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Ion selectivity using membranes comprising functionalized carbon nanotubes

Yue Chan · James M. Hill

Abstract In this paper, we use applied mathematical modelling to investigate the transportation of ions inside functionalized carbon nanotubes, and in particular the transport of sodium and chloride ions. This problem is important for future ion transport and detection, and also arises in ion diffusion inside complex biological channels. Some important future applications of the system for a solvent are ultra-sensitive biosensors and electrolytes for alkaline fuel cells. We model the interactions between the ions and the nanotube by the Lennard-Jones potential and the interactions between the ions and the functional group by the Coulomb potential, while the atomic interactions between the ions is modeled by both the Lennard-Jones and Coulomb potentials. We further assume that the carbon atoms, the charge of the functional group, and the ions are all evenly distributed on the surface of the nanotube, the entry of the nanotube and the envisaged ionic surface, respectively, so that we may use the continuous approximation to calculate the corresponding potential energies. For nanotubes located in salt water, the molecular effects arising from the bulk solution can be extracted from MD simulation studies. Assuming that the solvent is absent, we first determine the acceptance radii for the sodium or chloride ion entering the nanotube, both with and without a functional group, and we then determine the equilibrium positions of two identical ions inside the nanotube. Finally, the transportation time of an intruding ion through the nanotube is deduced from the total axial force. In the presence of a solvent,

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the molecular effects arising from the bulk solution are examined and we establish that the presence of a solvent stabilizes the selectivity of the ions.

Keywords   Sodium ion · Chloride ion · Carbon nanotube ·
Continuous approximation · Ion transportation

1 Introduction

Carbon nanotubes have been extensively investigated and may be used as water channels [1–12]. Recently, increasing attention has been given to the engineering design of ion-selective nanotubes that could be exploited as nanodevices, such as ultrasensitive biosensors and anion exchange components for alkaline fuel cells. Such knowledge would enhance our fundamental understanding of ion processes inside complex biological channels [13,14]. Ion-selective nanotubes have been extensively and theoretically investigated [15–18]. By decorating the nanotube rim with different functional groups at the nanotube entrance, they can be used to selectively permeate cations and anions [16,19]. In addition, normally when carbon nanotubes are cut, their dangling bonds react with the fluid environment, so that most nanotubes do indeed have functionalized ends. These theoretical studies recognize the possible use of carbon nanotubes as a means of ion transport, and an excellent survey of mass transport including ions, gases and liquids can be found in Majumder et al. [20].

In this paper, we use applied mathematical modelling to predict the ion selectivity (sodium and chloride ions) using functionalized (for example, carboxylic groups -COOH) carbon nanotube membranes [19,21]. Our principal contribution here is the use of applied mathematical modelling in contrast to the molecular dynamics simulations presented in [16,19]. Essentially, the modelling approach adopted here determines average or representative numerical values of the various physical quantities. Although the paper is an illustration of the expansion of mathematical modelling into the realm of nanotechnology for complex atomic interactions, this approach can never replace the detailed information that might be obtained from computational simulations such as MD. Here, the total axial forces for sodium and chloride ions are determined using a hybrid approach which combines both the discrete and the continuous approaches, so as to determine acceptance radii for the sodium and chloride ions. Accordingly, the ionic configuration and transportation times are determined inside functionalized nanotubes. The continuous approximation adopted in this paper has been successfully used to investigate the relative motion of certain nanostructures, such as the oscillation of fullerenes or ultra-small nanotubes inside a single-walled carbon nanotube [22,23], the encapsulation of drug molecules inside single-walled nanotubes for drug delivery [24,25], the diffusion and the storage of lithium ions between graphene sheets [26,27], the hydrogen storage inside the graphene-oxide frameworks [28], the transportation of water molecules inside ultra-small carbon nanotubes [12,29], the dynamics of molecular rotors and motors [30], and the shuttle memory nanodevice using metallofullerenes and carbon nanotubes [31].

In Sect. 2, we present the 6–12 Lennard-Jones continuous approximation and the required equations of motion in the context of the current investigation. Numerical
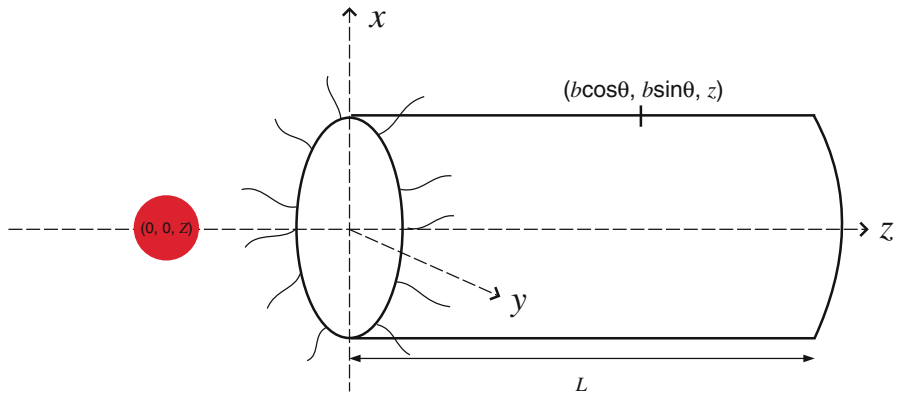
Fig. 1 Ion penetrating nanotube of length L decorated by functional group at entry

results and discussion are presented in Sect. 3 and a general conclusion is provided in the final section of the paper.

2 Theory

In this section, we present the theoretical background for the paper. First, we assume that the sodium and chloride ions to be a van der Waals gas, and we determine the acceptance radius for a sodium or chloride ion penetrating into a carbon nanotube. Certain physical effects have been ignored, including the cost of stripping water from ions, any movement of the proposed functional groups at the tube ends, and the image forces as the ions approach the narrow cylindrical opening of the nanotube. We next determine the equilibrium configurations for two identical ions inside the nanotube, from which a transportation time of an ion through a nanotube of a certain length can be subsequently deduced. We then model the van der Waals interactions between ions, and between the ion and the nanotube, using the standard non-bonded 6–12 Lennard-Jones potential, $V_L(\rho)$ which for two non-bonded atoms is given by [32] (Fig. 1)

$$V_L(\rho) = 4\varepsilon\left[-\left(\frac{\sigma}{\rho}\right)^6 + \left(\frac{\sigma}{\rho}\right)^{12}\right] = -\frac{A}{\rho^6} + \frac{B}{\rho^{12}}, \tag{1}$$

where ρ, ε and σ denote the distance between two arbitrary atoms, the potential well depth of two atoms, and the Lennard-Jones distance between two atoms, respectively. In addition, $A = 4\varepsilon\sigma^6$ and $B = 4\varepsilon\sigma^{12}$ denote the attractive and repulsive Lennard-Jones constants, respectively. We model the interactions between the intruding ion and the functional group by the Coulomb potential, and the interactions between ions using both the Lennard-Jones potential and the Coulomb potential, $V_E(\rho)$, which is given by

$$V_E(\rho) = \frac{q_1 q_2}{\epsilon\rho}, \tag{2}$$

where q_1, q_2 and ε denote the charge for the first atom, the charge for the second atom and the dielectric constant for the system, respectively. While the electrostatic interactions between ions are simply determined using the pairwise approach, we assume that the total charge of the functional group, the carbon atoms and the ion can be smeared over the nanotube entry, the surface of the nanotube of radius b and an envisaged spherical surface of radius a, respectively. In this way, the continuous approximation [22,23] can be used to determine the total Lennard-Jones interactions between the ions as well as between the ion and the nanotube, and the total electrostatic interactions between the ion and the functional group. First, we estimate the minimum radius of the nanotube for which an ion can be sucked into the nanotube without external forces and fluctuations, that is, we determine the acceptance radius as formulated by Cox et al. [22]. The authors of [22] show that the critical acceptance radius of the nanotube is the radius above which the acceptance energy E_a is positive, and is given by the expression

$$E_a = \frac{qQ}{\varepsilon}\left[\frac{1}{\sqrt{Z_0^2 + b^2}} - \frac{2}{b}\right] + \frac{8b\pi^2\eta_i\eta_t}{a^2\sqrt{b^2 - a^2}}\left[A(\Lambda_2 + 2\Lambda_3) - \frac{B}{5a^6}(5\Lambda_5 + 80\Lambda_6\right.$$
$$\left. + 336\Lambda_7 + 512\Lambda_8 + 256\Lambda_9)\right] - \int_{-\infty}^{Z_0}\mathcal{R}\,dZ, \tag{3}$$

where A, B, q, Q, η_i, η_t and $\mathcal{R}$ denote the attractive constant between the ion and the nanotube, the repulsive constant between the ion and the nanotube, the ion charge and the total charge of the functional group at the nanotube entry, the number density of ion, the number density of carbon atoms on the nanotube surface and the external forces and fluctuations, respectively. Further, the quantity $\mathcal{R}$ is assumed to have the following analytical form

$$\mathcal{R} = -\{1 - H(Z)\}\{1 - exp(Z)\}(\delta E/\delta Z)_B, \tag{4}$$

where $H(\cdot)$, and $(\delta E/\delta Z)_B$ denote the Heaviside step function, and the molecular force arising from the bulk solution, respectively. We comment that while the Heaviside function defines a cut-off effect which is outside the nanotube pore, the exponential function defines the strength of the force, which diminishes towards the nanotube entry. In addition, Λ_n and ψ_0 are defined respectively by $\Lambda_n = a^{2n}(b^2 - a^2)^{-n}\int_{-\pi/2}^{\psi_0}(\cos^{2n}\psi)d\psi$ and $\psi_0 = \tan^{-1}(Z_0/\sqrt{b^2 - a^2})$, and the value of Z_0 is the point where the axial force F_z is zero, and is determined from

$$F_z(Z) = \frac{8\pi^2\eta_i\eta_t b}{a^4\lambda^3}\left[A\left(1 + \frac{2}{\lambda}\right) - \frac{B}{5a^6\lambda^3}\left(5 + \frac{80}{\lambda} + \frac{336}{\lambda^2} + \frac{512}{\lambda^3} + \frac{256}{\lambda^4}\right)\right]$$
$$- \frac{qQ|Z|}{\varepsilon(Z^2 + b^2)^{3/2}} + \mathcal{R}, \tag{5}$$
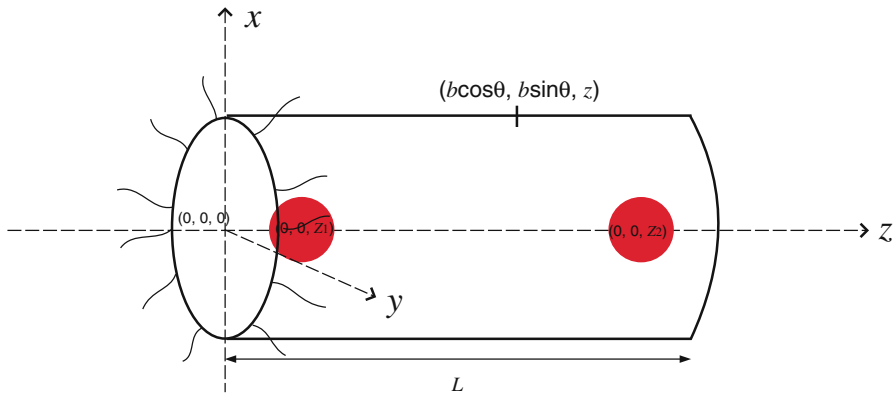
Fig. 2 Two ions positioned at symmetric minimum energy locations

where $\lambda = (b^2 - a^2 + Z^2)/a^2$. Given that the acceptance criteria is satisfied so that a single ion can be sucked into the nanotube, the subsequent flow possibilities are unlimited. Here, we assume that the tube length is such that two identical ions are located at the minimum energy positions at the tube extremities, which arises from the mutually repulsive electrostatic force between the ions and the proposed charges at the nanotube ends. This may be confirmed from the numerical results determined from the molecular dynamics simulations [19,33] and presented in Sect. 3. A schematic of the proposed system is as shown in Fig. 2.

Here, we determine the total energy of the system which is the sum of the interactions between ions, the ions and the functional group at the nanotube entry, as well as between the ions and the nanotube. We model the interaction between ions, that is $E_{i_1 i_2}$, where i_1 and i_2 denote the first and the second ion, respectively by both the Coulomb and Lennard-Jones potentials using the hybrid pairwise and continuous approaches. In addition, we model the interactions between the ion and the nanotube, that is $E_{i_1 t}$ and $E_{i_2 t}$, where t denotes the nanotube, by the Lennard-Jones potential using the continuous approximation. For the interactions between the ions and the functional groups at the nanotube entry, that is $E_{i_1 f}$ and $E_{i_2 f}$, we consider only the electrostatic energy using the continuous approximation. The total potential energy of the system E, assuming only two identical ions situated inside the nanotube, can therefore be written as

$$E = E_{i_1 i_2} + E_{i_1 t} + E_{i_2 t} + E_{i_1 f} + E_{i_2 f}, \tag{6}$$

where $E_{i_1 i_2}$, $E_{i_1 t}$, $E_{i_2 t}$, $E_{i_1 f}$ and $E_{i_2 f}$ denote respectively the following expressions:

$$E_{i_1 i_2} = \frac{\pi^2 a^2 \eta_i^2}{3r} \left\{ -A_i \left[\frac{1}{(2a+r)^3} - \frac{1}{(2a-r)^3} - \frac{2}{r^3} \right] + \frac{2B_i}{15} \left[\frac{1}{(2a+r)^9} - \frac{1}{(2a-r)^9} - \frac{2}{r^9} \right] \right\}$$
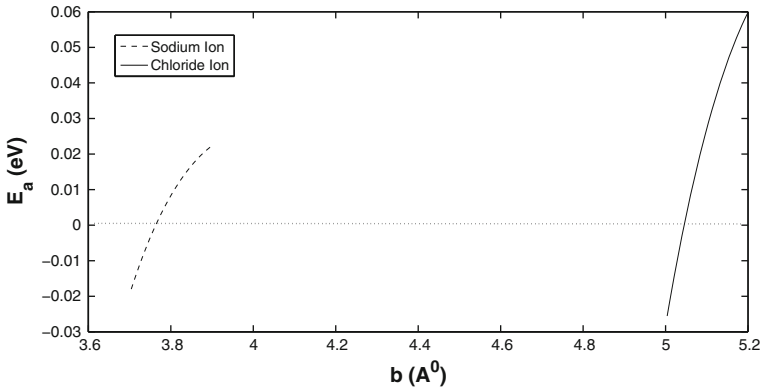$$+ \frac{q^2}{\varepsilon r},$$

Fig. 3 Acceptance energies for sodium and chloride ions for single-walled carbon nanotube

$$E_{i_1,i_2 t} = 4\pi^2 \eta_i \eta_t ab \int\limits_{z=0}^{L} \frac{1}{\rho} \left\{ \frac{A}{4} \left[\frac{1}{(a+\rho)^4} - \frac{1}{(a-\rho)^4} \right] - \frac{B}{10} \left[\frac{1}{(a+\rho)^{10}} - \frac{1}{(a-\rho)^{10}} \right] \right\} dz,$$

$$E_{i_1,i_2 f} = \frac{Qq}{\varepsilon\sqrt{Z^2 + b^2}},$$

where Z is either Z_1 or Z_2 (see Fig. 2), $r = Z_2 - Z_1$ and $\rho = \sqrt{b^2 + (z - Z)^2}$.

3 Numerical results and discussion

In this section, we present the numerical results arising from the theory presented in the previous section, with the numerical values of all the necessary parameters as given in Table 1. Using Eq. (3) we first determine the acceptance criteria for a sodium or chloride ion intruding axially into an infinitely long single-walled carbon nanotube. We comment that if water enters the tube with the ions, then for this combined problem the whole dynamics of acceptance would be changed, and such a calculation would need to be undertaken using molecular dynamics simulations.

3.1 Van der Waals gases

For simplicity, we first assume that both sodium and chloride ions are a van der Waals gas, by which we mean that a hypothetical gas whose molecules bounce off each other with perfect elasticity and possess negligible size, and the intermolecular forces acting between molecules are negligible while they are not in contact. By setting the total charge of the functional group $Q = 0$, the corresponding numerical results are as shown in Fig. 3.

If we only consider van der Waals gases, the charges between the ions cancel out in the reservoir, assuming $\mathcal{R}$ to be the normal atmospheric pressure, and the acceptance radii for the sodium and chloride ions are determined to be 3.78 and 5.02 Å, respectively. In other words, if the radius of the nanotube lies between 3.78
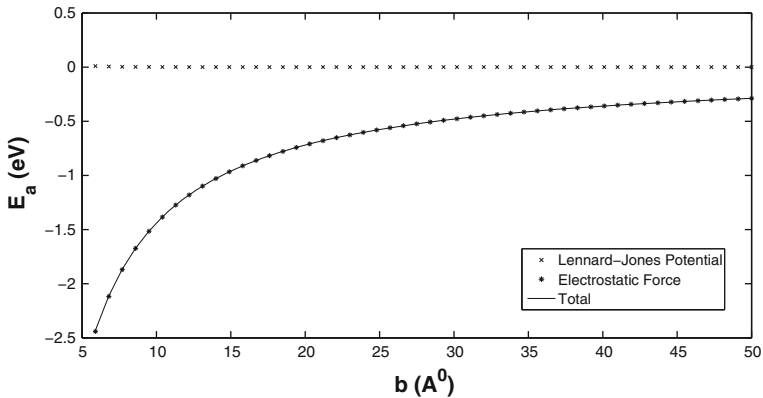
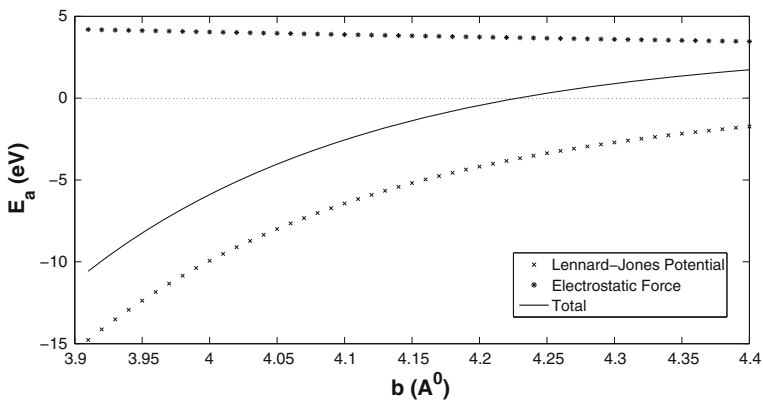**Fig. 4** Acceptance energy for sodium ion with functional group $Q = e$

Fig. 5 Acceptance energy for chloride ion with functional group $Q = e$

and 5.02 Å, only sodium ions can enter the nanotube spontaneously and above 5.02 Å both the sodium and chloride ions will pass through the nanotube. These results agree with Corry [11] who investigates seawater desalination using nanotube membranes and obtains the values 4.3 and 5 Å for the sodium and the chloride ions, respectively. However, the gap between such acceptance radii is so narrow, that in practice any small distortions at the nanotube entry would greatly affect ion selectivity and would be deemed useless. Here, we modify ion selectivity of nanotubes by covalently attaching an extra functional group at the nanotube entry, and to obtain some insight into such an effect, we first consider the two cases for total charges $Q = e$ and $Q = -e$ distributed evenly at the nanotube entry (see Fig. 1). Now, if all the terms of Eq. (3) are adopted, the numerical results for $Q = e$ for the sodium and the chloride ion are as given in Figs. 4 and 5, respectively. In order to facilitate the subsequent discussion, the electrostatic energy and the van der Waals forces are shown separately.

From Fig. 4, we observe that the repulsive electrostatic forces between the sodium ion and the functional group shift the acceptance radius to the right, i.e. increasing
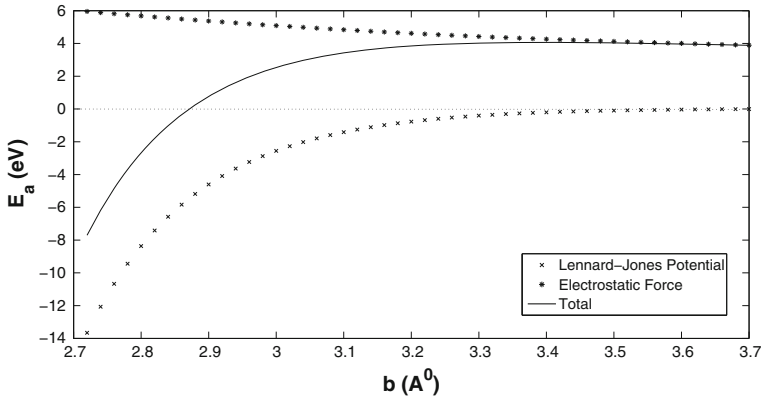
Fig. 6 Acceptance energy for sodium ion with functional group $Q = -e$
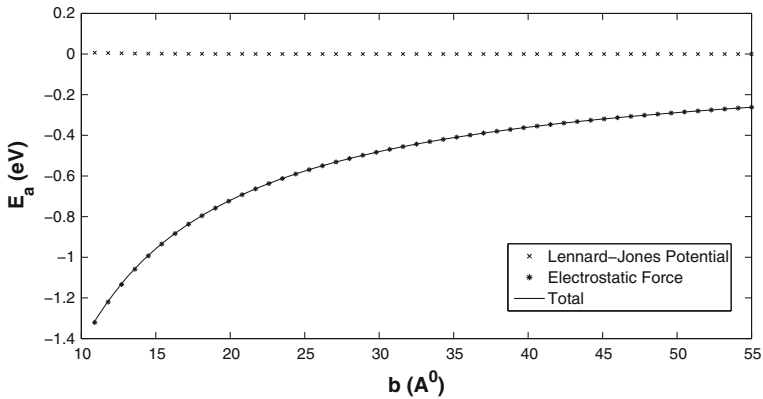

Fig. 7 Acceptance energy for chloride ion with functional group $Q = -e$

the value of the acceptance radius. However, since the Lennard-Jones forces diminish more rapidly than the electrostatic forces as the radius of the nanotube increases, the acceptance radius approaches infinity so that a sodium ion is unable to enter into the nanotube without the application of external forces. However, any fluctuations of approximate magnitude 0.4 eV arising from perhaps heat or collisions between ions or other sources such as ultrasonic waves will act to suck the sodium ion into large radii nanotubes. On the other hand, from Fig. 5, the additional attractive electrostatic forces between the chloride ion and the functional group moves the acceptance radius to the left from 5.02 to 4.23 Å, so that the chloride ion will now penetrate more easily into the decorated nanotube. Hence, the introduction of the functional group $Q = e$ will, for large enough radius, eventually accept chloride ions only and repel sodium ions. Next, we maintain the magnitude of the charge of the functional group unchanged, but we reverse the sign to become $-e$, and the numerical results for the sodium and the chloride ion are as given in Figs. 6 and 7, respectively.

From Fig. 6, due to the negative charge arising from the functional group at the entry, the functional group provides an additional attractive electrostatic force for the
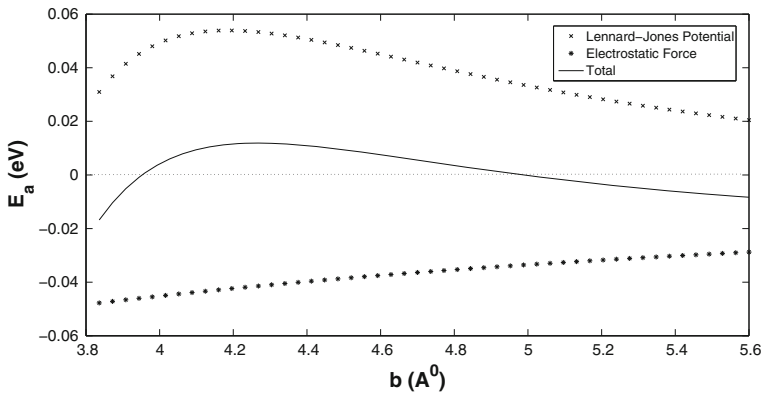
Fig. 8 Acceptance energy for sodium ion with functional group $Q = 0.01e$
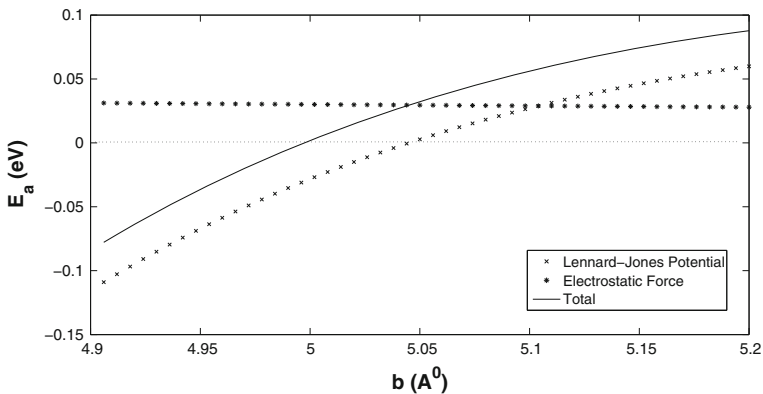

Fig. 9 Acceptance energy for chloride ion with functional group $Q = 0.01e$

sodium ion to enter the nanotube and the acceptance radius of the sodium ion reduces from 3.78 to 2.9 Å. From Fig. 7, since the Lennard-Jones forces diminish so rapidly as the nanotube radius increases, the chloride ion will always experience a repulsive force pushing it away from the nanotube. Our calculations predict that only chloride ions can penetrate into the nanotube of radius 4.23 Å which is decorated by the functional group with charge $Q = e$. Similarly, only sodium ions can penetrate into the nanotube of radius 2.9 Å which is decorated by the functional group with charge $Q = -e$. Our numerical results also predict that such phenomenon remains qualitatively unchanged for $Q = \pm 0.1e$ (see Table. 2). So that, for $|Q| \geq 0.1e$, depending upon the sign of the charge of the functional group, only sodium ions or chloride ions can be sucked into the decorated nanotube providing the sole ion selectivity for the nanotube. To observe the diminishing effect of the functional group, we assign $Q = 0.01e$ which although we appreciate may not be physically realistic, the corresponding numerical results for the sodium and chloride ions are as given in Figs. 8 and 9, respectively.

From Fig. 9 we observe that a small doped positive charge at the nanotube entry only affects the acceptance radius of the chloride ion marginally by 0.02 Å. However,
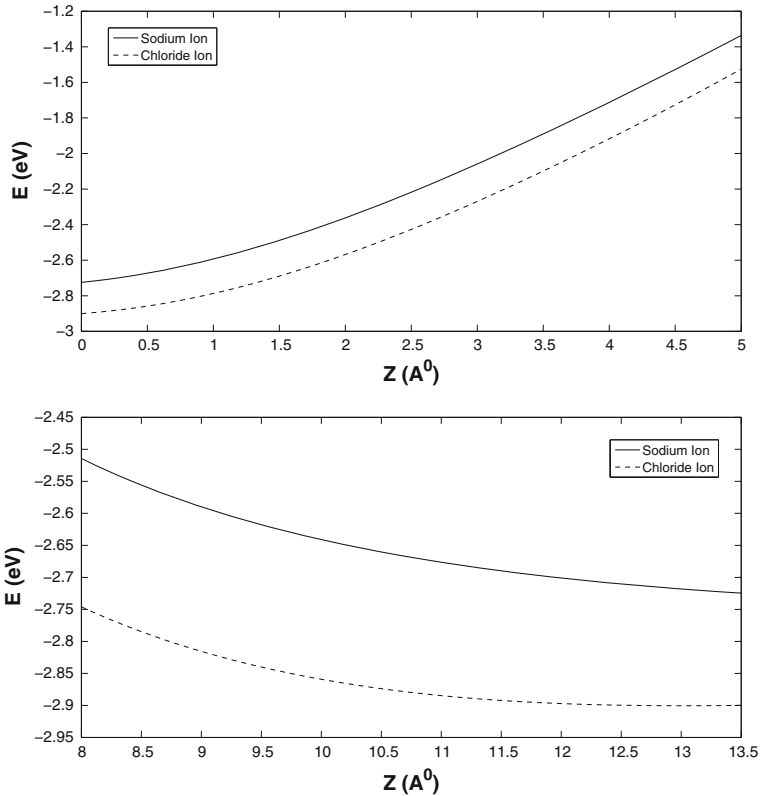
Fig. 10 Total energy of two sodium or chloride ions inside nanotube of radius 4.5 Å with functional groups $Q = -e$ and e, respectively

from Fig. 8 an intriguing phenomenon occurs, since the existence of the functional group neither completely repels the sodium ion nor sucks in the ion beyond a certain acceptance radius. Instead, the combination of the Coulomb and Lennard-Jones potentials is perfectly balanced such that it generates a range of radii, that is 3.95–4.98 Å for which the sodium ion can pass through the nanotube and blocks the sodium ion outside of this range. This phenomena reinforces the fact that the ion transport is sensitive to changes in any external charges and sources [13]. The new acceptance radii for the sodium and chloride ions arising from the total charge of the functional groups, that is Q, are summarized in Table. 2.

Since functionalized nanotubes tend to suck the counter-ion into the tube but repel the co-ion and the introduction of a functional group at the entry always reduces the acceptance radius of the counter-ion, we expect that two identical ions can penetrate into a nanotube of sufficiently large radius and they are separated by their intrinsic repulsive electrostatic forces. To verify this hypothesis, we use Eq. (6) and plot the total energy of two sodium and chloride ions inside a nanotube of radius 5.3 Å and length 13.5 Å with the functional group of total charge $Q = -e$ and $Q = e$, respectively which are as given in Fig. 10.
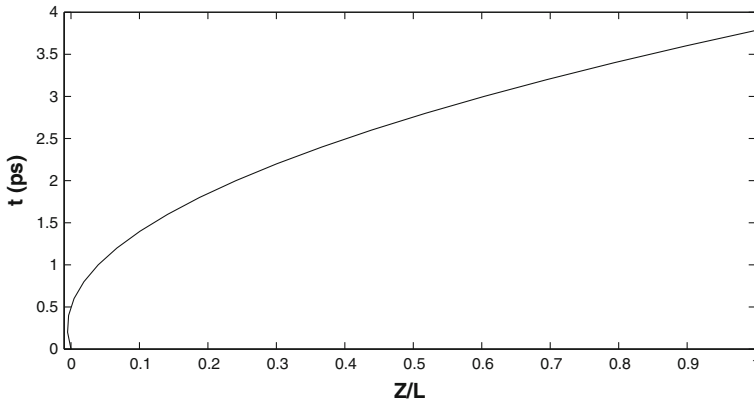
Fig. 11 Transportation times for sodium ions inside nanotube with functional group $Q = -e$
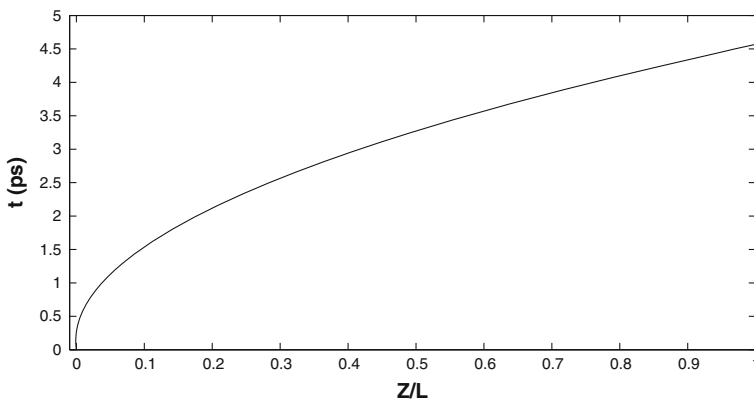

Fig. 12 Transportation times for chloride ions inside nanotube with functional group $Q = e$

We observe from Fig. 10 that both sodium or chloride ions are separated and located at the nanotube's extremities; that is the minimum energy configuration arising from the repulsive electrostatic force between two ions. The chloride ion possesses the higher binding energy in comparison to that of the sodium ion, which is in close agreement with results given by Hilder and Chung [33] and Hilder et al. [19]. Next, we calculate the transportation time of sodium and chloride ions passing through a nanotube of radius 5.3 Å and length 13.5 Å decorated by functional groups of total charge −e and e, respectively. As noted previously, the introduction of such functional groups is such that the nanotube completely accepts counter-ions but repels co-ions, and the nanotube of radius 5.3 Å (see Table 2) sucks in the corresponding counter-ions. Here, we only consider the simplest scenario that the first ion enters into the nanotube and becomes situated at the right-hand end of the nanotube. The entry of a second ion then propels the first ion out of the tube and travels on axis through the nanotube to reach the right-hand tube end, and we assume that the same process

continues indefinitely. The equation of motion, that is Eq. (5), can be decomposed into two first order differential equations that can be used to determine the transportation time of the ion through the nanotube, namely using $v = \dot{Z}$

$$
m\dot{v} = \frac{8\pi^2 \eta_i \eta_t b}{a^4 \lambda^3} \left[A\left(1 + \frac{2}{\lambda}\right) - \frac{B}{5a^6 \lambda^3}\left(5 + \frac{80}{\lambda} + \frac{336}{\lambda^2} + \frac{512}{\lambda^3} + \frac{256}{\lambda^4}\right) \right]
$$
$$
- \frac{qQ|Z|}{\varepsilon(Z^2 + b^2)^{3/2}} + \delta(t)\frac{q^2}{\varepsilon L^2}, \tag{7}
$$

where the dot, m and $\delta(t)$ denote the time derivative, the mass of the intruding ion and the usual Dirac delta function, respectively. The delta function arises from the instantaneous collision between the two ions which knocks the first ion out of the nanotube. Upon assuming that both the initial position and the velocity of the second ion are zero, Eq. (7) might be solved numerically using a fourth order Runge-Kutta numerical scheme [34] and the solution is as given in Figs. 11 and 12 for the case of the sodium and chloride ions, respectively.

The transportation times for the intruding sodium and chloride ions are calculated to be 3.8 and 4.6 ps, respectively. For the case of the sodium ion, we observe that the instantaneous collision between the two sodium ions knocks the first sodium ion temporarily out of the nanotube in the first 0.25 ps. After that, the attractive forces between the second sodium ion and the functionalized nanotube sucks the second ion back into the nanotube. The same phenomenon happens in the case of chloride ion. For this particular transport process, the numerical results indicate very fast transportation times of the ions inside the nanotube, which might be an interesting problem that could be verified by molecular dynamics simulations.

3.2 Ions in solvent

Here, we relax the assumption of zero external forces made in the previous subsection, and we assume that $\mathcal{R}$ has the form given by Eq. (4). According to Song and Corry [35], assuming a void nanotube interior, a hydrostatic pressure of 200 MPa and a net concentration of 250 mM NaCl, the molecular force arising from the bulk solution is found from curve fitting to be

$$
-\left(\frac{\delta E}{\delta Z}\right)_B = \begin{cases} -0.19 + 0.059b - 0.0061b^2, & \text{(Sodium ion)} \\ -0.38 + 0.14b - 0.016b^2, & \text{(Chloride ion)} \end{cases} \tag{8}
$$

and these relations are valid for $3.4 < b < 6.1$. Now, for simplicity, we ignore the functional group at the tube entry and we determine the axial force for both the sodium and chloride ions, that is Eq. (5) which is given in Fig. 13

Unlike the case of van der Waals gases, the acceptance radii of sodium and chloride ions can be determined by solely from the axial force diagram. We comment that the molecular effect arising from solution prevents both ions from entering the nanotubes. When $b = 4$ and 5.3 Å, respectively for sodium and chloride ions, the sodium and
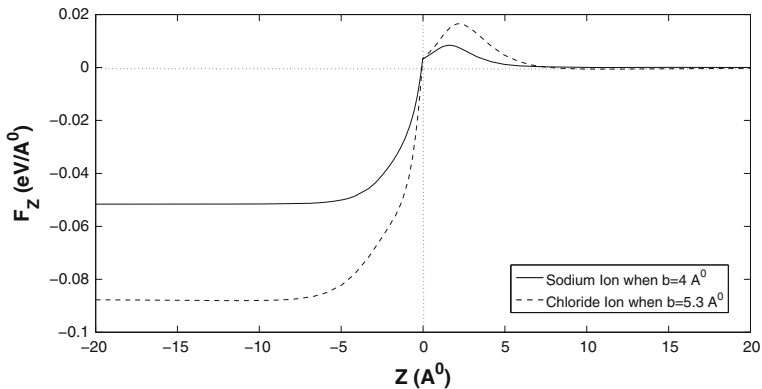
Fig. 13 Axial force for sodium and chloride ions for $Q = 0$ and taking into account of solvent effect

chloride ions start to experience a positive suction at the entry. In comparison to the van der Waals gases, the radius of nanotube needs to be larger to generate a smaller molecular barrier for both ions to enter the nanotube. Now, if we add the functional group, we find for $-e < Q < e$ that the solvent stabilizes the ion selectivity for both ions, the acceptance radii of sodium and chloride ions stay the same and the functional group starts to repel the sodium and chloride ions when $Q = 12e$ and $-28e$, respectively.

4 Conclusion

For the problem of ion selectivity through a carbon nanotube which has functional groups attached on the rim of the nanotube entry, we use the 6–12 Lennard-Jones and Coulomb potentials together with both the pairwise and continuous approaches to model the electrostatic and van der Waals forces between ions, the ion and the functional group, as well as between the ion and the nanotube. The acceptance radii of the sodium and chloride ions are determined with and without a functional group at the nanotube entry, and we find as might be expected, that the functional group tends to suck in counter-ions and repel co-ions, so that in principle single ion selectivity might be achieved. We also consider the co-existence of two identical ions at the extremities of a functionalized nanotube of sufficiently large radius, which gives rise to the simplest transportation phenomena of one-in and one-out and which provides the flow pattern producing the fastest transportation time. The presence of a solvent tends to stabilize the selectivity of the ions, so that an acceptance radii can be obtained for both sodium and chloride ions, assuming that the total charge of the functional group is non-zero.

5 Appendix

See Tables 1 and 2.

Table 1 Numerical values for A, B, A_i and B_i as determined by Lorentz-Berthelot mixing rules [36]

Description	Parameter	Value
Radius of sodium ion	a	1.16 Å
Radius of chloride ion	a	1.67 Å
Mass of sodium ion	m	23 m_μ
Mass of chloride ion	m	36 m_μ
Attractive constant Na–Na	A_i	1.31 eVÅ^6
Repulsive constant Na–Na	B_i	318.76 eVÅ^{12}
Attractive constant Cl–Cl	A_i	126.04 eVÅ^6
Repulsive constant Cl–Cl	B_i	915,813.31 eVÅ^{12}
Attractive constant Na-nanotube	A	7.19 eVÅ^6
Repulsive constant Na-nanotube	B	7,224.50 eVÅ^{12}
Attractive constant Cl-nanotube	A	62.57 eVÅ^6
Repulsive constant Cl-nanotube	B	304,015.33 eVÅ^{12}
Number density of graphene	η_C	0.381 Å^{-2}
Number density of sodium ion	η_{Na}	0.059 Å^{-2}
Number density of chloride ion	η_{Cl}	0.029 Å^{-2}

Table 2 Acceptance radii for various total charge of functional groups

Charge (Q)	Sodium ion (Å)	Chloride ion (Å)
e	Rejected	4.23
0.1 e	Rejected	4.75
0.01 e	4–5	5
0 e	3.78	5.02
−0.01 e	3.65	5.1–10.2
−0.1 e	3.32	Rejected
−e	2.9	Rejected

References

1. D.H.J. Mackay, K.R. Wilson, Possible allosteric significance of water structures in proteins. J. Biomol. Struct. Dyn. **4**, 491–500 (1986)
2. R.M. Lynden-Bell, J.C. Rasaiah, Mobility and solvation of ions in channels. J. Chem. Phys. **105**, 9266–9280 (1996)
3. M.S.P. Sansom, I.H. Shrivastava, K.M. Ranatunga, G.R. Smith, Simulations of ion channels watching ions and water move. Trends Biochem. Sci. **25**, 368–374 (2000)
4. N. Naguib, H. Ye, Y. Gogotsi, A.G. Yazicioglu, C.M. Megaridis, M. Yoshimura, Observation of water confined in nanometer channels of closed carbon nanotubes. Nano Lett. **4**, 2237–2243 (2004)

5. Y. Gogotsi, J.A. Libera, A.G. Yazicioglu, C.M. Megaridis, In situ multiphase fluid experiments in hydrothermal carbon nanotubes. Appl. Phys. Lett. **79**, 1021–1023 (2001)
6. K. Koga, G.T. Gao, H. Tanaka, X.C. Zeng, Formation of ordered ice nanotubes inside carbon nanotubes. Nature **412**, 802–805 (2001)
7. A. Berezhkovskii, G. Hummer, Single-file transport of water molecules through a carbon nanotube. Phys. Rev. Lett. **89**, 064503 (2002)
8. G. Zuo, R. Shen, S. Ma, W. Guo, Transport properties of single-file water molecules inside a carbon nanotube biomimicking water channel. ACS Nano **4**, 205–210 (2010)
9. A. Kalra, S. Garde, G. Hummer, Osmotic water transport through carbon nanotube membranes. PNAS **100**, 10175–10180 (2003)
10. B. Mukherjee, P.K. Maiti, C. Dasgupta, A.K. Sood, Single-file diffusion of water inside narrow carbon nanorings. ACS Nano **4**, 985–991 (2010)
11. B. Corry, Designing carbon nanotube membranes for efficient water desalination. J. Phys. Chem. B **112**, 1427–1434 (2008)
12. Y. Chan, J.M. Hill, A mechanical model for single-file transport of water through carbon nanotube membranes. J. Membr. Sci. **372**, 57–65 (2011)
13. M. Yu, H.H. Funke, J.L. Falconer, R.D. Noble, Gated ion transport through dense carbon nanotube membranes. JACS **132**, 8285–8290 (2009)
14. G. Merle, M. Wessling, K. Nijmeijer, Anion exchange membranes for alkaline fuel cells: A review. J. Membr. Sci. **377**, 1–35 (2011)
15. C. Peter, G. Hummer, Ion transport through membrane-spanning nanopores studied by molecular dynamics simulations and continuum electrostatics calculations. Biophys. J. **89**, 2222–2234 (2005)
16. S. Joseph, R.J. Mashl, E. Jakobsson, N.R. Aluru, Electrolytic transport in modified carbon nanotubes. Nano Lett. **3**, 1399–1403 (2003)
17. M. Majumder, N. Chopra, B.J. Hinds, Effect of tip functionalization on transport through vertically oriented carbon nanotube membranes. J. Am. Chem. Soc. **127**, 9062–9070 (2005)
18. J.H. Park, S.B. Sinnott, N.R. Aluru, Ion separation using a Y-junction carbon nanotube. Nanotechnology **17**, 895–900 (2006)
19. T.A. Hilder, D. Gordon, S.H. Chung, Synthetic chloride-selective carbon nanotubes examined by using molecular and stochastic dynamics. Biophys. J. **99**, 1734–1742 (2010)
20. M. Majumder, N. Chopra, B.J. Hinds, Mass transport through carbon nanotube membranes in three different regimes: Ionic diffusion and gas and liquid flow. ACS Nano **5**, 3867–3877 (2011)
21. F. Fornasiero, H.G. Park, J.K. Holt, M. Stadermann, C.P. Grigoropoulos, A. Noy, O. Bakajin, Ion exclusion by sub-2-nm carbon nanotube pores. PNAS. **105**, 17250–17255 (2008)
22. B.J. Cox, N. Thamwattana, J.M. Hill, Mechanics of atoms and fullerenes in single-walled carbon nanotubes. I. Acceptance and suction energies. Proc. R. Soc. Lond. Ser. A **463**, 461 (2007)
23. B.J. Cox, N. Thamwattana, J.M. Hill, Mechanics of atoms and fullerenes in single-walled carbon nanotubes. II. Oscillatory behaviour. Proc. R. Soc. Lond. Ser. A **463**, 477 (2007)
24. T.A. Hilder, J.M. Hill, Carbon nanotubes as drug delivery nanocapsules. Curr. Appl. Phys. **8**, 258–261 (2007)
25. T.A. Hilder, J.M. Hill, Theoretical comparison of nanotube materials for drug delivery. Micro Nano Lett. **3**, 18–24 (2007)
26. Y. Chan, J.M. Hill, Modelling interaction of atoms and ions with graphene. Micro Nano Lett. **5**, 247–250 (2010)
27. Y. Chan, J.M. Hill, Lithium ion storage between graphenes. Nanoscale Res. Lett. **6**, 203 (2011)
28. Y. Chan, J.M. Hill, Hydrogen storage inside graphene-oxide frameworks. Nanotechnology **22**, 305403 (2011)
29. Y. Chan, J.M. Hill, Modeling on ion rejection using membranes comprising ultra-small radii carbon nanotubes. Eur. Phys. J. B **85**, 56 (2012)
30. Y. Chan, J.M. Hill, Dynamics of benzene molecules situated in metal-organic frameworks. J. Math. Chem. **49**, 2190–2209 (2011)
31. Y. Chan, R.K.F. Lee, J.M. Hill, Metallofullerenes in composite carbon nanotubes as a nanocomputing memory device. IEEE Trans. Nanotechnol. **10**, 947–952 (2011)
32. J.E. Jones, On the determination of molecular fields. I. From the variation of the viscosity of a gas with temperature. Proc. R. Soc. **106A**, 441 (1924)
33. T.A. Hilder, S.H. Chung, Carbon nanotube as a gramicidin analogue. Chem. Phys. Lett. **501**, 423–426 (2011)

34. R.L. Burden, J.D. Faires, *Numerical Analysis*, 8th edn. (Thomson, Belmont, 2005)
35. C. Song, B. Corry, Intrinsic ion selectivity of narrow hydrophobic pores. J. Phys. Chem. B **113**, 7642–7649 (2009)
36. G.C. Maitland, M. Rigby, E.B. Smith, W.A. Wakeham, *Intermolecular Forces—Their Origin and Determination* (Clarendon Press, Oxford, 1981)