Deciphering the nature of ion-graphene interaction

Ke Zhou[✉] and Zhiping Xu**Applied Mechanics Laboratory, Department of Engineering Mechanics, Tsinghua University, Beijing 100084, China*

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Ion-specific interactions with materials are important for the design of ion-based energy and information devices, which are studied here with a focus on alkali-earth-metal and transition-metal ions in the context of carbon nanofluidics. Density functional theory calculations show that for the alkali-earth-metal ions, the nature of interaction is ionic, with charge transfer to and from graphene determined by the change in work function. In contrast, covalent bonding is identified for transition-metal ions adsorbed on graphene, showing hybridization near the Dirac point. The ion-graphene interaction is significantly stronger than van der Waals interactions and shows much higher contrast among the ions. We find that, surprisingly, these features are robust even with the presence of water solvation, where alkali-earth-metal ion-graphene interaction remains ionic with modified charge transfer, while covalent interaction with transition-metal ions turns into ionic. These understandings imply that the ion-wall interaction can be notably tuned by the external electric field, as verified by our calculations, and opens an avenue for the development of nanofluidics where the channel width is comparable with the range of ion-wall interaction.

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Charge-neutral, chemically inert surfaces such as graphene or graphite are well known to interact with many atoms or molecules via van der Waals interactions. These long-range, nonbonding interactions are not only weak in the strength but also less discernible between the absorbed species and lack of external control. Interestingly, recent studies in nanofluidics show that ions in graphene nanochannels demonstrate highly selective transport behaviors [1–6]. These unexpected findings were attributed to the contrast in the ion-wall interaction [5–7]. The high contrast in ion-wall or ion-pore interaction also indicates discernible activation energies for diffusive processes of ions, offering plenty of room for recognition and selectivity of ions [8–10]. For example, recent experiments show that nanopores decorated by crown ethers impressively promote the K^+/Na^+ selectivity to more than 50 [10].

The notion of *cation- π* interaction was proposed to explain the noncovalent and relatively strong (≈ 1.0 eV) interaction between (hydrated) cations and the aromatic rings [11–15]. The *cation- π* interaction stems from the interaction between the ion and induced dipole, quadruple moments of the π system [11–13], which allows the control of molecular recognition, catalysis, and physiological processes [11,12,16,17]. Moreover, it leads to one order-of-magnitude difference in the energy of adsorption [11–14]. This concept is referred to explain highly selective ion transport in nanochannels through the contrast in the ion-wall interaction

that contributes to the drag force [5–7]. However, the nature of *cation- π* ion-wall interaction in carbon nanofluidics has not been well elucidated. The effects of solvents are unknown, and how the interaction can be controlled through external cues has not been discussed. Exploration in this context could shed light on the design of ionic devices for mass and/or information transport, storage, and detection, offering fundamental understanding of physical processes in biology and chemistry [2,3,11,12,15–19].

In this Rapid Communication, we employed first-principles calculations at the level of density functional theory (DFT). The functional of strongly constrained and appropriately normed (SCAN) meta-generalized gradient approximation (meta-GGA) is used to probe the nature of ion-graphene interaction, the results of which are compared with other functionals, with or without van der Waals corrections [20–22]. A wide spectrum of cations including Na, K, Ca, Cu, Cr, Fe, and Ni were studied, covering distinct electronic structures and chemical binding behaviors. The strength of ion-wall interaction with graphene and the bonding characteristics were assessed, followed by discussion on the effects of solvent and external electric field (EEF), to address the robustness and tunability in practical applications.

To study the ion-wall interaction, we constructed a $4 \times 4 \times 1$ supercell of graphene (32 carbon atoms) with a lattice constant that is relaxed to 2.46 Å. A single metal atom is placed on top of the graphene, at three high-symmetry sites, the center of hexagons (*hexagon*, H), the top of carbon atoms (*top*, T), and the bond center (*bond*, B). The ion-graphene system is charge neutral. The vacuum layer thickness (H) in the z direction is set to 15 Å for bare graphene and that with ion absorption 20 Å for hydrated ions, as the diameter of hydration is ≈ 5 Å [23]. Spin-polarized calculations were performed using the Vienna *Ab Initio* Simulation Package (VASP) with a kinetic energy

*Corresponding author: xuzp@tsinghua.edu.cn

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FIG. 1. [(a), (b)] Binding energies (E_b) of Na, K, Ca, and Cu on graphene as calculated from 12-6 L-J potential functions [22] and DFT/SCAN + r VV10. The heteroatomic L-J force-field parameters are computed through the Lorentz-Berthelot mixing rules [22]. [(c), (f), (i)] Differential charge densities ($\Delta\rho$) of K|G, Fe|G, and Cu|G composites at the energy-favorable sites (H, H, and T, respectively). Isosurfaces are visualized at 1.0×10^{-3} e/bohr³ (yellow for gain and cyan for loss). [(d), (g), (j)] 2D slices of $\Delta\rho$. [(e), (h), (k)] Accumulated $\Delta\rho$ in the x - y plane. The line plots on the right show the values of $\Delta\rho$ along the z direction, which is averaged in the x - y plane.

cutoff of 500 eV [24,25] and dipole-moment corrections in the z direction [26]. A $9 \times 9 \times 1$, Γ -center Monkhorst-Pack mesh grid was used for Brillouin-zone integration. The projector augmented wave (PAW) method is used for the ion-electron interaction [27], and pseudopotentials for Na (K), Ca, Cu, Cr, Fe, and Ni contain the p^6s^1 , p^6s^2 , $d^{10}s^1$, d^5s^1 , d^6s^2 , and d^8s^2 shells, which are treated as valence states. To include the long-range van der Waals interactions in SCAN meta-GGA that can well describe intermediate-range van der Waals interactions [20,21], the revised Vydrovvan Voorhis nonlocal correlation (r VV10) is adopted [21].

The adatoms adsorbed on graphene are ionized [28,29], and the energy of binding or adsorption for ions, E_b , is calculated as $E_b = E_{M|G} - E_M - E_G$. Here $E_{M|G}$ is the total energy of geometrically optimized atomic structures of the composite system and E_G , E_M are those for isolated systems of graphene and the ion, respectively. The calculation results show that these ions can be divided into two categories according to the bonding characteristics of their interaction with graphene, which is ionic for Na, K, and Ca, but covalent for Cu, Cr, Ni, and Fe. The results show that the value of E_b is on the order of 1.0 eV (Table S1) [22], which is consistent with that of ions on benzene or other aromatic molecules [11,12,14]. In contrast, the value of E_b calculated from the 12-6 Lennard-Jones (L-J) potential functions that are parametrized in widely used force fields [22], ≈ 0.1 eV, is significantly lower (Fig. 1). The enhanced strength of adsorption, as attributed to the cation- π interaction in the literature, requires clarification of the ion-wall interaction and a more reasonable parametrization procedure in force-field development.

To understand the contrast in ion-graphene adhesion, we analyzed electronic structures of the M|G composites.

The work functions of single atoms (W_M) was calculated, which demonstrate a linear correlation with the ionization energy (IE) [22]. The values of W_M are compared with that of graphene ($W_G = 4.29$ eV), showing that, for alkali-earth-metal ions Cr and Ni ($W_M < W_G$), charge is transferred into graphene, in consistency with the conclusion from Bader charge analysis [22]. For transition-metal ions such as Cu and Fe, we have $W_M > W_G$, but the ion-wall interaction has a covalent nature, and thus graphene is not an electron donor. The shift in the work function, $W_{M|G} - W_G$, scales linearly with the electric-dipole moment, M [22,30]. To elucidate the bonding characteristics, the redistribution and transfer of charge densities in the real space were analyzed (Fig. 1). We define the charge-density difference as $\Delta\rho = \rho_{M|G} - \rho_M - \rho_G$, where $\rho_{M|G}$, ρ_M , and ρ_G are the charge densities of the composite and isolated atom-graphene system, respectively. From the three-dimensional (3D) isosurfaces and 2D slices plotted for $\Delta\rho$, we find signatures of ionic and/or covalent bonds. Specifically, interaction with the alkali and alkali-earth-metal atoms such as K is ionic. There is no charge accumulation between the atom and graphene in this situation, in contrast to the transition-metal atoms such as Fe and Cu, where covalent bonding features are identified. Moreover, the excess charge for K|G is spatially delocalized, spreading on the upper surface of graphene, while for Fe|G and Cu|G, it is localized on the carbon atoms next to the metal atom, also signaling a different bonding nature.

These arguments can be further validated by the electronic band structures, which were calculated by unfolding the results obtained for the supercells to the primitive cells [31,32]. The ion-graphene interaction can be characterized by the significance of Dirac points near the high-symmetry point

FIG. 2. Spin-resolved effective band structures (EBSs) of (a) K|G, (b) Fe|G, and (c) Cu|G composites. The color bar indicates the Bloch spectral weight [31,32].

K in the effective band structure (EBS) [30,31,33]. Charge transfer between the ion and graphene shifts the Dirac point up or down with respect to the Fermi level (corresponding to *n*- or *p*-type doping) [33]. Orbital projections show that electron accepting and donating is dominated by the p_z orbital in graphene for all the ions under consideration, although charge transfers between the *s* and *d* orbitals are also identified in the transition-metal atoms [22]. For ionic interaction, the Dirac cone is distinct. In contrast, the covalent interaction perturbs the EBS by blurring the Dirac cone structures, as also indicated by electron localization between the adatom and graphene (Fig. 2) [22]. Analysis of density of states (DOS) and orbital projections identify that the perturbation is resulted from the coupling between *d* electrons in the transition-metal atom and p_z in graphene [22]. We also find that the significance of perturbation is positively correlated to the binding strength, although the characteristics of atomic orbitals are also important. Specifically, for Fe and Ni with $E_b = 0.854$ and 1.289 eV, the Dirac cone feature is destroyed, while for Cu and Cr with $E_b = 0.879$ and 0.374 eV, the modification is gentle (Fig. 2) [22].

Recent experimental studies on selective ion transport through graphene nanochannels show that the cation-anion and/or cation-cation selectivity can be achieved through mechanisms such as charge exclusion, size sieving, and

cation- π interaction as we discuss here [2–7]. To address the ion-graphene interaction from the ion mobility measured experimentally, the solvent effects are crucial [28,29]. Although the bare cation- π interaction is notably stronger than van der Waals interactions, the strength of ion-water interaction in hydrated ions is on the same order [11,12]. The ion-wall interaction is thus expected to be weakened with the presence of solvation shells that separate the ion and graphene. By intercalating water molecules at the ion-graphene interface, we find that, surprisingly, the adsorption strength of the ion-water complex remains at the same order as that of the bare interface. This conclusion is preserved in calculations using several other functionals (Fig. S5), and is expected to hold for complexes with a larger hydration number, as validated by models with more than one solvation shell [22]. Water intercalation can modify the ionic degree of cations and the binding distance (Tables S3–S5) [22]. The binding strength E_b increases as the ion makes direct contact with graphene without water intercalated at the ion-graphene interface, as a result of the modified ionization of ions and graphene, but decreases for the complexes with water intercalation that screens out the interaction. The interaction between alkali-earth-metal ions and graphene remains ionic. For Fe and Cu, the interaction changes from covalent to ionic as the ion-graphene distance increases (Figs. 3, S6, and S7) [22]. The Dirac cones in the

FIG. 3. [(a)–(h)] Optimized structures of Na/water complexes on graphene. S, T, and B denote the configurations with water molecules on the side, top, and bottom sites of Na, respectively, in top and front views. The numerals before the letters indicate the number of water molecules. (i) Binding energies (E_b) calculated for Na, Fe, and Cu complexes. The dashed and undashed bars are the results for covalent and ionic interactions, respectively. The results for Na with more water molecules in the complex are shown in Table S3 and Fig. S8 [22].

FIG. 4. (a) Dipole moments (M), (b) Bader atomic charges (q_{Bader}) [35], (c) binding energies [$E_b = E_{\text{M|G}}(E) - E_{\text{M}}(E) - E_{\text{G}}(0)$], and (d) magnetic moments ($\mu_{\text{M|G}}$) of the M|G composites, plotted as a function of the strength E of the EEF [illustrated in the inset of panel (d)]. Here $E_{\text{M|G}}(E)$ and $E_{\text{M}}(E)$ are energies of the composite with a relaxed structure and an isolated ion under EEF, while $E_{\text{G}}(0)$ is the energy of graphene with $E = 0$.

EBSs of Na are distinct for all configurations. In contrast, for transition-metal ions such as Fe and Cu, the Dirac cone feature is lost in the $2S$ configuration, which, however, is recovered in the $2S-1B$ configurations as the d electrons decouple with p_z and the Dirac point is shifted (Figs. S6 and S7) [22].

The electrostatic nature of ion-graphene interaction suggests that the interaction can be engineered by applying the EEF [13,34]. Under an EEF in perpendicular to the basal plane of graphene with strength, E , ranging from -4 to 4 V/nm, the dipole moment of system (M) changes continuously with the field strength E , indicating a modified charge-transfer behavior [Figs. 4(a) and 4(b)]. DFT calculation results show that the binding strength can be tuned by up to three times in the range of field strength explored here. For Na, K, Fe, and Ni, E_b increases with the field strength for $E < 0$ and decreases for $E > 0$, along with changes in the Bader atomic charge [Fig. 4(c)]. The difference in the field-strength dependence of E_b indicates that EEF provide an effective way to control the selective ion transport process as have been achieved in recent experiments [36]. The magnetic moment ($\mu_{\text{M|G}}$) of the ion-graphene composite also change with E for alkali and alkali-earth-metal ions, while for transition-metal ions it remains relatively intact [Fig. 4(d)]. Notably for Na and K, $\mu_{\text{M|G}}$ increases from 0 to $\approx 0.5\mu_B$. This induced magnetic moment, although too weak to modify the ion-wall binding behaviors, implies potential applications of magnetoelectric effects in metal-free magnetic systems and single-atom magnetic storage [37,38]. The changes in the DOSs under EEF (Figs. S9–S11) [22] show that, for alkali composites of K and Na, the s orbitals are shifted, as a result of the charge transfer process. For transition-metal ions, the d and s orbitals of Fe and Ni are shifted, while for Cu and Cr, the s orbitals remains intact but the d orbitals are shifted. This contrast may explain the distinct field-strength dependence of

FIG. 5. Energy scales spanned by intermolecular (weak), intramolecular (strong), and cation- π interactions [11,13,14,28], the free energy of hydration and partial hydration of ions [2,39–41]. Specific values are annotated for the binding energy of Na on graphene (0.65 eV, Na|G using SCAN + rVV10) [22], K^+ on benzene (0.83 eV, $K^+|C_6H_6$) [11], Na^+ on graphite (2.35 eV, $Li^+|graphite$) [14], the strength of hydrogen bond in bulk water (0.24 eV) [42], strength of C-C covalent bond (3.57 eV) and Na-Cl ionic bond (8.16 eV) [43], free energy of partial hydration with the first hydration shell (1HS, ≈ 2 eV for Mg^{2+} and ≈ 0.2 eV for Na^+) [2,40,41], and free energy of hydration for H_3O^+ (1.73 eV), Na^+ (3.91 eV), and F^- (4.86 eV) [39].

E_b of Cu and Cr [Fig. 4(c)]. These findings suggest that, for carbon nanofluidics where the width of fluid channel is comparable with the range of ion-wall interaction, the selective ion transport or storage processes can be well controlled by external fields, which cannot be achieved with conventional knowledge in micro- and/or nanofluidics.

As the hydration free energy of ions ($\gtrsim 1.0$ eV) is comparable to the strength of ion-graphene interaction [39], there is a competition between ion-graphene binding and ion solvation (Fig. 5) [23,44]. We identify that the partial dehydration free energy of the first hydration shell (1HS, ≈ 2 eV for Mg^{2+} and ≈ 0.2 eV for Na^+) [2,40,41] is comparable to the strength of ion-graphene interaction and that of hydrogen bonds in water (0.24 eV [42]). Previous studies suggest that weakly hydrated ions such as Na^+ and K^+ can make direct contact with the graphene surface, but not for highly hydrated ions such as Ca^{2+} and Mg^{2+} [23,44]. In nanochannels, perturbation on HSs from complexity in the chemical environment [15,23], modification of water-structuring effects (structure-making, structure-breaking) [45], paired correlation of ions [36], and potential of external fields are coupled to the ion-wall interaction. The configurations of hydrated ions in the graphene nanochannels are thus not easy to predict. Recent advances in experimental techniques may advance our understandings beyond the theoretical arguments. For example, experiments using scanning tunneling microscopy (STM) and atomic force microscopy (AFM) demonstrated the feasibility of exploring HSs near a surface [46,47]. One can also use x-ray absorption spectroscopy (XAS), second-harmonic generation (SHG) microscopy, and other tools along with molecular dynamics (MD) simulations to probe the HSs indirectly [48,49]. Further experiments and simulations with more detailed information on the ion-wall interaction are needed to clarify these points. Since the specific, relatively strong, and robust interaction between ions and graphene stems from electrostatic interaction and/or covalent bonding

(compared to the van der Waals interaction), the polarization in ion-graphene composites requires an improved treatment far beyond the simple pair-form potentials such as the L-J and Morse function. Moreover, the delocalization of electrons transferred to and from graphene makes it challenging to describe the ion-graphene interaction [22]. Our work thus offers key insights to develop accurate force fields for classical MD simulations of ion dynamics confined in graphene channels where the ion-wall interaction becomes essential, which can be implemented by, for example, using the deep-learning-

based representation to address the accuracy versus efficiency dilemma [50].

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