

## Van der Waals coefficients for alkali metal clusters and their size dependence

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**Abstract.** In this paper we employ the hydrodynamic formulation of time-dependent density functional theory to obtain the van der Waals coefficients  $C_6$  and  $C_8$  of alkali metal clusters of various sizes including very large clusters. Such calculations become computationally very demanding in the orbital-based Kohn–Sham formalism, but are quite simple in the hydrodynamic approach. We show that for interactions between the clusters of the same sizes,  $C_6$  and  $C_8$  scale as the sixth and the eighth power of the cluster radius, respectively, and approach their classically predicted values for the large size clusters.

**Keywords.** Metal clusters; response properties; van der Waals coefficients.

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### 1. Introduction

The long-range van der Waals forces play an important role in the description of many physical and chemical phenomena such as adhesion, surface tension, physical adsorption, etc [1]. The correlations between electron density fluctuations at widely separated locations give rise to these forces. For clusters the knowledge of coefficients of van der Waals interaction is useful in describing the cluster–cluster collisions [2] and also for characterizing the orientation of clusters in bulk matter [3,4]. The van der Waals interaction coefficients, namely  $C_6^{AB}$  and  $C_8^{AB}$ , between small alkali metal particles within the spherical jellium background (SJB) model have been calculated in the past [5–7] using time-dependent density functional theory (TDDFT) [8]. In refs [5,6] time-dependent Kohn–Sham (TDKS) [8] formalism of TDDFT was employed to obtain  $C_6^{AB}$  and  $C_8^{AB}$ . On the other hand, in ref. [7], we employed a density-based method within TDDFT formalism to obtain the van der Waals coefficient  $C_6^{AB}$  for the clusters. The TDKS formalism is an orbital-based theory and involves calculation of these orbitals in a self-consistent manner. Thus, as the size of the system increases these calculations tend to become computationally cumbersome. On the other hand, the density-based approach scales in

a better manner with respect to the particle size as compared to the orbital-based TDKS approach. As a result of this, the calculations of cluster properties with density-based approach are computationally much easier than the corresponding orbital-based calculations.

The main aim of this paper is to extend our previous work [7,9,10] by applying the density-based hydrodynamic approach to calculate the higher-order van der Waals coefficient  $C_8^{AB}$  of alkali atom clusters characterizing the dipole–quadrupole interaction component of the long-range force. Further, we study the evolution of  $C_6^{AB}$  and  $C_8^{AB}$  with the size of the clusters. In addition to this we also calculate  $C_6^{AB}$  and  $C_8^{AB}$  coefficients for the pair interaction between potassium clusters of various sizes and between potassium and sodium clusters of different sizes.

Before proceeding further, it is important to note that density functional theory (DFT) in principle should give the exact ground-state properties including the long range van der Waals energies. However, the widely used local density approximation (LDA) [11,12] and generalized gradient approximations (GGA) [13–15] fail to reproduce the van der Waals energies. This is due to the fact that the LDA and the GGA cannot completely simulate the correlated motion of electrons arising from Coulomb interaction between distant non-overlapping electronic systems. It is only recently that attempts [16–18] have been made to obtain van der Waals energies directly from the ground-state energy functional by correcting the long-range nature of the effective Kohn–Sham potential. On the other hand, it is possible to make reliable estimates of the van der Waals coefficients by using expressions which relate these coefficients to the frequency-dependent multipole polarizabilities at imaginary frequencies [19,20]. We follow the latter route for the calculation of these coefficients.

The paper is organized as follows: In §2 we express  $C_6$  and  $C_8$  in terms of the dipole and the quadrupole dynamic polarizabilities. We then briefly describe our method of obtaining these polarizabilities employing hydrodynamic approach of TDDFT. Results of our calculations are presented and discussed in §3.

## 2. Methods of calculation

The non-retarded electrostatic interaction energy between two spherically symmetric electronic systems  $A$  and  $B$  separated by interaction distance  $R$  can be written as [19,20]

$$V_{AB}(R) = -\frac{C_6^{AB}}{R^6} - \frac{C_8^{AB}}{R^8} - \dots \quad (1)$$

The above expression has been obtained by assuming that  $R$  is very large so that the charge distributions corresponding to the two systems do not overlap. The coefficient  $C_6^{AB}$  describes the dipole–dipole interaction, and  $C_8^{AB}$  corresponds to the dipole–quadrupole interaction between systems  $A$  and  $B$ . These coefficients can be expressed in terms of the dynamic multipole polarizability  $\alpha_l(\omega)$  (where  $l$  denotes the index of multipolarity) by the following relations [21,22]:

$$\begin{aligned} C_6^{AB} &= C(A, 1; B, 1), \\ C_8^{AB} &= C(A, 1; B, 2) + C(A, 2; B, 1) \end{aligned} \quad (2)$$

with

$$C(A, l_1; B, l_2) = \frac{(2l_1 + 2l_2)!}{2\pi(2l_1)!(2l_2)!} \int_0^\infty d\omega \alpha_{l_1}^A(i\omega) \alpha_{l_2}^B(i\omega), \quad (3)$$

where  $\alpha_l^X(i\omega)$  is the multipole polarizability of system  $X$  ( $X = A$  or  $B$ ) at imaginary frequency  $u = i\omega$  and it is given by

$$\alpha_l(i\omega) = \sum_j \frac{f_j^l}{\omega_j^2 + \omega^2}. \quad (4)$$

In the above equation  $f_j^l$  is the oscillator strength for the  $2^l$ -pole transition from ground state to the  $j$ th excited state, and  $\omega_j$  is the corresponding transition energy. It is also evident from the above equation that  $\alpha_l^X(i\omega)$  is a real quantity. Note that  $\alpha_l^X(i\omega)$  does not have any physical significance. However, the expressions given by eqs (2) and (3) make the computation of  $C_6^{AB}$  and  $C_8^{AB}$  straightforward. Moreover, mathematically  $\alpha_l^X(i\omega)$  is better behaved than its real frequency counterpart  $\alpha_l^X(\omega)$ : it does not have any singularity and decreases monotonically from its static value  $\alpha_l^X(0)$  to zero as  $\omega \rightarrow \infty$ . Consequently, the quadrature in eq. (3) can be computed quite accurately. To determine the frequency-dependent polarizabilities appearing in eq. (3), we employ the variation-perturbation method within the hydrodynamic approach of TDDFT. We now describe the theory in brief. For details the reader is referred to [7,9,10]

The basic dynamical variables of the hydrodynamic theory are the time-dependent density  $\rho(\mathbf{r}, t)$  and the velocity potential  $S(\mathbf{r}, t)$ . The velocity of the electron fluid is given by  $\mathbf{v}(\mathbf{r}, t) = -\nabla S(\mathbf{r}, t)$ . Thus the total time-averaged energy can be expressed in terms of these two variables. For our purpose we need to evaluate the second-order change in the time-averaged energy as this is related directly to the frequency-dependent multipole polarizability by the relation

$$\alpha_l(\omega) = -4E_l^{(2)}. \quad (5)$$

The second-order time-averaged energy  $E_l^{(2)}$  in turn can be expressed as

$$E_l^{(2)} = \left\{ \frac{1}{2} \int \frac{\delta^2 F[\rho]}{\delta \rho(\mathbf{r}, t) \delta \rho(\mathbf{r}', t)} \rho^{(1)}(\mathbf{r}, t) \rho^{(1)}(\mathbf{r}', t) d\mathbf{r} d\mathbf{r}' \right. \\ \left. + \int v_{\text{app}}^{(l)}(\mathbf{r}, t) \rho^{(0)}(\mathbf{r}) d\mathbf{r} + \int \frac{\partial S^{(1)}(\mathbf{r}, t)}{\partial t} \rho^{(1)}(\mathbf{r}, t) d\mathbf{r} \right. \\ \left. + \frac{1}{2} \int (\nabla S^{(1)} \cdot \nabla S^{(1)}) \rho^{(0)}(\mathbf{r}) d\mathbf{r} \right\}, \quad (6)$$

where the curly bracket denotes the time averaging over a period of the applied oscillating field and  $\rho^{(0)}(\mathbf{r})$  represents the ground-state density. It has been shown that  $E_l^{(2)}$  is stationary with respect to the variations in the first-order induced density  $\rho^{(1)}(\mathbf{r}, t)$  and the induced current-density  $S^{(1)}(\mathbf{r}, t)$  [7]. Consequently,  $E_l^{(2)}$  can be determined by choosing appropriate variational forms for  $\rho^{(1)}(\mathbf{r}, t)$  and  $S^{(1)}(\mathbf{r}, t)$  and

making  $E_l^{(2)}$  stationary with respect to the parameters of  $\rho^{(1)}(\mathbf{r}, t)$  and  $S^{(1)}(\mathbf{r}, t)$ . In the above expression, the functional

$$F[\rho] = T_s[\rho] + E_H[\rho] + E_{XC}[\rho], \quad (7)$$

where  $T_s[\rho]$ ,  $E_H[\rho]$  and  $E_{XC}[\rho]$  denote the kinetic, Hartree and the exchange-correlation (XC) energy functionals respectively. The exact forms of  $T_s[\rho]$  and  $E_{XC}[\rho]$  are not known. Consequently, to perform any calculation one needs to use approximate forms for these functionals. On the other hand, the Hartree energy functional  $E_H[\rho]$  representing the classical Coulomb energy is known exactly and it is given by

$$E_H[\rho] = \frac{1}{2} \iint \frac{\rho(\mathbf{r}, t)\rho(\mathbf{r}', t)}{|\mathbf{r} - \mathbf{r}'|} d\mathbf{r}d\mathbf{r}'. \quad (8)$$

For the purpose of calculation the multipolar applied potential  $v_{\text{app}}^l(\mathbf{r}, t)$  is chosen to be

$$v_{\text{app}}^l(\mathbf{r}, t) = \mathcal{E}r^l P_l(\cos \theta) \cos \omega t, \quad (9)$$

where  $\mathcal{E}$ ,  $\omega$  represent the amplitude and the frequency of the applied electromagnetic field respectively and  $P_l(\cos \theta)$  is the Legendre polynomial of order  $l$ . In accordance with the above form of the applied potential the variational forms for  $\rho^{(1)}(\mathbf{r}, t)$  and  $S^{(1)}(\mathbf{r}, t)$  are chosen to be

$$\begin{aligned} \rho^{(1)}(\mathbf{r}, t) &= \rho^{(1)}(\mathbf{r}, \omega) \cos \omega t, \\ S^{(1)}(\mathbf{r}, t) &= \omega S^{(1)}(\mathbf{r}, \omega) \sin \omega t \end{aligned} \quad (10)$$

with

$$\begin{aligned} \rho^{(1)}(\mathbf{r}, \omega) &= \sum_i c_i r^i \rho^{(0)}(\mathbf{r}) P_l(\cos \theta), \\ S^{(1)}(\mathbf{r}, \omega) &= \sum_i d_i r^i(\mathbf{r}) P_l(\cos \theta), \end{aligned} \quad (11)$$

where  $\rho^{(0)}(\mathbf{r})$  is the ground-state density and  $c_i$  and  $d_i$  are the linear variational parameters obtained by minimizing time-averaged second-order energy  $E_l^{(2)}$ . For computation we have used ten parameters each for  $\rho^{(1)}(\mathbf{r}, \omega)$  and  $S^{(1)}(\mathbf{r}, \omega)$ . Adding more parameters does not affect the results significantly indicating their convergence. Substituting eq. (10) in eq. (6) and taking average over time we get

$$\begin{aligned} E^{(2)} &= \frac{1}{4} \int \frac{\delta^2 F[\rho]}{\delta \rho(\mathbf{r}) \delta \rho(\mathbf{r}')} \rho^{(1)}(\mathbf{r}, \omega) \rho^{(1)}(\mathbf{r}', \omega) d\mathbf{r}d\mathbf{r}' \\ &+ \frac{1}{2} \int v_{\text{app}}^{(1)}(\mathbf{r}) \rho^{(1)}(\mathbf{r}, \omega) d\mathbf{r} + \frac{\omega^2}{2} \int S^{(1)}(\mathbf{r}, \omega) \rho^{(1)}(\mathbf{r}, \omega) d\mathbf{r} \\ &+ \frac{\omega^2}{4} \int (\nabla S^{(1)} \cdot \nabla S^{(1)}) \rho^{(0)}(\mathbf{r}) d\mathbf{r}. \end{aligned} \quad (12)$$

At this point it is important to point out that the VP method discussed above is also applicable for the imaginary frequencies with  $\omega^2$  replaced by  $-\omega^2$  in eq. (12) [7]. This allows us to determine dynamic multipolarizability at imaginary frequencies ( $\alpha(i\omega)$ ) by exactly the same procedure as employed for getting  $\alpha(\omega)$ . All that is required for this is to change  $\omega^2$  to  $-\omega^2$  in eq. (12). This is done very easily in the numerical code written for determining dynamic polarizability at real frequencies.

As mentioned earlier, the calculation of  $E_l^{(2)}$  requires approximating the functionals  $T_s[\rho]$  and  $E_{XC}[\rho]$ . We choose the von Weizsacker [23] form for  $T_s[\rho]$  which is given as

$$T_W[\rho] = \frac{1}{8} \int \frac{\nabla\rho \cdot \nabla\rho}{\rho} d\mathbf{r}. \quad (13)$$

The von Weizsacker functional is well-suited for the description of response properties of closed shell systems [7,24]. Keeping this in mind we consider closed shell clusters for our calculation. For the XC energy, adiabatic local-density approximation (ALDA) [8] is accurate enough to describe the energy changes. Thus the exchange energy is approximated by the Dirac exchange functional [25]

$$E_x[\rho] = C_x \int \rho^{\frac{4}{3}}(\mathbf{r}) d\mathbf{r},$$

$$C_x = -\frac{3}{4} \left( \frac{3}{\pi} \right)^{1/3} \quad (14)$$

and for the correlation energy functional we employ the Gunnarsson–Lundqvist (GL) [26] parametrized form for it. Moreover, this choice of XC functional allows us to make a systematic comparison with the numbers of refs [5,6], which were also obtained by employing the same XC functional.

In the present paper the ground-state densities  $\rho^{(0)}(\mathbf{r})$  of clusters are obtained by employing purely density-based extended Thomas–Fermi (ETF) [27,28] method within the spherical jellium background model (SJBM) of metal clusters. This approach yields the ground-state densities of very large clusters (containing up to 1000 atoms) easily, thereby allowing us to study the evolution of van der Waals coefficients with the size of the clusters. For details of the ETF method and its application to study alkali–metal cluster, we refer the reader to [9,10,27–29]. In the next section we present the results for  $C_6^{AB}$  and  $C_8^{AB}$  of alkali metal clusters by employing the method described above.

### 3. Results and discussion

We perform calculations for the coefficients  $C_6^{AB}$  and  $C_8^{AB}$  between pairs of clusters made of either the same or different types of alkali atoms. Keeping in mind the better applicability of the hydrodynamic theory for the bigger clusters, the smallest cluster considered in this paper consists of eight atoms. For the purpose of calculation we consider clusters made of sodium ( $r_s = 4.0$  a.u.) and potassium ( $r_s = 4.86$  a.u.) atoms (where  $r_s$  is the Wigner–Seitz radius of the cluster defined

by  $r_s = (3/4\pi n_+)^{1/3}$ ,  $n_+$  is the positive background density). First to assess the accuracy of the numbers for  $C_6^{AB}$  and  $C_8^{AB}$  obtained by employing the hydrodynamic approach we make a detailed comparison of our results for the sodium clusters containing 8, 20, and 40 constituent atoms with the corresponding results of refs [5,6].

In tables 1 and 2 we present the results of our calculation for  $C_6^{AB}$  and  $C_8^{AB}$  respectively, between pairs of sodium clusters along with the corresponding results of refs [5,6] in parenthesis for clusters containing 8, 20 and 40 atoms. Table 1 clearly shows that the numbers obtained by employing the hydrodynamic approach are quite close to the corresponding numbers obtained by the TDKS method. The numbers obtained for  $C_6^{AB}$  by the hydrodynamic approach are systematically lower than the orbital-based TDKS results. The difference between the two results is nearly the same for all the sizes and this difference is of the order of 11%. Next we focus our attention on the results for  $C_8^{AB}$  between pairs of sodium clusters. In table 2 we present the results for the coefficient  $C_8^{AB}$ . It is evident from table 2 that values of  $C_8^{AB}$  obtained by the hydrodynamic approach are quite close to the corresponding TDKS results. In comparison to the results for  $C_6^{AB}$  our numbers

**Table 1.** Dispersion coefficient  $C_6^{AB}$  for sodium atom clusters in atomic units (a.u.). The numbers follow the notation  $3.60(3) = 3.60 \times 10^3$ . The numbers in parenthesis are results of refs [5,6].

$N$	8	20	40
8	3.54(4) (4.01(4))	8.42(4) (9.55(4))	1.64(5) (1.86(5))
20		2.03(5) (2.29(5))	3.93(5) (4.45(5))
40			7.70(5) (8.60(5))

**Table 2.** Dispersion coefficient  $C_8^{AB}$  for sodium atom clusters in atomic units (a.u.). The numbers follow the notation  $3.60(3) = 3.60 \times 10^3$ . The numbers in parenthesis are results of refs [5,6].

$N$	8	20	40
8	1.28(7) (1.32(7))	4.33(7) (4.59(7))	1.15(8) (1.25(8))
20		1.36(8) (1.44(8))	3.37(8) (3.67(8))
40			8.10(8) (8.82(8))

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**Table 3.** Dispersion coefficient  $C_6^{AB}$  for potassium atom clusters in atomic units (a.u.). The numbers follow the notation  $3.60(3) = 3.60 \times 10^3$ . The numbers in parenthesis are results of ref. [6].

$N$	8	20
8	7.70(4) (8.71(4))	1.87(5) (2.02(5))
20		4.55(5) (4.74(5))

**Table 4.** Dispersion coefficient  $C_8^{AB}$  for potassium atom clusters in atomic units (a.u.). The numbers follow the notation  $3.60(3) = 3.60 \times 10^3$ . The numbers in parenthesis are results of ref. [6].

$N$	8	20
8	3.97(7) (4.37(7))	1.38(8) (1.43(8))
20		4.36(8) (4.55(8))

for  $C_8^{AB}$  are closer to the corresponding TDKS values. However, for  $C_8^{AB}$  the difference between the two results is slightly higher for larger clusters than for smaller ones.

In order to test the accuracy of the results obtained via hydrodynamic approach for other alkali clusters we now apply it to calculate the van der Waals coefficients between pairs of small potassium clusters containing 8 and 20 atoms. We present the results of these calculations in tables 3 and 4. Again two tables clearly show that the values of both  $C_6^{AB}$  and  $C_8^{AB}$  between two potassium clusters are obtained quite accurately by employing the density-based hydrodynamic approach. The numbers obtained by us for the potassium clusters are also lower than the corresponding TDKS results. Tables 3 and 4 also show that the difference between the hydrodynamic and the TDKS results is lower for the larger clusters than for smaller ones. On the other hand, for sodium clusters the difference between the two results remains nearly the same as the cluster size increases.

Next we present in tables 5 and 6 the results for  $C_6^{AB}$  and  $C_8^{AB}$  respectively, for the pair interaction between sodium and potassium clusters with 8 and 20 constituent atoms. Once again we see from these two tables that the hydrodynamic numbers are quite close to the corresponding TDKS results except for the number for  $C_6^{AB}$  between the 8-atom sodium and the 8-atom potassium clusters. Tables 5 and 6 also show that like the numbers for  $C_8^{AB}$  between clusters of identical atoms the value of  $C_8^{AB}$  obtained by hydrodynamic approach for two clusters made of different atomic species is closer to the TDKS when compared to the corresponding  $C_6^{AB}$  results.

**Table 5.** Dispersion coefficient  $C_6^{AB}$  for the pair interaction between sodium clusters (values of  $N$  along the column) and potassium clusters (values of  $N$  along the row) in atomic units (a.u.). The numbers follow the notation  $3.60(3) = 3.60 \times 10^3$ . The numbers in parenthesis are results of ref. [6].

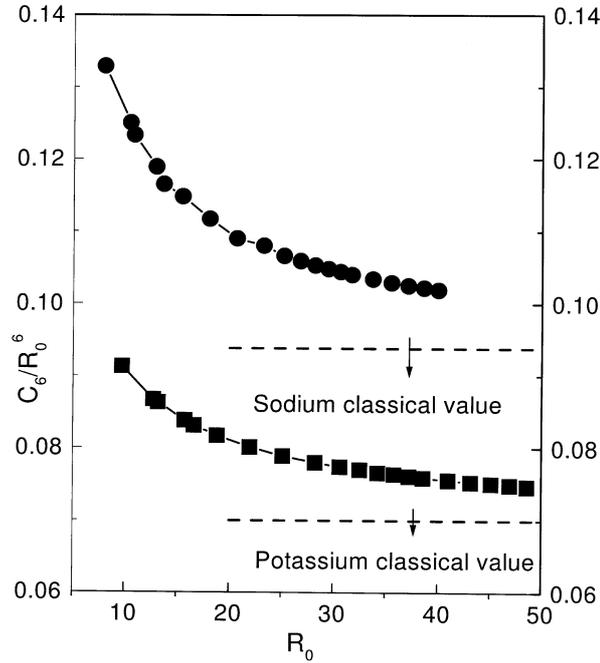
$N$	8	20
8	5.18(4) (8.05(4))	1.26(5) (1.88(5))
20	1.24(5) (1.40(5))	3.00(5) (3.26(5))

**Table 6.** Dispersion coefficient  $C_8^{AB}$  for the pair interaction between sodium clusters (values of  $N$  along the column) and potassium clusters (values of  $N$  along the row) in atomic units (a.u.). The numbers follow the notation  $3.60(3) = 3.60 \times 10^3$ . The numbers in parenthesis are results of ref. [6].

$N$	8	20
8	2.27(7) (2.91(7))	8.29(7) (1.12(8))
20	7.30(7) (7.75(7))	2.45(8) (2.57(8))

The results presented above very clearly indicate that the hydrodynamic approach gives reasonably accurate numbers for the van der Waals coefficients of small sodium and potassium clusters with comparatively less numerical effort than the calculation involving the TDKS approach. Encouraged by this we now employ the hydrodynamic approach to evaluate the van der Waals coefficients for much larger clusters. Using these results we study the evolution of van der Waals coefficients as the size of cluster is increased, specially focusing attention on the asymptotic behaviour. To this end we perform calculations for clusters with the number of constituent atoms ranging from 8 to 1000 atoms. This range of number of atoms translates to the size of cluster from around  $R_0 = 5$  a.u to  $R_0 = 40$  a.u., where  $R_0 = r_s N^{1/3}$  and  $N$  denotes the number of atoms. To study the size dependence of van der Waals coefficients we plot in figures 1 and 2,  $C_6^{AB}/R_0^6$  and  $C_8^{AB}/R_0^8$  respectively, as functions of  $R_0$ . These two figures clearly exhibit that as the size of the cluster increases the values of coefficients  $C_6^{AB}/R_0^6$  and  $C_8^{AB}/R_0^8$  saturate to constants numbers, indicating that  $C_6^{AB}$  and  $C_8^{AB}$  scale as the sixth and the eight power of the radius  $R_0$  of the cluster respectively. This trend is consistent with the fact that the properties of metal clusters approach their corresponding classical values as the size of the cluster is increased. The classical expressions for  $C_6^{AB}/R_0^6$  and  $C_8^{AB}/R_0^8$  between clusters of the same sizes can be written as [6]

$$C_6^{AB}/R_0^6 = \frac{3}{4}\omega_{\text{Mie}},$$



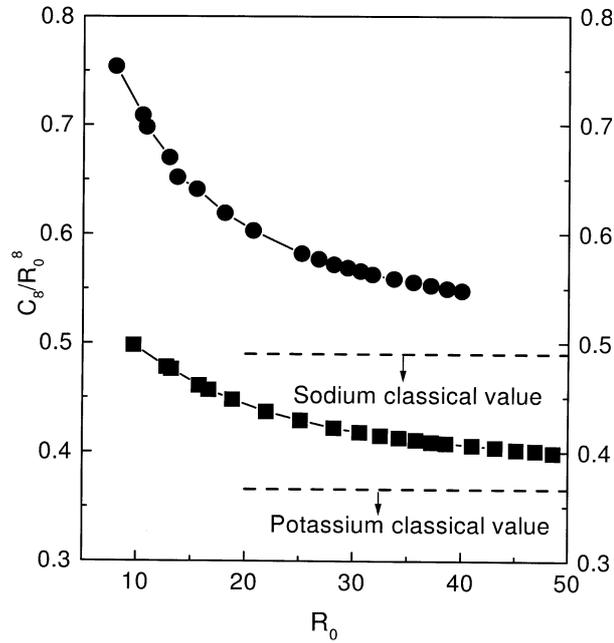
**Figure 1.** Plot of van der Waals coefficient  $C_6^{AB}$  in units of  $R_0^6$  of alkali metal clusters: sodium (solid circles) and potassium (solid squares) as a function of  $R_0$ . The lines connecting data points are drawn as a guide to the eye and the horizontal dashed lines represent the corresponding classical values of van der Waals coefficient.

$$C_8^{AB}/R_0^8 = \frac{15}{2} \frac{\sqrt{5}}{\sqrt{5} + \sqrt{6}} \omega_{\text{Mie}}. \quad (15)$$

Here  $\omega_{\text{Mie}}$  is the Mie resonance frequency given by

$$\omega_{\text{Mie}} = \sqrt{\frac{1}{r_s^3}} \quad (16)$$

and it is equal to  $1/\sqrt{3}$  of the bulk plasmon frequency. These expressions for  $C_6^{AB}/R_0^6$  and  $C_8^{AB}/R_0^8$  given above are derived in ref. [6] by assuming that all the strength of the respective multipole resonance is concentrated in a single peak. By substituting the values of  $r_s$  in eq. (15) we get  $C_6^{AB}/R_0^6 = 0.094$  and  $C_8^{AB}/R_0^8 = 0.49$  for sodium clusters whereas for potassium clusters  $C_6^{AB}/R_0^6 = 0.07$  and  $C_8^{AB}/R_0^8 = 0.37$ . These classical numbers for  $C_6^{AB}/R_0^6$  and  $C_8^{AB}/R_0^8$  are shown by the asymptotic straight lines in figures 1 and 2. We see from figures 1 and 2 that the values of the coefficients  $C_6^{AB}$  and  $C_8^{AB}$  obtained by hydrodynamic method asymptotically approach toward their classical values as given by eq. (15). To reach the asymptotic regime we need to calculate van der Waals coefficients between larger clusters.



**Figure 2.** Plot of van der Waals coefficient  $C_8^{AB}$  in units of  $R_0^8$  of alkali metal clusters: sodium (solid circles) and potassium (solid squares) as a function of  $R_0$ . The lines connecting data points are drawn as a guide to the eye and the horizontal dashed lines represent the corresponding classical values of van der Waals coefficient.

To conclude, we have extended the applicability of the hydrodynamic approach within TDDFT to the calculation of higher order van der Waals coefficient  $C_8^{AB}$  between clusters of various sizes and different species. Our results for both  $C_6^{AB}$  and  $C_8^{AB}$  are quite close to the more accurate orbital-based TDKS approach. In particular, we have found that the numbers obtained by hydrodynamic approach for  $C_8^{AB}$  are more accurate than that of  $C_6^{AB}$ . For both sodium and potassium clusters we have been able to calculate  $C_6^{AB}$  and  $C_8^{AB}$  coefficients for clusters containing up to 1000 atoms. Thus we have been able to get the evolution of these coefficients as a function of cluster size and have shown that they asymptotically tend to their respective classical values.

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