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Modelling interaction of atoms and ions with graphene

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Abstract

In this Letter, the authors investigate the interaction of various atoms/ions with a graphene sheet and two parallel graphene sheets using the continuous approximation and the 6–12 Lennard-Jones potential. The authors assume that the carbon atoms are smeared across the surface of the graphene sheet so that the total interaction between the single atom/ion and the graphene sheet can be approximated by a surface integration over the graphene sheet. They determine the equilibrium position for the atom/ion on the surface of the graphene sheet and the minimum intermolecular spacing between two graphene sheets. This minimum spacing is by symmetry twice the value for the equilibrium positions for a single graphene sheet and is such that the atom/ion undergoes no net force. The same methodology together with basic statistical mechanics are also employed to investigate the diffusion of the atom/ion from a central location to the edge of the graphene sheet at different temperatures. The results presented in this Letter are consistent with a similar study adopting a molecular dynamics simulation approach. Possible applications of the present study might include the development of future drug delivery systems and future high-performance alkali battery design using nanomaterials as components.

Keywords

ions, atoms, graphene, interaction, modelling

Disciplines

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Modelling interaction of atoms and ions with graphene

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In this Letter, the authors investigate the interaction of various atoms/ions with a graphene sheet and two parallel graphene sheets using the continuous approximation and the 6–12 Lennard-Jones potential. The authors assume that the carbon atoms are smeared across the surface of the graphene sheet so that the total interaction between the single atom/ion and the graphene sheet can be approximated by a surface integration over the graphene sheet. They determine the equilibrium position for the atom/ion on the surface of the graphene sheet and the minimum intermolecular spacing between two graphene sheets. This minimum spacing is by symmetry twice the value for the equilibrium positions for a single graphene sheet and is such that the atom/ion undergoes no net force. The same methodology together with basic statistical mechanics are also employed to investigate the diffusion of the atom/ion from a central location to the edge of the graphene sheet at different temperatures. The results presented in this Letter are consistent with a similar study adopting a molecular dynamics simulation approach. Possible applications of the present study might include the development of future drug delivery systems and future high-performance alkali battery design using nanomaterials as components.

1. Introduction: Carbon nanomaterials, such as fullerenes, carbon nanotubes and graphene sheets, have been extensively investigated not only for manufacturing new nanoscale devices, such as sensors, actuators, memory devices and electromechanical switches [1, 2], but also for fabricating biomechanical systems [3, 4]. Carbon nanomaterials, especially carbon nanotubes and graphene, are ideal candidates for the encapsulation of drugs, nanofiltration membranes, atomic/molecular encapsulation, containment of carbon dioxide for tackling climate change, and hydrogen storage for powering green vehicles.

Some ions such as Mn^{2+} and Gd^{3+} are well known agents for magnetic resonance imaging [5, 6]. Interaction with a graphene sheet turns out to be crucial for developing future drug delivery systems for identifying and controlling drug location (nanovectors). The demonstration of the diffusion process for metals and alkali ions on a graphene surface has been experimentally observed by high-resolution transmission electron microscope [7]. Krashennnikov *et al.* [8] have also used density functional theory to investigate the structure, bonding and magnetic properties of metal atoms embedded between graphenes, which are crucial for developing high-performance alkali batteries [9, 10]. More recently, Wang *et al.* [11] experimentally demonstrate that graphene nanosheets can enhance the lithium storage capacity in lithium ion cells and hence produce improved cyclic battery performance.

In this Letter, we adopt the approach employed by Cox *et al.* [12, 13] who employ the 6–12 Lennard-Jones (L-J) potential and further assume that carbon atoms are evenly distributed across the surface of carbon nanostructures so that the total potential energy between various non-bonded carbon nanomolecules can be determined analytically by performing a surface integral. Such total potential energy can be used to investigate the relative motions of quite complicated nanostructures, such as the oscillatory motion of a fullerene inside a single-walled carbon nanotube. In addition, the same methodology has successfully been used to study the encapsulation of drug molecules inside single-walled nanotubes as the ‘magic bullet’ [14, 15] and the encapsulation of hydrogen atoms inside metal-organic frameworks for hydrogen storage [16].

Here, the interaction of various metals/ions with a graphene sheet is investigated. Particular interest centres around manganese ion (Mn^{2+}), gold atom (Au), platinum (Pt), sodium ion (Na^{1+}) and lithium ion (Li^{1+}). While Mn^{2+} is an ideal candidate for drug delivery, Li^{1+} is a common element for high-energy density rechargeable alkali batteries. Further, other elements such as Au, Pt and

Na^{1+} are selected as a benchmark for comparison purposes. The continuous approach is employed to approximate the van der Waals interactions between a single atom/ion and a graphene such that the equilibrium position of the atom/ion on the surface of the graphene sheet, h , can be determined and the minimum intermolecular spacing between two parallel graphenes, $2h$, can be subsequently estimated, for which no net force is exerted on the atom/ion. Such minimum intermolecular spacing might be used, for example to determine the smallest possible battery size and the maximum battery capacity for Li^{1+} alkali batteries. Furthermore, the diffusion of the atom/ion on the surface of the graphene sheet is investigated using the energy conservation principle and simple statistical mechanics, which could form theoretical basis for designing future high-performance alkali batteries by improving the intercalation between lithium ions and graphene sheets inside the cathode of the rechargeable batteries. The present authors believe that apart from the respective shapes and sizes of the microstructure, knowledge of the dynamics of ion transport on a graphene sheet could be used to improve the design of such structures. At present, these structures, size and shape are designed mainly empirically and these approaches might achieve a more rational battery design. The authors also acknowledge that although some detailed physical effects such as electron charge exchanges, optical properties of the graphene sheet and structural effects, for example the local deficits of graphene, are ignored in the current work, average physical quantities such as the minimum intermolecular spacing and the diffusion time for various atoms/ions can be predicted almost instantaneously using simple formulae and yet still yield reasonable results in comparison to that of molecular dynamics simulation methodologies.

Wherever possible, the merits and the limitations of this methodology are discussed in comparison to the more comprehensive calculations, for example density functional theory and molecular dynamics simulation approaches.

2. Theory: In this Section, the authors determine the equilibrium position, h , and the minimum intermolecular spacing, $2h$ for Mn^{2+} , Au, Pt, Na^{1+} and Li^{1+} on the surface of a $n = 19$ carbon graphene sheet, where n denotes the number of hexagon on the graphene sheet, followed by the diffusion for the single atom/ion on the surface of the graphene sheet. The schematic diagram for the proposed systems is given in Fig. 1. The molecular interaction between the atom/ion and the graphene is modelled by the usual

6–12 L-J potential [17], which is given by

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

where ρ , ϵ and σ denote the atomic distance between two arbitrary atoms, the potential well depth of two atoms and the L-J distance, respectively. In addition, A and B denote the attractive and repulsive Hamaker constants, respectively. The authors comment that following the L-J description for atomic interaction by Jones [18], many theoretical efforts have been made to improve the accuracy of the results by taking into account dielectric properties of the surface [19].

Next, it is assumed that the carbon atoms are smeared across the surface of the graphene sheet and the continuous approach developed by Cox *et al.* [12, 13] is adopted to determine the total potential energy of the single atom/ion and the graphene sheet system, which is stated as

$$E = \eta \int_s V(\rho) dS \tag{2}$$

where η and dS denote the atomic number density (number of carbon atoms per Å²) and the surface area element of the graphene sheet, respectively. There are a finite number of geometric approximations that can be made to calculate the surface area of a graphene sheet. Cox *et al.* [20] approximate the graphene surface by a rectangular shape, but here it is analytically convenient to approximate the graphene sheet by a circular shape, for which $dS = 2\pi r dr$. Since the L-J potential decays rapidly beyond the van der Waals distance, the authors accurately approximate the graphene sheet by an infinite circular shape without serious loss of numerical accuracy.

Figure 1 Schematic for interaction between atom/ion and graphene sheet

Table 1 L-J potential parameters

Atom/ion–graphene	Kinetic diameter σ , Å	Well depth ϵ , eV	Attractive constant A , eV Å ⁶	Repulsive constant B , eV Å ¹²
Mn ²⁺ –C [22]	2.250	0.00994	5.159	669.312
Au–C [23]	3.187	0.00210	8.786	9206.081
Pt–C [15]	3.134	0.00718	27.168	25 717.910
Na ¹⁺ –C [24]	2.935	0.00230	5.886	3762.605
Li ¹⁺ –C [25]	2.473	0.00433	3.959	904.438

L-J parameters for graphene are determined from [12, 13]

Under these assumptions, (2) becomes

$$E = \eta \pi \left(-\frac{A}{2h^4} + \frac{B}{5h^{10}} \right) \tag{3}$$

where h denotes the perpendicular distance of the atom/ion above the graphene sheet (see Fig. 1). The authors comment that (3) can be easily used by engineers and chemists and the attractive constant A and the repulsive constant B of the system can be determined by individual elements using the Lorentz–Berthelot mixing rule [21]. All the L-J parameters used in this Letter are summarised in Table 1.

3. Numerical results and discussions: Upon substituting these L-J parameters into (3), one can determine the total potential energy of various atoms/ions in terms of the perpendicular distance h above the graphene sheet, which is plotted in Fig. 2. The equilibrium positions for Mn²⁺, Au, Pt, Na¹⁺ and Li¹⁺, where minimum potential energies occur are reported as 2.25, 3.30, 3.25, 2.91 and 2.5 Å, respectively. For example, the equilibrium position for Mn²⁺ is comparable to the density functional theory numerical result, which is 2.46 Å given by Abe *et al.* [9]. The above study is ready to predict the minimum intermolecular spacing of two parallel graphenes $2h$ (the factor of 2 is utilised because of the symmetry between graphenes) so that the embedded atom/ion, for example Li¹⁺ undergoes no net force. Such a value for Li¹⁺ is estimated to be 5 Å. For anything below this value, the two parallel graphene sheets strongly influence Li¹⁺ and therefore becomes unstable for delivering reliable battery functionalities. The minimum intermolecular spacing could be used to determine the minimum possible size and the maximum possible capacity of a battery.

Next, the authors investigate the diffusion process for a single atom/ion above the surface of a graphene sheet. Such diffusion process is simply caused by the chemical potential difference between the atom/ion at the centre and on the edge of the graphene sheet. The minimum potential energies for Mn²⁺, Au, Pt, Na¹⁺ and Li¹⁺ at the centre can be read off from Fig. 2 as 0.0723, 0.0306, 0.101, 0.0285 and 0.038 eV, respectively. However, the atom/ion only observes roughly half of the above potential energies on the edge, from which one can use the conservation of energy by equating the potential and the kinetic energy of the atom/ion to determine the diffusion time at absolute zero. For this calculation, the authors have approximated the velocity of the atom/ion by the radius of the graphene sheet, which is 11 Å over the diffusion time. Upon taking into account of the temperature effect using the simple Boltzmann distribution function, that is, $\exp(-E/k_B T)$, where k_B denotes the Boltzmann’s constant, one can determine the average diffusion time for the atom/ion, provided that $kT \ll E$ is satisfied. The numerical results are plotted in Fig. 3. It is observed that the diffusion time for Mn²⁺ at $T = 300$ and 600 K are comparable to those obtained by Abe *et al.* [9]. However, the small discrepancy between these results and the results given by Abe *et al.* [9] may arise from the ignorance of other physical mechanisms, for example electron charge exchanges during the diffusion process, the optical properties of the graphene sheet and the edge effects at

Figure 2 Total potential energy for proposed systems

Figure 3 Diffusion time for proposed systems at different equilibrium temperature

the nanoscale. In addition, for the case of magnesium ion interacting with graphene, Tachikawa [25] shows that the magnesium ion vibrates in a hexagonal site and the diffusion process does not occur even at $T = 1000$ K. However, this model still predicts reasonable average diffusion times for the proposed systems, a calculation that otherwise might take a very large computational time using molecular dynamics calculations and easily accessible by engineers and chemists. From Fig. 3, it is observed that Li^{1+} constitutes the minimum diffusion time and hence generating the highest battery performance (better intercalation) in comparison to other elements such as Na^{1+} . From Fig. 2, Li^{1+} also possesses the smaller intermolecular spacing than that of Na^{1+} and hence the smaller battery size and the higher battery capacity could be possibly achieved.

4. Conclusions: The determination of molecular interaction between atoms/ions and a graphene sheet could be crucial for developing future drug delivery systems and high-performance batteries. In this Letter, the authors adopt the 6–12 L-J potential together with the continuous approach employed by Cox *et al.* [12, 13] to evaluate such interactions and find that although the methodology provides only average values for the intermolecular spacing and the diffusion time, these results are comparable to those obtained from time-consuming molecular dynamics simulation. Although some subtle physical effects are ignored using the current methodology, it can be seen to provide reasonable predictions, for example the minimum possible battery size, the maximum battery capacity and better battery performance. The authors can also obtain corresponding results from the same methodology but for nanosheets of different materials, for example silicon. The authors also comment that the present methodology can be easily extended to small metal clusters on the graphene sheet by further adopting the continuous approximation either on the surface or throughout the volume of the metal cluster.

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