Does water dope carbon nanotubes?

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(Received 30 June 2014; accepted 8 October 2014; published online 27 October 2014)

We calculate the long-range perturbation to the electronic charge density of carbon nanotubes (CNTs) as a result of the physisorption of a water molecule. We find that the dominant effect is a charge redistribution in the CNT due to polarisation caused by the dipole moment of the water molecule. The charge redistribution is found to occur over a length-scale greater than 30 Å, highlighting the need for large-scale simulations. By comparing our fully first-principles calculations to ones in which the perturbation due to a water molecule is treated using a classical electrostatic model, we estimate that the charge transfer between CNT and water is negligible (no more than 10^{-4} e per water molecule). We therefore conclude that water does not significantly dope CNTs, a conclusion that is consistent with the poor alignment of the relevant energy levels of the water molecule and CNT. Previous calculations that suggest water *n*-dopes CNTs are likely due to the misinterpretation of Mulliken charge partitioning in small supercells. © 2014 AIP Publishing LLC. [<http://dx.doi.org/10.1063/1.4898712>]

I. INTRODUCTION

The unique electronic properties of carbon nanotubes (CNTs) make them a promising material for novel applications¹ including highly sensitive chemical sensors,^{2,3} light-weight electrical wires,^{4–6} and nanoscale electronic devices.^{1,7,8}

Optimal performance of these devices often requires the CNTs to have a particular electronic character, whether semiconducting or metallic, which is determined by the CNT chirality. The control of chirality during CNT synthesis is challenging, which has led to the development of alternative in-solution techniques for separating bulk-grown CNT samples with respect to electronic type. Examples include density gradient ultracentrifugation,^{9,10} polymer wrapping,^{11,12} and chromatography.^{13,14}

As a consequence of this post-processing, residual water may remain adsorbed to the CNTs. Therefore, it is vital to understand the influence that water has on the electronic structure of CNTs.

Experimental investigations of the effect of water vapour on the conductivity of mats and fibres of CNTs have been contradictory with both increases^{15–19} and decreases^{20–22} in conductivity observed. The lack of agreement may be attributable to an abundance of factors, including the CNT sample composition and purity, the presence of impurities and their composition, contact resistances with external electrodes and between the CNTs themselves, and the alignment and connectivity of CNTs in the mat/fibre network. The relative contribution of these factors, and their dependence on local water concentration, may be significantly different between the different samples used in the reported experiments, and are difficult to isolate.

Theoretical calculations based on density functional theory (DFT)^{23,24} have shown that water interacts weakly with CNTs, binding through physisorption.^{21,25–28} This weak inter-

action has been shown to cause little scattering, and the conductance of individual CNTs when hydrated is little changed from when dry.^{26,29}

Charge transfer analyses, also performed within DFT, have suggested that water may *n*-dope CNTs.^{21,25–28} The conductance of semiconductor CNTs is sensitive to the amount of doping, and in Ref. 19 a mechanism based on charge transfer between water and CNTs has been proposed to explain the experimental observations.

There are, however, several issues with the charge transfer analyses used to determine this mechanism. Most fundamentally, there is no unique formalism to partition the DFT-derived ground-state charge density among different species in a system. The magnitude of charge transfer is sensitive to the details of the calculations, including the choice of functional for exchange and correlation,³⁰ the basis set,^{31–33} and the partitioning method used.^{31,33} Changing the partitioning method will often alter the computed partial charges by 0.1 e or more,^{32,33} which is comparable to the proposed water/CNT charge transfer.^{21,25–28} These theoretical calculations may still, therefore, be consistent with no charge transfer or even *p*-doping. Indeed, it has been suggested that there is no overall charge transfer.^{20,27,34}

Regardless of the method used to determine the charge partitioning, it is also not clear that charge doping can be determined by considering only the total partial charge of the CNT, as used in previous studies.^{21,25–28} In principle, doping is manifested by additional or reduced electron charge density, as compared to the bulk, far from the defect that may be causing the doping, such that all electrostatic perturbations have been screened. Only this *delocalised* charge transfer can result in doping and contribute to conductance; localised charge transfer will in fact act to scatter current and decrease the conductance. Accordingly, the long-range spatial distribution of the electron charge density must be considered to determine whether doping occurs.

Neither experiment nor theory, therefore, has reached agreement over the interaction between CNTs and water and further analysis of the calculated charge transfers is required to support a doping hypothesis. In this work, we revisit the problem of charge transfer between water and CNTs. Working directly with the charge density, derived from first-principles calculations, we calculate the long-range perturbation to the CNT charge density due to the water molecule. Our main result is that the interaction is a long-ranged electrostatic polarisation that arises due to the dipole moment of the water molecule which cannot be fully captured within a small simulation cell. We isolate the contribution to the density perturbation due to the water dipole moment by using a simple classical model for the water electrostatics. This allows us to estimate the residual charge transfer between a CNT and water molecule which we find to be negligible. We therefore conclude that water does not *n*-dope CNTs.

The remainder of this paper is organised as follows: we first give details of our methods; Sec. III analyses the electrostatic interaction between the CNT and water molecule; we then discuss the wider context of these conclusions in Sec. IV.

II. METHODS

We consider supercells containing a single water molecule adsorbed on one of two CNT structures: 16 unit-cells of a semiconducting (10, 0) CNT; and 28 unit-cells of a metallic (5, 5) CNT. The overall length of each supercell is 68.5 Å and 69.1 Å, respectively.

Electronic structures are calculated using the ONETEP linear-scaling DFT code,³⁵ which uses a small set of localised numerical orbitals called non-orthogonal generalised Wannier functions (NGWFs).³⁶ In this work, we use four NGWFs per carbon and oxygen atom and one per hydrogen atom. Each NGWF is represented in terms of an underlying basis of *psinc* functions,³⁷ equivalent to a set of plane-waves, that enables them to be optimised *in situ* for their unique chemical environment as the calculation proceeds. Throughout this work, we use a localisation radius of 5.3 Å for the NGWFs in order to capture charge polarisation accurately.

Equivalent plane-wave kinetic energy cutoffs of 1000 eV and 4000 eV are used for the *psinc* basis sets representing the NGWFs and charge density, respectively, and the Brillouin zone is sampled at the Γ point only. Core electrons are described using norm-conserving pseudopotentials in Kleinman-Bylander form.³⁸

In this work, all calculations employ the PBE generalised gradient approximation for exchange and correlation;³⁹ our conclusions are unchanged when equivalent calculations are performed using the local density approximation (LDA).⁴⁰

Periodic boundary conditions are used along the CNT axis, which is denoted as the *z*-direction; directions perpendicular to the axis are treated with the supercell approximation with at least 12 Å separating periodic images.

The atomic structures of the CNT unit cells are determined using the plane wave DFT package CASTEP.⁴¹ A fully converged Brillouin zone sampling scheme of 16 and 28 equally spaced *k*-points, including the Γ point, for the (10, 0)

and (5, 5) CNTs, respectively. The states sampled are equivalent to those sampled in the larger supercell. The same pseudopotentials and parameter set, as far as possible, are used as for the ONETEP calculations.

After relaxation, the maximum residual forces and stress are 5 meV/Å and 0.02 GPa, respectively. Calculated C–C bond lengths are 1.424 Å and 1.432 Å for the (10, 0) CNT, and 1.429 Å and 1.431 Å for the (5, 5) CNT; and the relaxed periodic unit cell lengths are 4.279 Å and 2.469 Å, respectively.

The water molecule is similarly relaxed in isolation in a 22 Å cubic simulation cell within the supercell approximation. Previous calculations have shown that the change to the structure of CNT and water is negligible when water is adsorbed,²⁸ therefore the geometry of the composite structure is not relaxed further. We have verified for a selection of structures that our conclusions are unaffected by this choice.

Maximally localised Wannier functions (MLWFs)^{42,43} used for the point charge model of Sec. III A are calculated using the QUANTUM ESPRESSO⁴⁴ interface to WANNIER90.⁴⁵

III. RESULTS AND DISCUSSION

A. Computing the CNT charge polarisation

Our key result is given in Fig. 1 where we show the long-range electron density redistribution for a (10, 0) semiconducting CNT with a single water molecule adsorbed (solid lines). The supercell is 68 Å in length along the CNT axis and the oxygen ion of the water molecule is directly above a carbon site, at a distance of 3.20 Å which is approximately the average equilibrium binding distance of these orientations, and is positioned at the centre of the CNT supercell ($z \approx 34$ Å). The water molecule is oriented such that the normal to the atomic plane makes an angle θ to the radial vector of the CNT as shown in Fig. 2. The four panels show different orientations of the water molecules that are thermally

FIG. 1. The laterally integrated density difference profile for a 68 Å (10, 0) CNT supercell with a single water molecule adsorbed (full DFT calculation, solid lines). Also shown (dashed lines), the corresponding induced polarisation when the water molecule treated as classical Wannier charges (see main text). The angle θ corresponds to the angle between the water dipole vector and the normal to the CNT surface as shown in Fig. 2.

FIG. 2. The structure of the water molecule adsorbed on a (10,0) CNT. The water oxygen ion is situated 3.20 Å above a carbon, with the water dipole making an angle θ to the CNT axis. Shown here is $\theta = 90^\circ$. Only the part of the CNT closest to the water molecule is shown, the CNT extends for an additional ≈ 30 Å in both directions to form the full supercell.

accessible at room temperature. As we will show shortly, the precise CNT/water geometry does not strongly affect the interactions present, precluding the need for a detailed thermodynamic analysis.

The induced density polarisation is calculated through the charge density difference, defined as the difference between the density for the CNT and water combined $n_{1,2}(\mathbf{r})$, and the isolated CNT and water molecule alone $n_1(\mathbf{r})$, $n_2(\mathbf{r})$

$$\Delta n(\mathbf{r}) = n_{1,2}(\mathbf{r}) - n_1(\mathbf{r}) - n_2(\mathbf{r}). \quad (1)$$

Three separate calculations per configuration are performed to determine the density difference. The periodicity due to the underlying atomic lattice is smoothed out by convolving this quantity with a window function $w(z)$ with width equal to the CNT unit cell length L_{uc} . In order to smooth out the large variations due to the underlying ionic lattice, we integrate this quantity over planes perpendicular to the CNT axis defining an electron density difference per unit length,

$$\lambda(z) = \int \Delta n(x', y', z') w(z - z') dx' dy' dz', \quad (2)$$

$$w(z) = \begin{cases} 1/L_{uc} & |z| < L_{uc}/2 \\ 0 & \text{otherwise} \end{cases}. \quad (3)$$

The charge redistribution shown in Fig. 1 is remarkably long-ranged, occurring over a length-scale greater than 30 Å. As this is much larger than the CNT unit cell, this long-range polarisation cannot be observed in the smaller supercells used in previous calculations.^{21,25–28}

The form of the charge polarisation is strongly dependent of the orientation of the water molecule, but correlates well with the direction of the water dipole. For example, at $\theta = 0^\circ$, the dipole points away from the CNT and electron

density is repelled; at $\theta = 180^\circ$, the dipole is towards the CNT and electron density is attracted. Equivalent calculations (not presented here) show similar behaviour when varying the water-CNT binding distance.

The dominant effect of the water molecule on the CNT appears to be purely electrostatic in origin. In order to demonstrate this more rigorously, we calculate the charge polarisation of the system using a purely electrostatic model for the water molecule, i.e., without explicit inclusion of the real electron density of the water molecule in the system. The water molecule is treated as a set of point charges, whose influence appears as a correction to the local Kohn-Sham potential⁴⁷

$$\delta V_{loc}(\mathbf{r}) = \sum_i \frac{q_i}{|\mathbf{r} - \mathbf{r}_i|}, \quad (4)$$

where $\mathbf{r}_i$ and q_i are the position and magnitude, respectively, of each point charge. Positive (ionic) charges are located at the ionic positions with magnitudes given by those of the corresponding pseudo-ions. For the negative (electronic) charges, the positions are the centres of the MLWFs^{42,45} obtained by subspace rotation of the manifold of occupied eigenstates of an isolated water molecule.⁴⁶ The magnitude of each electronic charge is then the integrated charge density of each MLWF. Due to the unitarity of the Wannier transformation, this gives $-2e$, with the factor of two being a result of spin degeneracy. In practice, to prevent unphysical “charge-spilling” into the deep Coulombic potential, these point charges are smeared with a Gaussian function of half-width 0.16 Å.⁴⁷ The geometry of the MLWF centres in relation to the ionic positions is shown in Fig. 3 (bottom left). Our method is similar in spirit to that of Ref. 48, but differs in that the procedure is parameter free and requires no fitting.

The difference in electronic density induced by this classical electrostatic model for the water molecule can be calculated using the equivalent of Eq. (1) and is shown in Fig. 1 (dashed lines). The agreement with the full DFT calculation (solid lines) is excellent for all configurations. Additional calculations (not shown) modifying the binding distance show that the Wannier charge model accurately describes charge redistribution for thermally accessible geometries. To achieve a large difference in the long-range density difference in the $\theta = 0^\circ$ orientation, for example, the water molecule must have a binding distance less than 2.5 Å. Such small separations, however, incur a serious energy penalty of at least 200 meV (or $8k_B T$ at ambient temperature) and therefore the contributions from these configurations can be neglected under the ambient conditions that experiments are performed. The success of the MLWF model can be explained by comparing the long-range electrostatic potential corresponding to the MLWF model and that of the water molecule from DFT. This comparison is shown in the top two panels of Fig. 3. The classical model reproduces the potential to high accuracy, with only small differences very close to the water molecule where the detailed charge density distribution is important. Equivalent calculations (not shown) performed on a metallic (5, 5) CNT produce similar results, providing evidence for the general applicability of our model.

FIG. 3. Top panels: a comparison between the electrostatic potential (local ionic and Hartree) for the isolated full DFT water molecule (left), and the classical Wannier charge representation (right). Contours are in steps of 20 meV, in the plane 3.20 Å below the water molecule, where the surface of the CNT would be when the water is in the 90° orientation. The water oxygen ion is located at the origin. The inset in the bottom right panel gives the difference between the two potentials in the region indicated by the dashed box. Contours are in steps of 5 meV, and the shading gives the absolute difference between 0 meV (white) and 50 meV (black). Outside the region shown, the difference between the potentials is less than 5 meV. Bottom panel, left: the positions of the Wannier charge centres (blue spheres) and oxygen/hydrogen ions.

It is interesting to note that simpler models for the water electrostatics also well reproduce the density polarisation. In Fig. 4, we compare the density polarisation induced in a metallic (5, 5) CNT within three different models. The left panel gives the Wannier charge model which most accurately reproduces the DFT induced polarisation. The central panel

FIG. 4. Comparison of the different electrostatic models for the water molecule adsorbed on a (5, 5) CNT in the $\theta = 45^\circ$ orientation. Left panel: point charge (MLWF) model for the water molecule; centre panel: dipole model for the water molecule; right panel: classical conducting cylinder model (see main text for details). In all cases, the dashed blue line gives the full DFT result.

uses a classical dipole model for the water potential, with classical charges of magnitude $\pm 8e$ at the centres of positive and negative charge of the isolated water molecule; the CNT is still treated using DFT. The agreement between this model and the DFT induced polarisation is still excellent, however differences between the classical and DFT electrostatic potential in the near-field produce a small lateral shift in the polarisation along the z -direction. The right panel shows the induced charge density for the simplest model where the CNT is treated as a classical conducting cylinder. The water molecule is described as a series of classical point charges as in the Wannier charge model, with the induced density calculated by solving the classical Poisson equation, as detailed in the Appendix. We note that the classical induced polarisation calculated by this crude final model captures well the main form of the full DFT induced polarisation supporting the conclusion that the dominant interaction is electrostatic.

Similar results (not shown) are obtained for the (10, 0) CNT, including for the classical conducting cylinder model despite the CNT being semiconducting.

Finally, we note that we do not expect that our conclusion will change in the presence of multiple water molecules. The shallow binding energy between CNT and water should not change with additional water molecules as the dominant interaction in this case is not the relatively weak physisorption between CNT and water, but instead the much stronger hydrogen bonding between the individual water molecules themselves. The short (< 2.5 Å) binding distances required to potentially achieve charge transfer will remain thermally inaccessible at ambient conditions in this case as well.

B. Estimating the residual charge transfer

In any calculation of the electronic density, the difference in charge density given by Eq. (1) consists of both charge polarisation $\Delta n_p(\mathbf{r})$ and charge transfer $\Delta n_t(\mathbf{r})$ components,

$$\Delta n(\mathbf{r}) = \Delta n_p(\mathbf{r}) + \Delta n_t(\mathbf{r}). \quad (5)$$

A convincing indicator of charge transfer would be additional charge delocalised in the CNT, far from the water molecule. As shown by the results above, however, the charge polarisation induced by the water dipole moment is very long-ranged. In principle, the charge transfer contribution could be determined by increasing the system size to screen the electrostatic perturbation, and considering regions where $\Delta n_p(\mathbf{r}) \rightarrow 0$.⁵⁰ Such an approach is impractical, especially for low-dimensional systems such as CNTs in which the relatively weak screening necessitates the use of very large systems. The larger the system size, the more accurately the charge densities must be determined as any charge transfer ΔQ becomes delocalised over a larger volume V , and the associated density difference becomes smaller: $\Delta n_t(\mathbf{r}) \sim \Delta Q/V$. Discerning small amounts of charge transfer accurately in this way is challenging from a computation point of view.

Instead, we approximate the polarisation contribution to the charge density difference in the full DFT calculation $\Delta n_p(\mathbf{r})$ (Fig. 4, dashed lines) as exactly the density difference

calculated by the Wannier charge model $\Delta n^{\text{WF}}(\mathbf{r})$ (Fig. 4, left panel, solid line) in which the charge density difference is due entirely to electrostatic polarisation: i.e., $\Delta n_p(\mathbf{r}) \approx \Delta n^{\text{WF}}(\mathbf{r})$. The residual charge transfer is then approximated as

$$\Delta n_t(\mathbf{r}) \approx \Delta n(\mathbf{r}) - \Delta n^{\text{WF}}(\mathbf{r}). \quad (6)$$

Summing $\Delta n_t(\mathbf{r})$ over the unit cell furthest from the water molecule provides an estimate of the charge transfer between the CNT and the water molecule, which we find to be no more than $|\Delta Q| \lesssim 10^{-4} e$, independent of orientation. This is three orders of magnitude lower than the value calculated by Mulliken population analysis, and shows that there is negligible charge transfer in this system.

C. Considerations of the electronic energy level alignment

Finally, we consider the evidence for charge transfer in terms of the energy levels of the CNT and water systems.

Previous calculations have shown that water interacts weakly with a CNT.^{21,25–28} As there is little chemical bonding, the eigenstates of the isolated water and CNT are expected to be little perturbed.

This is confirmed in Fig. 5, which compares the density of states of a 16 unit cell (10, 0) semiconductor CNT and a water molecule when mutually isolated, and the corresponding CNT/water local density of states (LDOS)⁴⁹ with the water adsorbed. Indeed, the LDOS/DOS of the CNT are indistinguishable. Equivalent calculations surrounding the CNT with a cluster of water molecules result in the same conclusion.

For significant charge transfer between CNT and water to occur, charge must transfer from the highest occupied molecular orbital (HOMO) of the water molecule to the CNT conduction band. As the water HOMO lies almost 4 eV below the CNT conduction band, this transfer would involve a large

FIG. 5. A comparison of the density of states (LDOS) for a (10,0) CNT and water molecule when isolated (dashed red/blue, respectively), and the local density of states of the CNT and water molecule (solid red/blue) when the water is adsorbed 3.20 Å above the CNT in the 90° configuration. A Gaussian smearing of 0.1 eV has been used. The CNT LDOS and DOS are indistinguishable. For each calculation, energies have been aligned by the potential far into the vacuum.

energy penalty, the magnitude of which is dependent on the CNT band gap.

The energy penalty for metallic CNTs is smaller than for semiconducting CNTs, and so calculations for these systems should show a large difference in either the binding energy or the charge transferred to the CNT. As neither of these effects are observed in calculation,^{25,28} we conclude that if charge transfer occurs then it must be very small, consistent with our estimation from Sec. III B. We also conclude that the Mulliken population analysis reported in previous calculations^{21,25–28} is not suitable for determining charge transfer in this system.

Whilst the energy levels calculated by Kohn-Sham DFT do not correspond to the true quasi-particle energy levels, the many-body correction to the energy levels is likely to be smaller than the large difference between water and CNT states. Moreover, the correction to the DFT band gap will increase the energy difference between the occupied water states and the CNT conduction band. Therefore, we do not believe that this conclusion will change under a higher level of theory. For other adsorbed molecules, significant charge transfer would be possible if the molecular levels better align with the CNT states. For example, molecular oxygen in the triplet spin state has been calculated to have an unoccupied molecular level that sits within the CNT band gap.⁵¹ We therefore do not dispute the conclusion that oxygen may *p*-dope semiconductor CNTs.^{34,52}

IV. CONCLUSIONS

Using linear-scaling density-functional theory, we have calculated the long-range electronic effects of a water molecule adsorbed onto a CNT. We have shown that the interaction is described very well with classical electrostatics: the permanent dipole moment of the water molecule induces a polarisation of the electronic charge density of the CNT that is remarkably long-ranged, occurring over a length-scale greater than 30 Å.

By comparing our full DFT calculations with ones in which the water molecule is treated as a classical charge distribution defined by its Wannier charge centres, we estimate that the charge transfer between CNT and a water molecule is no more than $10^{-4} e$. We therefore conclude that water does not significantly dope CNTs. This conclusion is supported by the poor alignment of the relevant energy levels of the water molecule and the CNT, and contrasts with previous results, based on Mulliken charge partitioning in small supercells, that suggest much greater charge transfer.

As a consequence of the lack of charge transfer and the weak interaction between CNT and water, we conclude that water has a very weak effect on the conductivity of *individual* CNTs.^{26,29} In order to understand the origin of the humidity-dependent conductivities observed in experiments on CNT fibres and mats, therefore, it is vital to go beyond the effect of water on individual CNTs, and also consider the effect of water on the conductivity of *networks* of CNTs, i.e., on the conductivity between CNTs. For example, in Ref. 53 we recently proposed a mechanism that greatly improves the conductance between different CNTs through momentum-resonant

scattering. The resonance can be achieved using a weak, long-ranged perturbation to the CNTs, which may be provided, for example, by water molecules weakly adsorbed to the CNT surface.

Finally, it is worth emphasising that our results highlight the importance of using supercells that are sufficiently large to capture long-ranged charge polarisation effects and that enable the disentanglement of charge polarisation from charge transfer. Beyond the immediate application to water on CNTs, these ideas are relevant more generally to the determination of charge polarisation and charge transfer resulting from adsorption of molecular species on bulk surfaces and layered materials.

ACKNOWLEDGMENTS

The authors would like to thank N. D. M. Hine for useful discussions. This work was performed using the Darwin Supercomputer of the University of Cambridge High Performance Computing Service funded by Engineering and Physical Sciences Research Council (U.K.) (EPSRC(GB)) under Grant No. EP/J017639/1. R.A.B. acknowledges financial support from British Telecommunications and EPSRC; M.C.P. acknowledges support from EPSRC under Grant No. EP/J017639/1; and A.A.M. acknowledges support from the Thomas Young Centre under Grant No. TYC-101.

APPENDIX: CLASSICAL ELECTROSTATIC MODEL

In Sec. III A, we model the interaction between a CNT and an adsorbed water molecule as a classical conducting cylinder interacting with point charges.

The cylinder radius is set as the radius of the CNT. The water molecule is modelled as point charges placed at the centres of the Wannier/ionic charges, as described in Sec. III A.

We calculate the charge density profile induced in the conducting cylinder due to the classical charges.

The electric potential is calculated by solving for the Green's function to the Poisson equation subject to the constant potential Dirichlet boundary condition on the cylinder

$$\nabla^2 \phi(\mathbf{r}) = 4\pi \sum_i q_i \delta(\mathbf{r} - \mathbf{r}_i), \quad (\text{A1})$$

where we have adopted atomic units.

In the limit of an infinite radius cylinder, the conductor becomes an infinite conducting plane and the solution is obtained using the method of images in a simple analytic form. For a single charge at position $\mathbf{r}_i = (x_i, 0, 0)$ above a conductor in the yz plane, the potential is

$$\phi(\mathbf{r}) = \frac{q}{|\mathbf{r} - \mathbf{r}_i|} - \frac{q}{|\mathbf{r} - \mathbf{r}_i^m|}, \quad (\text{A2})$$

where $\mathbf{r}_i^m = (-x_i, 0, 0)$ is the position of the mirror charge if the conductor lies on the yz -plane.

The surface charge of the conductor is calculated using Gauss' law giving $\sigma(y, z) = 1/(2\pi)E_x|_{x=0}$, where $E_x|_{x=0}$ is the electric field perpendicular to the plane, evaluated at the plane. The charge density per unit length of CNT is given by

the sum of the surface charge along a direction perpendicular to the CNT axis, i.e.,

$$\lambda(z) = \int dy \sigma(y, z) = \frac{q}{\pi} \frac{x_i}{z^2 + x_i^2}. \quad (\text{A3})$$

The charge density due to multiple charges is generated through superposition. To compare to the charge polarisation derived from the DFT calculations, this quantity is convolved with the same window function given in Eq. (3).

Whilst the shape of the induced density calculated using this model is in excellent qualitative agreement with our DFT calculations, the amplitude is an order of magnitude too large. Heuristically, this can be understood to arise from the difference in screening in the metallic cylinder as compared to a real CNT. We account for this by including a single parameter to the model that scales all the classical charges by the same factor, and choose its value such that the best fit to the DFT data is obtained. For the calculation shown in the right panel of Fig. 4, the fitted scaling factor is 0.13.

Treating the finite radius of the CNT explicitly by calculating the Green's function for the cylindrical geometry⁵⁴ is found to little change the form of the induced density profile. This observation is reasonable as the CNT diameter ($\approx 8 \text{ \AA}$) is much larger than the distance between point charges and CNT surface ($3.20 \text{ \AA}$). Regardless, we find that the classical model captures well the main features of the charge polarisation due to the water molecule.

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