

Then, we require that

$$\frac{1}{16\pi} \frac{e^2 v L}{\sigma_{2d} a R} \left[1 - 3.32 \left(\frac{d}{a} \right)^2 \right] > k_B T. \quad (23)$$

For sea water, $P_{\text{osm}} = (7.26 \times 10^{26} \text{ m}^{-3})(0.4 \times 10^{-20} \text{ J}) = 2.90 \times 10^6 \text{ Pa}$. Then, for a flow velocity of $v = 1 \text{ m/s}$, we find that the above equality will be satisfied if $L/R = 1.51 \times 10^4$. Again, we have been using for the conductivity one conductivity quantum. For smaller conductivity for the nanotube, the friction coefficient will be larger, and hence ion separation

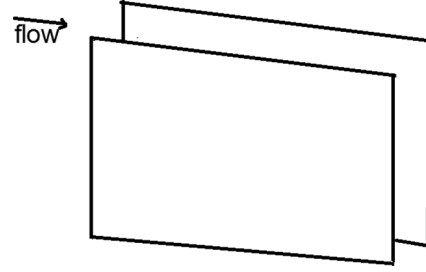


FIG. 2. Illustration of desalination by having salt water flow between two electrically conducting walls.

from the water can be accomplished for smaller values of L/R . For example, if the conductivity were smaller by a factor of 440, we would have $L/R = 34.3$.

Filtration of salt ions in carbon nanotubes will probably not be a large enough effect to be useful because salt that is removed will eventually clog the tube. If salt water is made to flow between an array of closely spaced graphene sheets (containing imperfections to increase their electrical resistance), however, the salt that is removed can be prevented from clogging the system because if the plates are vertical, the precipitated salt will be removed by gravity from between the plates.

Then, consider filtration resulting from two graphene sheets of length L along the flow direction, width W , and spacing ℓ , as illustrated in Fig. 2. The mean force on a single water molecule is due to a wall a distance h away, which from the previous expression from a single water molecule of a given dipole moment is given by

$$\langle f \rangle = \frac{\langle p^2 \rangle v}{12\pi \sigma_{2d} h^4}, \quad (24)$$

and the force on an ion was shown in Appendix B [Eq. (B6)] to be given by

$$f = \frac{q^2 v}{16\pi \sigma_{2d} h^2}. \quad (25)$$

Then, the difference between the total force that the walls exert on the ions and the water molecules that they replace (because they are dissolved) is given by

$$\begin{aligned} F_i - F_w &= LW \int_a^{\ell-a} dh \rho_i \left(\frac{q^2 v}{16\pi \sigma_{2d} h^2} - \frac{\langle p^2 \rangle v}{12\pi \sigma_{2d} h^4} \right) \\ &\approx \left[1 - \frac{4}{9} \left(\frac{d}{a} \right)^2 \right] \frac{LW e^2 \rho_i v}{16\pi \sigma_{2d} a}, \end{aligned} \quad (26)$$

where a is the distance of closest approach of the ions and molecules to a wall and d is defined by $p = ed$. In order to filter out the salt ions, we require that the pressure due to the above force (i.e., the above force divided by the area $W\ell$) must exceed the osmotic pressure that keeps the salt dissolved, $\rho_i k_B T$. This gives the condition

$$k_B T < \left[1 - \frac{4}{9} \left(\frac{d}{a} \right)^2 \right] \frac{L}{\ell} \frac{e^2 v}{16\pi \sigma_{2d} a}. \quad (27)$$

Since in mks units, $\varepsilon_0 v / \sigma_{2d}$ is dimensionless, the right-hand side has units of joules. For sea water, we estimate that this inequality is satisfied if $L/\ell > 2.36 \times 10^5$, for $v = 1$ m/s. If σ_{2d} were smaller by a factor of 440 (the value at which this friction mechanism would give the slip length reported in Ref. [20]), this inequality would be satisfied for $L/\ell > 536$. Perhaps we should use on the left-hand side the measured heat of solution instead of the osmotic pressure divided by ρ_i . The heat of solution is about 3×10^3 J/mol and since the number of moles per cubic meter is given by ρ_i divided by Avogadro's number, or $7.26 \times 10^{26} \text{ m}^{-26} / (6.02 \times 10^{23}) = 1.21 \times 10^3 \text{ mol/m}^3$, the heat of solution per unit volume is equal to $(3 \times 10^3 \text{ J/mol})(0.603 \times 10^3 \text{ mol/m}^3) = 3.62 \times 10^6 \text{ J/m}^3$, compared to the osmotic pressure, which is given by $\rho_i k_B T = (7.26 \times 10^{26} \text{ m}^{-3})(0.4 \times 10^{-20} \text{ J}) = 2.90 \times 10^6 \text{ J/m}^3$.

When the left and right side of Eq. (27) are equal

$$v = v_i = \frac{k_B T \ell}{\Gamma L}, \quad (28)$$

where v is the velocity of the water, v_i is the velocity of the ions, and

$$\Gamma = \left[1 - \frac{4}{9} \left(\frac{d}{a} \right)^2 \right] \frac{q^2}{16\pi\sigma_{2d}a} \approx 1.7 \times 10^{-24} \text{ J}, \quad (29)$$

for $\sigma_{2d} = 10^{-6} \Omega^{-1}$. The value of v_i when the inequality in Eq. (27) is satisfied is obtained by setting the difference between the total friction force due to the walls acting on the ions and its value acting on the water molecules replaced by the ions equal to the sum of the force due to osmotic pressure and the friction force that the flowing water exerts on the ions,

$$LW \rho_i \Gamma v_i = W \ell \rho_i k_B T + LW \ell \rho_i \gamma (v - v_i), \quad (30)$$

where γ is the proportionality constant between the friction drag force that the water exerts on an ion and the difference between the water and ion velocities. Equation (30) can be solved for $v - v_i$,

$$v - v_i = \frac{\Gamma}{\ell \gamma} \left(v_i - \frac{k_B T \ell}{\Gamma L} \right). \quad (31)$$

The magnitude of γ (which is the inverse ion mobility) can be estimated from typical measured values of the ion diffusion constant D using the Einstein relation, $\gamma = k_B T / D$, where $D \approx 1.16 \times 10^{-9} \text{ m}^2/\text{s}$ [28]. The electrical conductivity of a sodium chloride solution with salt concentration equal to that in sea water is reduced by a factor of 0.615 from its zero concentration value because of the attraction of oppositely charged ions [29]. Since the diffusion constant of the ions is proportional to the conductivity, it is also reduced by this factor. The friction constant is given by $\gamma = k_B T / D = 0.345 \times 10^{-11} \text{ N s/m}$. This value of γ , however, includes the attraction between oppositely charged ions mentioned above. Since the value of γ that we need here describes the force due to the water moving past the ions, which does not push the positive and negative ions in opposite directions, as occurs in ionic conduction and the diffusion of ions in salt solution, we need to multiply the above value by 0.615, giving $\gamma \approx 0.212 \times 10^{-11} \text{ N s/m}$. For the above value of Γ , we obtain $\Gamma / \ell \gamma \approx 6.94 \times 10^{-5} v$. The attractive force between each ion and its polarization charge in a wall will pull the ions towards the walls. Therefore, if as a result of this attractive force the

ions are concentrated within a distance $\Delta h \approx 1$ nm or less, the value of ρ_i used in the integral in Eq. (26) to calculate the value of Γ that occurs in Eq. (30) will increase by a factor of $\ell / \Delta h$, which can be about an order of magnitude. It takes a time L/v for all the water molecules to travel through the tube, whereas it takes a time L/v_i for the salt ions to travel through the tube. In that time, the ions presently dissolved in the water between the plates will have only moved a distance $(v_i/v)L$. Within this distance, the ion concentration has increased by at least a factor L divided by $(v_i/v)L$, or v/v_i . When the salt concentration exceeds its solubility, salt will precipitate out and drop into the region below the plates, which could contain water to wash away the precipitated salt. Further along the plates, the water will be pure. This cannot occur for the parameters that we used in Eq. (31) to calculate v_i , however. In order for desalination to occur, we would need to use a material with σ_{2d} a factor of 10^3 smaller. Alternatively, if instead of using a two-dimensional conductor like graphene we used a three-dimensional conductor, we would use Boyer's expression for the force of friction acting on an ion [16–18],

$$f = \frac{q^2}{16\pi\sigma_{3d}h^3}, \quad (32)$$

in Eq. (26), where σ_{3d} denotes the conductivity of a three-dimensional conductor. Then, we would need to use a material with $\sigma_{3d} = 1.67 (\Omega \text{ m})^{-1}$ or less. The advantages of this method over other desalination methods are that there are no filters to get blocked by salt that is filtered out of porous capacitor plates (in capacitive desalination) that must have ions removed from them periodically, as well as its simplicity.

Alternatively we could use image charge forces to desalinate water using the same parallel plate geometry. The ions will be attracted to the plates, and if the salt concentration exceeds the solubility of the salt, it will precipitate out of solution. The salt might then be pulled out from between the plates by gravity. This method might be more effective than the previously discussed method that uses electronic friction, because the attractive image charge forces acting on the ions are orders of magnitude larger than the electronic friction. More details will be given in a future publication.

For high salt concentrations, as occur in sea water, the Debye-Huckel screening length can be comparable to a , so that Debye-Huckel screening can have an effect on the friction due to Ohm's law heating. In order to calculate its effect we apply the image charge method to the screened potential

$$V(r) = \frac{1}{4\pi\epsilon} \frac{q}{r} e^{-k_s r}, \quad (33a)$$

where $r = [(x - vt)^2 + y^2 + (z - h)^2]^{1/2}$. Its image potential is given by

$$V_{\text{imag}}(r) = -\frac{1}{4\pi\epsilon} \frac{q}{r'} e^{-k_s r'}, \quad (33b)$$

where $r' = [(x - vt)^2 + y^2 + (z + h)^2]^{1/2}$. The resulting charge distribution induced in a wall is given by

$$\begin{aligned} \sigma(\vec{r}) &= -\epsilon \frac{\partial}{\partial z} [V(r) - V_{\text{imag}}(r)]_{z=0} \\ &= \frac{1}{4\pi} \left[\frac{k_s h}{(r'^2 + h^2)} + \frac{h}{(r'^2 + h^2)^{3/2}} \right] e^{-2k_s (r'^2 + h^2)^{1/2}}, \quad (34) \end{aligned}$$

where $r'^2 = (x - vt)^2 + y^2$. Then, using the procedure used in Eq. (4), we obtain

$$f(h) = \sigma_{2d}^{-1} \frac{v\pi}{(4\pi)^2} \int_0^\infty du \left[\frac{k_s^2 h^2}{(u + h^2)^2} + \frac{h^2}{(u + h^2)^3} + \frac{k_s h^2}{(u + h^2)^{5/2}} \right] e^{-2k_s(u+h^2)^{1/2}}, \quad (35)$$

where $u = r'^2$. The total force on the ions is given by

$$F_x = LW \rho_i \int_a^\infty dh f(h), \quad (36)$$

which, when integrated numerically for $k_s^{-1} = a$, we obtain a value which is about 1/4 of what was obtained without screening.

IV. CONCLUSIONS

It is shown theoretically that when salt water flows through conducting nanotubes or between closely spaced graphene sheets, it is subject to forces of friction acting on the water molecules and the salt ions due to Ohm's law heating resulting from a charge distribution induced in the conducting walls, which is dragged along with the flowing water and ions. Because this friction force acting on the ions is larger than that acting on the water molecules, this can be an effective mechanism for filtering ions out of the water. A mechanism is provided for how this friction due to Ohm's law heating could explain the observed rapid increase in the slip length reported in Ref. [20], for water flowing in carbon nanotubes.

APPENDIX A: CORRECTIONS TO REF. [19]

In Ref. [19], it was proposed that the observation of a rapid increase of the slip length with decreasing nanotube radius reported in Ref. [20] could be accounted for by the decrease in the number of conduction electrons as the tube radius decreases, resulting in a decrease in the friction experienced by the water flowing in the tube due to intraband excitation of conduction electrons. Here it will be pointed out that, at least on the basis of the usual theoretical treatment of the electronic states of single-wall carbon nanotubes, the contribution of electronic excitations to the friction is too small to explain the experiments. The slip length is given by $L_s = \eta/\lambda$, where η is

the viscosity of the water and λ is the friction coefficient for the force of friction exerted by the walls on the water, which is given by the mechanism discussed in Ref. [19] by

$$\begin{aligned} \lambda &= \frac{e^2 p^2 k_e^2}{24\pi^2 \hbar R^2} I \frac{\langle G_x^2 \rangle^{1/2}}{k_B T} \rho \frac{\hbar}{v_F R} \sum_{\alpha, \pm} |\alpha \pm 1/3| \\ &\times \exp\left(-\frac{|\alpha \pm 1/3| g_0}{k_B T}\right) \\ &= \frac{e^2 p^2 k_e^2}{24\pi^2 R^2} I \frac{\langle G_x^2 \rangle^{1/2}}{k_B T} \rho \frac{1}{v_F R^3} x^3 \sum_{\alpha, \pm} |\alpha \pm 1/3| \\ &\times \exp(-|\alpha \pm 1/3|x), \end{aligned} \quad (A1)$$

or

$$\lambda = \lambda_0 x^3 \sum_{\alpha, \pm} |\alpha \pm 1/3| \exp(-|\alpha \pm 1/3|x), \quad (A2)$$

where $x = R_0/R$, where R is the tube radius, $R_0 = g_0 R/(k_B T)$, and α is summed from 1 to infinity and

$$\lambda_0 = \frac{k_e^2 p^2 e^2 I \langle G_x^2 \rangle^{1/2} \rho}{24\pi^2 R_0^3 k_B T v_F}. \quad (A3)$$

This is a corrected version of the expression for λ which includes the R dependence of the circumference and the effective mass, which was not included in the expression for it in Ref. [19]. For $v_F = 8 \times 10^5$ m/s, $R_0 = 13.3$ nm, $\lambda_0 = 0.129$ N s/m³. At $R = R_0 = 13.3$ nm, $\lambda = 1.74$ N s/m³, which for $\eta = 10^{-3}$ N s/m², gives a slip length (if this were the only source of friction) of 0.575 mm compared with the observed slip length at this radius of 300 nm = 0.3×10^{-3} mm. Also, for single-walled carbon nanotube electronic structure used in Ref. [19], the gap becomes much smaller than $k_B T$ at much smaller values of R than the values at which the rapid increase in the slip length reported in Ref. [20] is observed to occur.

APPENDIX B: A DIRECT CALCULATION OF THE FORCE ON A MOVING MOLECULE OR ION DUE TO BOYER'S OHM'S LAW HEATING FRICTION

The x component of the electric field on the wall due to a charge q moving at velocity v is given by

$$E_x = \frac{q}{4\pi\epsilon} \left[\frac{x - vt}{[(x - vt)^2 + y^2 + h^2]^{3/2}} - \frac{x - 2\Delta x - vt}{[(x - 2\Delta x - vt)^2 + y^2 + h^2]^{3/2}} \right] \approx -\frac{q}{4\pi\epsilon_0} \frac{2\Delta x}{[(x - vt)^2 + y^2 + h^2]^{3/2}}. \quad (B1)$$

Then, since by Ohm's law

$$\sigma_{2d} E_x = v\sigma(\vec{r}), \quad (B2)$$

we have

$$\sigma_{2d} \frac{q}{2\pi\epsilon} \frac{\Delta x}{[(x - vt)^2 + y^2 + h^2]^{3/2}} \approx \frac{q\hbar v}{2\pi[(x - vt)^2 + y^2 + h^2]^{3/2}}, \quad (B3)$$

or

$$\frac{\Delta x}{h} \approx \frac{\varepsilon v}{\sigma_{2d}}, \quad (\text{B4})$$

where $\sigma_{2d}/\varepsilon = (0.451 \times 10^7 \text{ m/s})(\varepsilon_0/\varepsilon) = 0.151(\varepsilon_0/\varepsilon)c$, for $\sigma_{2d} = 0.4 \times 10^{-4} \Omega^{-1}$, where c is the speed of light. [It is equal to $0.0169c (\varepsilon_0/\varepsilon)^{1/2}$ for $\varepsilon/\varepsilon_0 = 80$, where $c(\varepsilon_0/\varepsilon)^{1/2}$ is the speed of light in the water.] Thus, the amount of lag of the image charge behind the ion due to retardation effects is considerably smaller than the amount of lag due to Ohm's law considered here. (σ_{2d} is likely smaller than the value used here.) Let us now calculate the field due to the image charge at the location of the point charge, in order to determine the friction force on the point charge. Evaluating the contribution due to the image charge in the above expression for E_x evaluated at the coordinates of the point charge [i.e., $(vt, 0, h)$], we obtain

$$E_x(vt, 0, h) = \frac{q\Delta x}{2\pi\varepsilon_0} \frac{1}{[\Delta x^2 + (2h)^2]^{3/2}} \approx \frac{q\Delta x}{16\pi\varepsilon h^3} = \frac{q}{16\pi\varepsilon h^3} \left(\frac{\varepsilon h v}{\sigma_{2d}} \right) = \frac{qv}{16\pi\sigma_{2d}h^2}, \quad (\text{B5})$$

giving a force of friction

$$F_x = qE_x = \frac{q^2 v}{16\pi\sigma_{2d}h^2}. \quad (\text{B6})$$

A similar thing must happen for a moving dipole, because Δx is independent of the sign of the charge. Thus each charge in the dipole will need to move ahead of its image charge by the same amount Δx , implying that the dipole must move ahead of the charge distribution that it produces in the tube wall.

Let us determine the friction acting on a moving dipole due to Ohm's law heating by calculating the electric field acting on the dipole due to its electrical image. Since if the image dipole were directly below the moving dipole above the wall, the component of the electric field at the moving dipole due to its image charge would be zero, the image must lag behind the moving dipole above the wall by an amount $2\Delta x$, so that the charge induced in the wall lags behind by Δx , with Δx chosen so that the moving charge density induced in the wall satisfies Ohm's law. Then, the electrical potential due to both the dipole above the wall and its image is given by

$$V = \frac{1}{4\pi\varepsilon_0} \left[\frac{\vec{p} \cdot \vec{r}'}{r'^3} + \frac{\vec{p}' \cdot \vec{r}''}{r''^3} \right], \quad (\text{B7})$$

where $\vec{p} = (p_x, p_y, p_z)$, $\vec{p}' = (-p_x, -p_y, p_z)$, $\vec{r}' = [x - vt, y, z - h]$, and $\vec{r}'' = [x - vt - 2\Delta x, y, z + h]$. Then,

$$\begin{aligned} \sigma(\vec{r}) &= -\varepsilon \frac{\partial V}{\partial z} \Big|_{z=0} = \frac{1}{4\pi} \left[\frac{2p_z}{r'^3} - \frac{3[p_x(x - vt) + p_y y - p_z h](-h)}{r'^5} - \frac{3h[-p_x(x - vt - 2\Delta x) - p_y y + p_z h]}{r''^5} \right] \\ &= \frac{1}{2\pi} \left[\frac{p_z r'^2 + 3h[p_x(x - vt) + p_y y - p_z h]}{r'^5} \right], \end{aligned} \quad (\text{B8})$$

to zeroth order in Δx . Also,

$$\begin{aligned} E_x|_{z=0} &= -\frac{\partial V}{\partial x} \Big|_{z=0} \\ &= -\frac{1}{4\pi\varepsilon} \left[\frac{p_x}{r'^3} - \frac{p_x}{r''^3} - \frac{3[p_x(x - vt) + p_y y - p_z h](x - vt)}{r'^5} - \frac{3[-p_x(x - vt - 2\Delta x) - p_y y + p_z h](x - vt - 2\Delta x)}{r''^5} \right] \\ &\quad \times \frac{1}{4\pi\varepsilon_0} \left[\frac{10p_x(x - vt) + 6p_y y - 6p_z h}{r'^5} \right] \Delta x = \frac{1}{2\pi\varepsilon_0} \left[\frac{5p_x(x - vt) + 3p_y y - 3p_z h}{r'^5} \right] \Delta x. \end{aligned} \quad (\text{B9})$$

From Ohm's law

$$\sigma_{2d} E_x = j_x = v\sigma(\vec{r}), \quad (\text{B10})$$

we get

$$\Delta x = \frac{\varepsilon V}{\sigma_{2d}} \frac{p_z r'^2 + 3h[p_x(x - vt) + p_y y - p_z h]}{5p_x(x - vt) + 3p_y y - 3p_z h} = \frac{2\varepsilon v h}{3\sigma_{2d}} \quad (\text{B11})$$

on the wall (i.e., for $x = vt$, $y = 0$, $z = 0$). The frictional force acting on the moving dipole is given by

$$f = \frac{\partial}{\partial x} (\vec{p} \cdot \vec{E}_{\text{image}}) \Big|_{x=vt, y=0, z=h}, \quad (\text{B12})$$

where

$$\vec{E}_{\text{image}} = \frac{1}{4\pi\epsilon} \left[\frac{3(\vec{p}' \cdot \vec{r}'')\vec{r}''}{r''^5} - \frac{\vec{p}'}{r''^3} \right]. \quad (\text{B13})$$

Then,

$$\vec{p} \cdot \vec{E}_{\text{image}} = \frac{1}{4\pi\epsilon} \left[\frac{3(\vec{p} \cdot \vec{r}'')(\vec{p}' \cdot \vec{r}'')}{r''^5} - \frac{\vec{p} \cdot \vec{p}'}{r''^3} \right]. \quad (\text{B14})$$

Hence,

$$f = \frac{\partial}{\partial x} (\vec{p} \cdot \vec{E}_{\text{image}}) = \frac{1}{4\pi\epsilon} \left[\frac{3\vec{p} \cdot \vec{p}'(x - vt - 2\Delta x)}{r''^5} + \frac{3[p_x'(\vec{p} \cdot \vec{r}'') + p_x(\vec{p}' \cdot \vec{r}'')]}{r''^5} - \frac{15(\vec{p}' \cdot \vec{r}'')(\vec{p} \cdot \vec{r}'')(x - vt - 2\Delta x)}{r''^7} \right], \quad (\text{B15})$$

evaluated at the location of the dipole ($x = vt$, $y = 0$, $z = h$). Then,

$$\begin{aligned} f &\approx \frac{1}{4\pi\epsilon} \left[\frac{12p_x^2}{32h^5} + \frac{30p_z^2}{32h^5} - \frac{6(2p_z^2 - p^2)}{32h^5} \right] \Delta x = -\frac{1}{4\pi\epsilon} \left[\frac{18p_z^2 + 12p_x^2 + 6p^2}{32h^5} \right] \Delta x|_{x=vt, y=0, z=0} \\ &= \frac{3}{2\pi\epsilon} \left[\frac{3p_z^2 + 2p_x^2 + p^2}{32h^5} \right] \Delta x|_{x=vt, y=0, z=0} \end{aligned} \quad (\text{B16})$$

to first order in Δx , or

$$f = \frac{3}{2\pi\epsilon} \frac{3p_z^2 + 2p_x^2 + p^2}{32h^5} \frac{2\epsilon v h}{3\sigma_{2d}} = \frac{1}{\pi} \frac{3p_z^2 + 2p_x^2 + p^2}{32\sigma_{2d} h^4} v. \quad (\text{B17})$$

The average of this force over all directions of \vec{p} gives

$$\langle f \rangle = \frac{\langle p^2 \rangle v}{12\pi\sigma_{2d} h^4}. \quad (\text{B18})$$

In the above calculation of F_x , Δx was evaluated at $z = 0$ for all values of x and y , which choice guarantees that

$$\sigma_{2d} E_x|_{z=0} = v\sigma(\vec{r}). \quad (\text{B19})$$

The force normal to the wall is given to lowest order in Δx by

$$\begin{aligned} F_z &= \frac{\partial}{\partial z} (\vec{p} \cdot \vec{E}') = \frac{1}{4\pi\epsilon} \left[3 \frac{p_z'(\vec{p} \cdot \vec{r}'') + p_z(\vec{p}' \cdot \vec{r}'')}{r''^5} - \frac{3\vec{p}' \cdot \vec{p}}{r''^5} \right] = \frac{1}{4\pi\epsilon} \left[\frac{18p_z^2}{32h^4} + \frac{6(p_z^2 - p_x^2 - p_y^2)}{32h^4} \right] \\ &= \frac{3}{\pi\epsilon} \left[\frac{2p_z^2 - (p_x^2 + p_y^2)}{32h^5} \right]. \end{aligned} \quad (\text{B20})$$

When this expression (B21) is averaged over all directions of \vec{p} , we obtain $\langle F_z \rangle = 0$.

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