C$_3$ coefficients for the alkali atoms interacting with a graphene layer and carbon nanotube

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Abstract
We evaluate separation dependent van der Waals dispersion (C$_3$) coefficients for the interactions of the Li, Na, K and Rb atoms with a graphene layer and with a single walled carbon nanotube (CNT) using the hydrodynamic and Dirac models. The results from both the models are evaluated using accurate values of the dynamic polarizabilities of the above alkali atoms. Accountability of accurate dynamic polarizabilities of the alkali atoms to determine the C$_3$ coefficients are accentuated by comparing the obtained coefficients using the precise values of the dynamic dipole polarizabilities against the values estimated from the single oscillator approximation that are generally used in the earlier calculations. For a practical description of the atom–surface interaction potentials, the C$_3$ coefficients are given for a wide range of separation distances between the considered ground states of the atoms and the wall surfaces and also for different nanotube radii. The coefficients for the graphene layer are fitted to a logistic function of the separation distance. For CNT, we find a paraboloid kind of fit dependence both on the separation distances and radii of the CNT.

Keywords: dispersion interaction, reflection coefficients, atomic polarizabilities

(Some figures may appear in colour only in the online journal)

1. Introduction

In the past decade, a considerable amount of attention has been drawn both towards the experimental and theoretical studies of the internal scattering of atoms with a graphene layer, and with various carbon nanostructures [1–3]. Owing to the fact that these nanostructures are endowed with exceptional electronic, optical, mechanical, thermal and magnetic properties that are of vested interest to the modern communication engineering technologies [4, 5], their applications are in demand both in the scientific and industrial laboratories. Graphene, in particular, manifests unique properties incurring its honeycomb-lattice structure that could maximize the interactions of the atoms on the layer. In fact, the knowledge of the atom-graphene interactions has been very useful in the construction of the hydrogen storage devices [6–8] and also plays an important role in understanding different physical, chemical and biological processes [9–12]. Moreover, these interactions are connected to the phenomenon of quantum reflections whose studies are useful to many experimentalists and theoreticians for explaining their exact behavior [13–16]. In addition to this, gaining insights into the atom-graphene contacts are crucial in the development of graphene based electronics. Metals adsorbed on graphene can form different types of structures and can rejuvenate graphene’s electronic behavior, instigating the observation of fascinating physical phenomenon [17–20]. Among the metals that can be adsorbed on graphene, study for the Li atom is categorically important for the applications in the storage of hydrogen gas [21, 22], improving efficiencies of Li-ion batteries [23, 24], and making superconductors [25, 26]. K atoms have also been used to tune the electronic structures of the graphene bilayers [27, 28]. A graphene layer rolled to make a carbon nanotube (CNT) has some very peculiar properties and has been
gaining world-wide attention [29–31]. Interaction of the alkali atoms with the single walled CNTs have profound applications in the purification of the CNTs [32]. Adsorbed alkali atoms have been demonstrated to act as chemical dopants on the CNTs and have been used to fabricate field effective transistors [33].

Accurate measurement of the $C_3$ coefficient of any atomic system with a graphene layer and with a CNT is extremely difficult. A number of theoretical methods have been performed, particularly using the density functional theories [34–37], lower order many-body methods [38], Lifshitz theory [13, 39–43], etc, to uncover the nature of the interactions of carbon nanostructures with various materials. Klimchitskaya et al have used Lifshitz theory to explain the interaction of the graphene layer with different materials, including metal plate [44–46] and atomic systems such as H [13], Na, Rb, Cs [13, 43], H$_2$ molecule [13], He$^+$ ion [13, 43], etc. Interactions of CNT with the H atom and H$_2$ molecule have also been explained by them in great detail [13]. However, these calculations for the graphene layer have been basically carried out by employing the dynamic polarizabilities obtained from the single oscillator model (SOM). In view of the fact that these interactions play crucial roles in a number of applications, and keeping in mind their vast experimental use, it would be expedient to carry out more accurate theoretical analysis of the interactions of the graphene layer and CNT with the alkali atoms. Our aspiration in this paper is to contemplate calculations of the $C_3$ coefficients to describe the interactions of the alkali atoms with a graphene layer by using precise values of the dynamic polarizabilities of the atoms. For this purpose, we assert that graphene is characterized at zero temperature and the interactions are well valid in the small separation region with the proviso of perceiving the importance of using accurate values of the polarizabilities.

The interaction between an atom and a wall is usually modeled by calculating the interaction between the atom and its image charge (reflection) in the wall. The reflection coefficients required for such calculations are well described by the widely celebrated Lifshitz theory which expresses these quantities as the functions of the dynamic dielectric permittivity of the wall and of the dynamic dipole polarizabilities of the atoms [47–51]. Although accurate evaluation of the dynamic dipole polarizabilities in the atomic systems require sophisticated many-body methods, their values for the alkali atoms, which are the utmost used atoms in the ultra-cold atomic experiments, are now known reliably at least with sufficient precision at this stage of interest [52, 53]. In contrast, the dynamic dielectric permittivity values are generally known to provide insufficient accuracy in the material mediums due to their strenuous procedure of evaluation, and to determine them precisely could prove a tedious task over a long period. In particular, the nanostructures with thickness of the size of an atom such as the considered graphene layer and single walled CNT do not have well defined dielectric permittivity. This entails the need for adopting suitable models to estimate the $C_3$ coefficients by introducing some effective parameters that can substitute the role of the dielectric permittivity of the wall in the Lifshitz theory. In this context, the two most popular models often employed for theoretical determination of the dispersion coefficients are the hydrodynamic model [54–58] and the Dirac model [59]. Here, we intend to apply both the models and would like to compare the obtained results using accurate values of the dynamic dipole polarizabilities. We also plan to present a very handy functional form of the radial dependent dispersion coefficients so that they can be easily derived for any arbitrary values of the atom-wall distance and the CNT radius for their convenient use in practical applications.

This paper is organized as follows: in section 2, we present the modified Lifshitz theory for the reflection coefficients on the graphene layer and CNT in the hydrodynamic and Dirac models framework. This is followed by a brief description of the method of calculations of the dynamic dipole polarizabilities in section 3 which are later used in the evaluation of the dispersion coefficients. Calculated results for the $C_3$ coefficients using accurate values of the dynamic polarizabilities and using SOM are given in section 4. In the same section, we present the dispersion coefficients for the graphene layer and CNT determined by employing both the hydrodynamic and Dirac models, and we compare them with the results obtained for an ideal conducting medium, Au, and SiO$_2$ wall. Unless stated explicitly, the results are given in atomic units (au) throughout the paper.

## 2. Theory of the dispersion coefficient

For a CNT with radius $R$ the dispersion coefficient ($C_3(a, R)$) is expressed using the proximity force approximation (PFA) as [47, 58, 60]

$$C_3(a, R) = \frac{1}{16\pi} \sqrt{\frac{R}{R + a}} \int_0^\infty d\xi \alpha(\xi) \int_{2aR\xi}^\infty d\gamma \, \gamma e^{-\gamma} \times \left\{ y = \frac{a}{2(R + a)} \right. \times \left. 2r_{TM} - \frac{4a^2 R^2}{y^2} (r_{TM} + r_{TE}) \right\}.$$

(1)

where $a_0$ is the fine structure constant, $a$ is the separation distance between the atom and the surface, $\alpha(\omega a)$ is the dynamic polarizability of the atom with imaginary argument, $r_{TM}$ and $r_{TE}$ are the reflection coefficients of the electromagnetic oscillations on CNT for the transverse magnetic and electric polarizations of the electromagnetic field. It has been shown in [61] that the relative differences between the exact and PFA results could be within 4% for the condition $\frac{1}{2} < \frac{a}{R} < \frac{3}{7}$.

For a thin single layer of graphene with limit $R \rightarrow \infty$, we can simplify the above expression to [13]

$$C_3(a) = \frac{1}{16\pi} \int_0^\infty d\xi \alpha(\xi) \int_{2aR\xi}^\infty d\gamma \, \gamma e^{-\gamma} \frac{2r_{TM} - \frac{4a^2 R^2}{y^2} (r_{TM} + r_{TE})}{y^2}.$$

(2)

The separation distance dependent $C_3$ coefficients given above
include both the retarded and non-retarded interaction energies which are applicable up to the separation distances where the thermal effects are not significant (typically ~1 μm) [39, 62]. However, the thermal effects are non-negligible in the determination of the $C_1$ coefficients at the larger separations, as has been shown by Gomez-Santos [63]. The results of our above approximation are suitable for use either for the zero-temperature experiments or for the room-temperature experiments performed at very short separation distances. Nevertheless, this would expound the role of using accurate values of the dynamic polarizabilities in the calculations of the $C_1$ coefficients.

The most difficult part in the evaluation of the above expressions is to get the $r_{TM}$ and $r_{TE}$ reflection coefficients correctly. Two widely used models to describe the electronic structure of graphene are the hydrodynamic model and the Dirac model. Within the framework of the hydrodynamic model, the reflection coefficients for a graphene layer or CNT are given as [54–58]

$$r_{TM} = \frac{q k}{q k + \alpha \psi}$$

and

$$r_{TE} = -\frac{k}{k + q},$$

with the wave number of graphene sheet $k = 6.75 \times 10^4$ m$^{-1}$ and $q = \frac{v_f \Delta}{\pi}$. In this model, graphene is considered as an infinitesimally thin positively charged sheet carrying a homogeneous fluid with some mass and negative charge densities. The energy of the quasi-particles in graphene is quadratic with respect to their momenta. Therefore this model works well at the large energies and fails at the low energies (where actual energy of the quasi-particles is a linear function of momentum). This model is an approximate one and does not take into account the Dirac character of the charge carriers in graphene.

Within the framework of the Dirac model to describe the electronic structure of graphene, the quasi-particle fermion excitations in graphene are treated as massless Dirac fermions moving with a Fermi velocity. It takes into account the properties of the graphene which are valid at the low energies of the quasi-particles in graphene; specifically, energies which are linear functions of momenta. The explicit relations for the reflection coefficients, considering the electronic structure of the graphene or CNT according to the Dirac model, are given as: [59]

$$r_{TM} = \frac{af(\hat{q})}{2\hat{q}^2 + af(\hat{q})}$$

and

$$r_{TE} = -\frac{af(\hat{q})}{2\hat{q} + af(\hat{q})},$$

where the function $f(\hat{q})$ determines the polarization tensor in an external electromagnetic field in the three dimensional space-time coordinate and is given as [59]

$$f(\hat{q}) = 4 \left( \alpha_{\nu} \Delta + \frac{\hat{q}^2 - 4\alpha_{\nu}\Delta^2}{2\hat{q}} \arctan \left( \frac{\hat{q}}{2\alpha_{\nu}\Delta} \right) \right),$$

where $\Delta$ is known as the mass gap parameter. The exact value of $\Delta$ remains unknown; however, its commonly accepted upper bound value quoted in the literature is 0.1 eV [25, 59].

The parameter $\hat{q}$ in the above equation is defined in terms of the Fermi velocity $v_f \sim 10^6$ m s$^{-1}$ as

$$\hat{q} = \left[ \frac{\alpha_v v_f^2 v_f^2}{4\alpha^2} + \left( 1 - \alpha_v^2 v_f^2 \right) \alpha_v^2 v_f^2 \right]^{1/2}.$$  

In the next section, we shall briefly discuss the method of calculations for the dynamic polarizabilities which are required for evaluating the $C_1$ coefficients as discussed above, and would like to compare them with the results obtained considering the SOM results. We also compare the results of the present work with those for the interaction of the alkali atoms with the materials having planar structures, such as a prefect conductor, a metal (Au), a semi conductor (Si) and a dielectric (SiO$_2$) which have been reported by us earlier [64].

### 3. Evaluation of the dynamic polarizabilities

The dynamic dipole polarizabilities of the ground state ($\Psi_i$) of an alkali atom for the corresponding principal quantum number $n$ due to the direct current electric field with the frequency $\omega$ is given by (e.g. see [52, 65])

$$\alpha(\omega) = \alpha_c(\omega) + \alpha_v(\omega) + \alpha_c(\omega),$$

where $\alpha_c$, $\alpha_v$, and $\alpha_c$ are known as core, core-valence and valence correlation contributions, respectively.

The advantage of using the expression given by equation (7) is that the dynamic of the dominant contribution $\alpha_c$ can be evaluated using the formula

$$\alpha_c(\omega) = \frac{2}{3} \left( \frac{2J_z + 1}{2J_z + 1} \right) \sum I \left( E_I - E_J \right) \left( \frac{\langle \Psi_I | D | \Psi_J \rangle}{E_I - E_J} \right)^2,$$

where $J_z = 1/2$ is the total angular momentum of the corresponding ground state, sum over $I$ represents all possible allowed intermediate states for the dipole transition, $E$s are the energies of the corresponding states and $\langle \Psi_I | D | \Psi_J \rangle$ is the electric dipole (E1) reduced matrix element of the dipole operator $D$ between the states $\Psi_I$ and $\Psi_J$.

In fact, the E1 matrix elements for many important transitions of the alkali atoms are now well studied and known to provide quite reasonable accuracy [52, 53, 66–68]. Using these matrix elements along with the experimental energies will certainly give more precise contributions to $\alpha_c$, and contributions from the higher singly and doubly excited states (tail) can be accounted approximately using a lower-order theory. It has also been found in the previous studies...
that the core and core-valence contributions are smaller than the valence contributions in the evaluation of the polarizabilities of the ground states of the alkali atoms (e.g. see [52, 53] and references therein). We account these later contributions using the Dirac–Fock (DF) method.

Among the important E1 matrix elements between the low-lying states, the matrix elements for a few primary transitions in the Na, K and Rb atoms have been obtained using a fitting procedure from the precise measurements of the lifetimes and the static dipole polarizabilities of the first few low-lying excited states, as have been given in [52, 53]. For instance, the E1 matrix elements of the 3s–3p transition are taken from the compiled data list of [69]. The other important matrix elements whose values were not deducible accurately from the measured quantities are evaluated by employing a relativistic coupled-cluster (RCC) theory. In our RCC method, we express the atomic wave function with the valence electron ν as

\[ |Ψ_ν⟩ = e^\tau (1 + S) |Φ⟩, \]

where |Φ⟩ is the DF wave function and T and S operators account for the correlation effects to all orders through the excitations of the electrons from the core orbitals alone and together from the valence and core orbitals, respectively. We consider here the singly and doubly excited configurations with important triple excited configurations in the well-known CCSD(T) method framework for calculating the atomic wave functions.

We calculate the E1 reduced matrix elements between the states \( |Ψ_ν⟩ \) and \( |Ψ_i⟩ \) to be used in the sum-over-states approach using the following RCC expression

\[ \langle Ψ_i|D|Ψ_ν⟩ = \frac{\langle ϕ|\{1 + S'_ν\}|ψ⟩}{\sqrt{N'_ν N}}, \]

where \( D = e^\tau D e^\tau \) and \( N' = \langle ϕ| e^\tau e^\tau + S'_ν e^\tau e^\tau S |ϕ⟩ \) involve two non-truncating series in the above expression. Calculation procedures of these expressions are discussed elsewhere [77, 78].

Following equation (8), we can write

\[ α(ιω) = \frac{2}{3(2I + 1)} \times \sum_{I} \frac{|\langle Ψ_i|D|Ψ_ν⟩|^2}{(E_I - E_ν)\left(1 + \frac{ιω}{E_I - E_ν}\right)^2}. \]

By assuming that there is only one principal dominating intermediate state, \( k, \) for which \( E_ν - E_k = ω_k \gg (E_ν - E_i) \) for the intermediate states \( I \neq k, \) the dynamic polarizability can be approximately estimated in SOM by

\[ α(ιω) \approx \frac{α(0)}{1 + \left(\frac{ω_k}{ω_ν}\right)^2}. \]

Table 1. Absolute values of the E1 matrix elements in the Li, Na, K, and Rb atoms in \( e_ν. \) Those which are extracted from the measured quantities are given in bold fonts; otherwise they are calculated using the coupled cluster single double (triple) (CCSD(T)) method. Estimated uncertainties in the CCSD(T) results are given in the parentheses.

| Transition       | Li E1 matrix elements | Transition       | Na E1 matrix elements |
|------------------|-----------------------|------------------|-----------------------|
| 2s_{1/2} → 2p_{1/2} | 3.182(2)              | 2s_{1/2} → 3p_{1/2} | 3.5246(23)           |
| 2s_{1/2} → 3p_{1/2} | 0.182(2)              | 3s_{1/2} → 4p_{1/2} | 0.304(2)             |
| 3s_{1/2} → 4p_{1/2} | 0.159(2)              | 3s_{1/2} → 5p_{1/2} | 0.107(1)             |
| 3s_{1/2} → 5p_{1/2} | 0.119(4)              | 3s_{1/2} → 6p_{1/2} | 0.056(2)             |
| 3s_{1/2} → 6p_{1/2} | 0.092(2)              | 3s_{1/2} → 7p_{1/2} | 0.035(2)             |
| 3s_{1/2} → 7p_{1/2} | 0.072(1)              | 3s_{1/2} → 8p_{1/2} | 0.026(2)             |
| 3s_{1/2} → 8p_{1/2} | 4.692(5)              | 3s_{1/2} → 3p_{1/2} | 4.9838(4)            |

4. Results and discussion

As mentioned above, we use the most precise values of the E1 matrix elements compiled in [52, 53] for the few important \( ns → np \) transitions of the Na, K and Rb atoms. These values are given in bold fonts in Table 1. In the same table, we also present the E1 matrix elements for other transitions calculated using our CCSD(T) method required for the evaluation of the polarizabilities that are already discussed at length in our earlier work [52, 53]. In Table 2, we present the contribution to the static dipole polarizabilities of the considered atoms and the characteristic frequencies are generally atom dependent. Sometimes, the \( ω_k \) value is chosen by fitting the above equation into the data available for the \( α(0) \) and \( α(ω) \) of an atom; for example see [40, 60].
obtained using these matrix elements as valence contributions $\alpha_v$ and the core, core-valence and tail contributions are given from the \textit{ab initio} calculations using the DF method. In this table, we also compare our final polarizability results with the available theoretical and experimental results and the values used in the earlier work for SOM [43]. As can be seen from the table, our static polarizability values match well with the values given in [70], where these polarizability values were obtained by combining the experimental data with the relativistic linearized coupled-cluster method limited to the single and double (SD) excitations. Extensive calculations of the dipole polarizabilities in the alkali atoms were also done by Marinescu \textit{et al} [71] using an empirical $l$- dependent model potential approach for the motion of a valence electron in the presence of a frozen core. In this work, the infinite second-order sums in the polarizability calculations were transformed into integrals over the solutions of two coupled inhomogeneous differential equations, and the integrals were carried out using the Numerov integration method. Our values are clearly in better agreement with experimental values as compared to the values given in [71]. Thus, this table clearly testifies the preciseness of our estimated static polarizabilities and ensures the quality of the dynamic polarizabilities that are obtained using our method. In order to compare our dynamic polarizability results with the SOM, we plot them in figure 1, which shows large differences at the smaller values of frequency. Employing these dynamic polarizabilities, we calculate the $C_3$ coefficients for the interactions of the alkali atoms with the graphene layer. As discussed before, we have chosen the upper bound for the gap parameter of graphene as $\Delta = 0.1$ eV in our calculations to render the intention of the present work. To depict the importance of using accurate polarizability values in these calculations, we plot in figure 2 the $C_3$ coefficients of the Na and Rb atoms against the separation distance from the graphene layer using polarizabilities from the RCC method and SOM. Our results for the Na atom using the polarizabilities calculated using the RCC method are not very different from the results given in [13] that are obtained using the polarizabilities from SOM. However, there seem to be significant differences in the results for the heavier Rb atom. The discrepancy seems to be due to the accuracies of our dynamic polarizability values than the latter.

Next, we use our polarizability values to determine the $C_3$ coefficients for the interactions between the alkali atoms with the graphene layer and CNT using the hydrodynamic and Dirac models by substituting expressions given by equations (3) and (4), respectively, in equations (2) and (1). We plot these values against different separation distances $a$ in figure 3 for all the considered atoms using both the models and the $C_3$ coefficients for a perfect conducting surface, Au and SiO$_2$ wall that have been reported elsewhere [64].

### Table 2. Static dipole polarizabilities (in au) of the ground states of the Li, Na, K and Rb alkali atoms and their comparison with the available theoretical and experimental results. Values used in the SOM for the evaluation of the dynamic polarizabilities in the previous works are also given at the bottom of the table.

| Contribution | Li   | Na   | K    | Rb    |
|--------------|------|------|------|-------|
| $\alpha_v$   | 162.6| 161.4| 284.3| 309.3 |
| $\alpha_c$   | 0.22 | 0.9  | 5.5  | 9.1   |
| $\alpha_{cv}$| $\sim$0| $\sim$0| $-0.13$| $-0.26$|
| $\alpha_{tail}$| 1.2 | 0.08 | 0.06 | 0.11 |
| Total        | 164.1| 162.4| 289.8(6)| 318.3(6) |
| [70]         | (7)  | (2)  |       |       |
| [71]         | 164.0| 159.2| 292.8| 319.2 |
| Experiment   | 164.2| 162.7| 290.58| 318.79|
| (11)$^a$     | (8)$^b$| (1.42)$^c$| (1.42)$^d$|
| Values used  | 162.7| 293.6| 319.9|
| in SOM       | (8)$^e$| (6.1)$^f$| (6.1)$^f$|

$^a$[72].

$^b$[73].

$^c$[74].

$^d$[74].

$^e$[73].

$^f$weighted average from [75] and [76].

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![Figure 1](image1.png)

**Figure 1.** Dynamic polarizabilities of the Na and Rb atom interacting with a graphene layer in the Dirac model calculated using the dynamic polarizabilities obtained from the RCC calculations and from the SOM.

![Figure 2](image2.png)

**Figure 2.** $C_3$ coefficients of the Na and Rb atom interacting with a graphene layer in the Dirac model calculated using the dynamic polarizabilities obtained from the RCC calculations and from the SOM.
this figure, it can be observed that there are discrepancies in the results obtained using the hydrodynamic and Dirac models for graphene. From the physical ground, we argue that the results obtained from the Dirac model are more accurate [13], and the hydrodynamic model appears to over-estimate the results in graphene. As can be seen from the figure, the interactions between an atom and the graphene layer is appreciable only at the small distances and reaches a negligible value for large separations. The interaction of an alkali atom is strongest with a perfect conductor, as expected, for the same separation distance as compared to the interaction of the atom with a graphene layer. However, an interesting observation that can be inferred from this figure is that the $C_3$ coefficients of the K and Rb atoms interacting with the graphene layer are more than the interactions of the atoms with the theoretically presumed ideal conductor at very small separation distances (say around 1–3 nm). This drives us to arrive at the conclusion that, at these distances, graphene can offer tighter potentials to K and Rb atoms which can find applications in a number of experiments. A similar graph comparing the Dirac and hydrodynamic models for the interactions between the atoms and CNT with $R = 6$ nm as a function of separation distance ‘$a$’ (between 1 to 5 nm) is shown in figure 4. For the above chosen radius of CNT and at this separation range, it has been observed that the exact results and the PFA results do not deviate much with respect to each other [13, 61].

Another motivation to carry out this study is to find out the dependence of the atom-wall interactions on the radius of CNT. For this purpose, we present the results computed for the $C_3$ coefficients as a function of distance ‘$a$’ and radius ‘$R$’ of CNT in table 3. The range for $R$ and $a$ have been chosen in accordance with the validity range of PFA. From the table, we notice that the $C_3$ coefficients increase slowly with an increase in the CNT radii. However the rate of increase is not very great. With a three-fold increase in the radius, it raises $C_3$ coefficients only about one and half times. As expected, these coefficients get stronger as the size of the atom increases, i.e. from Li to Rb for a given separation distance ‘$a$’. We also compare our fitted $C_3$ coefficient values (column labeled II) with those calculated using equations (1) and (4) (column labeled I). We see a deviation of less then 4% at all the separation distances. We were unable to find any previous

*Figure 3.* The $C_3$ coefficients (in au) using both the Dirac (shown in solid line) and hydrodynamic (shown in long-dashed line) models for the alkali atoms as a function of the atom-layer separation distance $a$ interacting with the graphene layer along with the results for a perfect conductor (shown in short-dashed line), Au (shown in dotted line) and SiO$_2$ (shown in the dotted-dashed line).

*Figure 4.* The $C_3$ coefficients (in au) using both the Dirac (solid line) and hydrodynamic (dashed line) models for the alkali atoms as a function of the atom-layer separation distance ‘$a$’ interacting with CNT of radius $R = 6$ nm.
work to compare our results with. However, we have exercised cross-checking between our results for the H atom and H₂ molecule independently with the results reported in [58] for CNT to ascertain this calculation procedure.

A lot of research work is devoted to experimental investigation of the behavior of interactions between the trapped atoms with graphene layers or CNTs [79–84]. For simplification of reproducing the surface interaction potentials from our reported C₃ coefficients, and for any comparison of our results with the future theoretical calculations, we give a logistic fit for the interaction potential of the atom-graphene layer using the following form

\[ U(a) = \frac{A_0}{a^2} \left( a + B_0 \right), \]  

(13)

where \( A_0 \) (in au) and \( B_0 \) (in nm) are the fitting parameters that depend on the properties of the atom. A list of these fitting parameters for the Li, Na, K and Rb atoms are given in table 4. The above equation is a useful tool to predict interactions between the alkali atoms and a graphene layer for any given separation distance ‘a’. Our fitting parameters for interaction between the graphene and Na atom are considerably different from those calculated in [13] (\( A_0 = 7.11 \) au and \( B_0 = 9.77 \) nm). As mentioned previously, our results are more reliable and use of our fitting parameters is recommended in extrapolating the interaction potentials for the graphene-alkali atom interactions. Similarly, we also fit the \( U(a, R) \) results for interaction of these atoms with CNT. However, a logistic equation does not serve as a suitable fit for CNT. Instead, we use a rational Taylor equation to fit the results in the following functional form

\[ U(a, R) = \frac{C_0 + Aa + BR + CA^2 + DR^2}{a^3} \]  

(14)

and present the respective fitting coefficients in table 4.

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### Table 3. Calculated (column labeled I) and fitted (column labeled II) values obtained using equation (14) for \( C_3 \) coefficients (in au) for the atom-CNT interaction. Values for \( R \) and \( a \) are given in nm.

| \( R \) | Li | Na | K | Rb |
|-------|----|----|----|----|
|       | 1  | 1  | 1  | 1  |
|       | 0.71| 0.782| 1.212| 1.371|
| 6     | 0.681| 0.757| 1.172| 1.325|
| 8     | 0.797| 0.884| 1.37| 1.548|
| 10    | 0.775| 0.858| 1.33| 1.502|
| 2     | 0.679| 0.744| 1.154| 1.298|
| 4     | 0.676| 0.647| 1.0| 1.127|
| 6     | 0.648| 0.646| 1.0| 1.125|
| 8     | 0.668| 0.646| 1.0| 1.087|
| 10    | 0.68| 0.628| 1.1| 1.087|
| 12    | 0.65| 0.628| 1.022| 1.087|
| 14    | 0.59| 0.59| 0.929| 0.979|
| 16    | 0.55| 0.55| 0.919| 0.98|
| 18    | 0.52| 0.52| 0.848| 0.892|
| 20    | 0.51| 0.51| 0.804| 0.875|
| 22    | 0.51| 0.51| 0.804| 0.897|

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Table 3. Calculated (column labeled I) and fitted (column labeled II) values obtained using equation (14) for \( C_3 \) coefficients (in au) for the atom-CNT interaction. Values for \( R \) and \( a \) are given in nm.
Table 4. Our fitting parameters for $C_{r}(a)$ coefficients with a graphene layer and CNT and their comparison with those in [13].

| Graphene layer | Li   | Na   | Na [13] | K     | Rb    |
|----------------|------|------|---------|-------|-------|
| Present        |      |      |         |       |       |
| A₀ (au)        | 7.4355 | 7.6136 | 7.11    | 12.5622 | 13.7257 |
| B₀ (nm)        | 8.3648 | 7.7463 | 9.77    | 8.41002 | 8.19064 |
| CNT Li Na K Rb |      |      |         |       |       |
| C₀ (au)        | 0.79556 | 0.89764 | 1.3852 | 1.5806 |
| A(au/mm)       | -0.27172 | -0.31559 | -0.48514 | -0.5628 |
| B(au/mm)       | 0.07338 | 0.07988 | 0.12444 | 0.13918 |
| C(au/mm²)      | 0.02902 | 0.03436 | 0.05293 | 0.06213 |
| D(au/mm²)      | -0.00445 | -0.00484 | -0.00754 | -0.00844 |

5. Summary

To outline the present work, we have investigated the dispersion coefficients that are valid at low temperatures for the atom-graphene and atom-carbon nanotube interactions using the more accurate dynamic polarizabilities of the Li, Na, K and Rb atoms. The interaction potentials for the considered alkali atoms are studied using both the hydrodynamic and the Dirac models as functions of distances between the atoms and a graphene layer, along with the separation distances between the atoms from the nanotube and its radius. We also compare these results with previously reported results, especially for the heavier atoms, where the dynamic polarizabilities were estimated using the single oscillator model. We also show the dependency of the dispersion coefficients of all the considered atoms on the radius of the nanotube explicitly. We find a steady but slow rise in the dispersion coefficients with increasing values of the radii of the nanotube and this behavior is enhanced with the size of the atom. Readily usable functional forms for the interaction potentials are suggested for the easy extrapolation and comparison of the experimental results with the theoretical values.

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