The Reaction Field Energy of a Non-Ideal Dipole

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The reaction field energy of a non-ideal dipole directed along the radius vector in a spherical cavity has been formulated and compared with that of a point dipole located in the center of the cavity for two special cases. Thus, the validity of approximation of the point dipole used widely is investigated.

The famous Onsager reaction field[1] of a non-polarizable point dipole located in the center of a spherical cavity with radius a in a continuous dielectric of relative permittivity ε_r, has long been applied in many fields. The Onsager reaction field $\boldsymbol{R}$ of the point dipole $\boldsymbol{\mu}$ is written as

$$\boldsymbol{R} = \frac{2(\varepsilon_r - 1)}{2\varepsilon_r + 1} \times \frac{\boldsymbol{\mu}}{a^3}. \tag{1}$$

The reaction field is described in the most detail in Böttcher's book.[2] According to this book, the definition of the ideal (point) dipole is as follows: The distance l between two point charges $-e$ and $+e$ is replaced by l/n and the charge e by ne. The limit approached as the number n tends to infinity by keeping el=a constant, is the ideal (point) dipole. Moreover, in the book, the reaction field of an eccentric point-dipole is presented.

It is, however, not necessarily always proper to apply the reaction field of the point dipole located in the center of the cavity: For example, it is obviously improper to apply the Onsager reaction field to a charge-transfer complex composed of two nonpolar molecules different in molecular sizes, because the positive and negative charges resulting from formation of the complex are separately localized at the different molecules and the middle point between the two molecules may not be in the center of the cavity. The positive and negative charges are separated in polar molecules. It is not necessarily always proper to take the position of the point dipole for the polar molecule at the center of the spherical cavity.

There has been no study on the difference between the reaction fields of ideal and non-ideal dipoles except for the special case of Huis et al.[3] As described below, their treatment is not complete. In this paper, therefore, an attempt has been made to derive an equation for calculation of the reaction field energy of the non-ideal dipole directed along the radius vector in a spherial cavity in order to compare the energy with that of the ideal dipole located in the center or shifted from the center of the cavity.

Theoretical

As described in Böttcher's book,[2] in most cases the computation of the reaction field at an arbitrary position of the ideal dipole is very intricate, except for the case of an eccentric dipole directed along the radius vector in a spherical cavity. In this case, therefore, we also consider the non-ideal dipole directed along the radius vector in a spherical cavity.

The origin O is chosen in the center of the spherical cavity (of radius a) embedded in a continuous dielectric medium (of relative permittivity ε_r) and the positive z-axis is taken through the non-ideal dipole, whose moment is $\mu = q(r_A + r_B)$ in the direction of the positive z-axis, as shown in Fig. 1. In Fig. 1, the negative and positive charges ($-q$ and $+q$) of the dipole are located at the point A ($z = r_A$) and at B ($z = -r_B$), respectively, on the z-axis. The distances from these charges to an arbitrary point P are written by $\overline{PA}$ and $\overline{PB}$. The distance from the origin to P is denoted by r and the angle between the vector $\boldsymbol{r}$ and the positive z-axis is denoted by θ. Then, assuming that $r > r_A$ and $r > r_B$, we obtain:

$$\frac{1}{\overline{PA}} = (r^2 + r_A^2 - 2r_A r\cos\theta)^{-1/2} = \sum_{n=0}^{\infty} P_n(\cos\theta)\frac{r_A^n}{r^{n+1}}, \tag{2}$$

$$\frac{1}{\overline{PB}} = (r^2 + r_B^2 - 2r_B r\cos(\pi - \theta))^{-1/2} = \sum_{n=0}^{\infty} (-1)^n P_n(\cos\theta)\frac{r_B^n}{r^{n+1}}. \tag{3}$$

Here $P_n(\cos\theta)$ is the Legendre polynomial and $P_n(-\cos\theta) = (-1)^n P_n(\cos\theta)$. We write the potential at the position of r outside and inside the cavity as $\phi_1(r)$ and $\phi_2(r)$, respectively. From the general solution of Laplace's equation for the case of at least axial symmetry,[2] $\phi_1(r)$ and $\phi_2(r)$ are written as

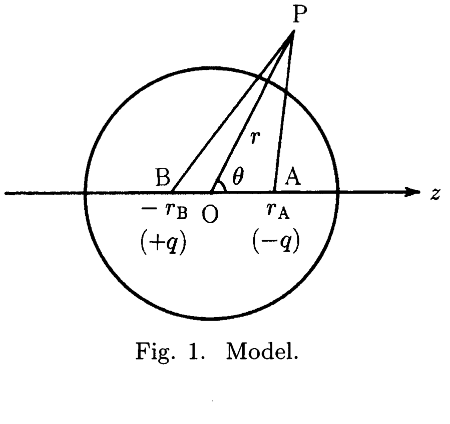

Fig. 1. Model.

$$\phi_1(r) = \sum_{n=0}^{\infty} \left(A_n r^n + \frac{B_n}{r^{n+1}}\right) \mathrm{P}_n(\cos\theta) \quad (r > a), \tag{4}$$

$$\phi_2(r) = \sum_{n=0}^{\infty} \left(C_n r^n + \frac{D_n}{r^{n+1}}\right) \mathrm{P}_n(\cos\theta) \quad (r_\mathrm{A} \text{ or } r_\mathrm{B} < r < a). \tag{5}$$

The constants of A_n, B_n, C_n, and D_n in Eqs. 4 and 5 can be calculated by the same procedure as in the case of the eccentric point-dipole in Böttcher's book[2] as follows: The terms of $\Sigma(D_n/r^{n+1})P_n(\cos\theta)$ in ϕ_2 are due to the field of the permanent dipole in the cavity and are obtained from the potential $\phi(r)$ $(\phi(r)=(-q)/\overline{\mathrm{PA}}+(+q)/\overline{\mathrm{PB}})$ in the absence of the dielectric. Then, we obtain $D_n = q\{(-1)^n r_\mathrm{B}^n - r_\mathrm{A}^n\}$. From the boundary condition of $(\phi_1)_{r\to\infty}=0$, we obtain $A_n=0$ for every n. Here we write B_n as $B_n = B'_n \times q\{(-1)^n r_\mathrm{B}^n - r_\mathrm{A}^n\}$. From the boundary conditions of $(\phi_1)_{r=a} = (\phi_2)_{r=a}$ and $\varepsilon_\mathrm{r}(\partial\phi_1/\partial r)_{r=a} = (\partial\phi_2/\partial r)_{r=a}$, we can obtain B'_n and C_n. Thus, we obtain:

$$\phi_1(r) = \sum_{n=0}^{\infty} \frac{2n+1}{(n+1)\varepsilon_\mathrm{r}+n} \times \frac{q\{(-1)^n r_\mathrm{B}^n - r_\mathrm{A}^n\}}{r^{n+1}} \times \mathrm{P}_n(\cos\theta), \tag{6}$$

$$\begin{aligned}\phi_2(r) = &-\sum_{n=0}^{\infty} \frac{(n+1)(\varepsilon_\mathrm{r}-1)}{(n+1)\varepsilon_\mathrm{r}+n} \\ &\times \frac{q\{(-1)^n r_\mathrm{B}^n - r_\mathrm{A}^n\} r^n}{a^{2n+1}} \times \mathrm{P}_n(\cos\theta) \\ &+ \sum_{n=0}^{\infty} \frac{q\{(-1)^n r_\mathrm{B}^n - r_\mathrm{A}^n\}}{r^{n+1}} \times \mathrm{P}_n(\cos\theta).\end{aligned} \tag{7}$$

According to Böttcher's book,[2] therefore, we obtain the reaction field potential $\phi^\mathrm{R}(r)$ for the whole cavity as

$$\begin{aligned}\phi^\mathrm{R}(r) = \\ -\sum_{n=0}^{\infty} \frac{(n+1)(\varepsilon_\mathrm{r}-1)}{(n+1)\varepsilon_\mathrm{r}+n} \times \frac{q\{(-1)^n r_\mathrm{B}^n - r_\mathrm{A}^n\} r^n}{a^{2n+1}} \times \mathrm{P}_n(\cos\theta).\end{aligned} \tag{8}$$

In Eq. 8, the values of $r=r_\mathrm{A}$ and $\cos 0=1$ (i. e., $\mathrm{P}_n(1)=1$) and ones of $r=r_\mathrm{B}$ and $\cos\pi=-1$ (i. e., $\mathrm{P}_n(-1)=(-1)^n$) should be used for the reaction potential of $\phi^\mathrm{R}(\mathrm{A})$ at the position of A and for the potential of $\phi^\mathrm{R}(\mathrm{B})$ at B, respectively. By using Eq. 8 in this way, the energy (E) of the non-ideal dipole $\boldsymbol{\mu}$ in its own reaction field is given by the following equation, as long as the permittivity of the dielectric is constant:[2]

$$\begin{aligned}E &= \frac{1}{2}\{(-q)\phi^\mathrm{R}(\mathrm{A}) + (+q)\phi^\mathrm{R}(\mathrm{B})\} \\ &= -\frac{\varepsilon_\mathrm{r}-1}{2\varepsilon_\mathrm{r}+1} \times \frac{\mu^2}{a^3} \\ &\quad -\frac{\varepsilon_\mathrm{r}-1}{2} \times \frac{q^2}{a^3} \sum_{n=2}^{\infty} \frac{n+1}{(n+1)\varepsilon_\mathrm{r}+n} \times \frac{\{(-1)^n r_\mathrm{B}^n - r_\mathrm{A}^n\}^2}{a^{2(n-1)}}.\end{aligned} \tag{9}$$

Assuming that $r_\mathrm{A} > r_\mathrm{B}$, we adopt the following parameter t:

$$\frac{r_\mathrm{B}}{r_\mathrm{A}} = t. \tag{10}$$

Using Eq. 10, we can write Eq. 9 as

$$\begin{aligned}E = &-\frac{\varepsilon_\mathrm{r}-1}{2\varepsilon_\mathrm{r}+1} \times \frac{\mu^2}{a^3} \\ &\times \left[1 + \frac{2\varepsilon_\mathrm{r}+1}{2(1+t)^2} \sum_{n=2}^{\infty} \frac{n+1}{(n+1)\varepsilon_\mathrm{r}+n} \left(\frac{r_\mathrm{A}}{a}\right)^{2(n-1)} \right. \\ &\left. \times\{(-1)^n t^n - 1\}^2\right].\end{aligned} \tag{11}$$

Equation 11 is the final equation. In the next section, we apply Eq. 11 for two special cases.

Applications

In the Case of $r_\mathrm{A}=r_\mathrm{B}$ (t=1). In this case, we can write $\mu = q\times(2r_\mathrm{A})$. Putting $t=1$ into Eq. 11, we obtain

$$E = -\frac{\varepsilon_\mathrm{r}-1}{2\varepsilon_\mathrm{r}+1} \times \frac{\mu^2}{a^3} \times (1+u), \tag{12}$$

where

$$u = (2\varepsilon_\mathrm{r}+1)\left(\frac{r_\mathrm{A}}{a}\right)^4 \sum_{n=2}^{\infty} \frac{n}{2n\varepsilon_\mathrm{r}+(2n-1)} \times \left(\frac{r_\mathrm{A}}{a}\right)^{4(n-2)}. \tag{13}$$

By using the Onsager reaction field of Eq. 1, we obtain for the energy of the point dipole ($\boldsymbol{\mu}$ located in the center of the spherical cavity) in its own reaction field:

$$E = -\frac{1}{2}\boldsymbol{\mu}\cdot\boldsymbol{R} = -\frac{\varepsilon_\mathrm{r}-1}{2\varepsilon_\mathrm{r}+1} \times \frac{\mu^2}{a^3}. \tag{14}$$

From the comparison of Eq. 12 with Eq. 14, the u value of Eq. 13 indicates the degree of difference in the E values between the non-ideal dipole and the point dipole located at the origin. The values of $(1+u)$ for several values of r_A/a and ε_r are given in Table 1. The table shows that the $(1+u)$ value does not change very much from unity at the range of r_A smaller than 0.5. In the case of $r_\mathrm{A}=r_\mathrm{B}$, therefore, the reaction field of the point dipole (Eq. 1) may be satisfactorily used for the r_A/a value smaller than 0.5.

In the Case of $r_\mathrm{B}=0$ (t=0). In this case, we can write $\mu = qr_\mathrm{A}$, because the positive charge of the B point is located at the origin. Putting $t=0$ into Eq. 11, we obtain:

$$E = -\frac{\varepsilon_\mathrm{r}-1}{2\varepsilon_\mathrm{r}+1} \times \frac{\mu^2}{a^3} \times (1+v), \tag{15}$$

where

$$v = \frac{(2\varepsilon_\mathrm{r}+1)}{2}\left(\frac{r_\mathrm{A}}{a}\right)^2 \sum_{n=2}^{\infty} \frac{n+1}{(n+1)\varepsilon_\mathrm{r}+n} \times \left(\frac{r_\mathrm{A}}{a}\right)^{2(n-2)}. \tag{16}$$

The v value indicates the degree of difference in the E values between this non-ideal dipole and the point dipole located at the origin. The values of $(1+v)$ for several values of r_A/a and ε_r are shown in Table 2. The table shows that the $(1+v)$ value considerably increases with the increasing value of r_A/a from unity and slightly depends on the ε_r value for the same r_A/a value. From Table 2, it is known that Eq. 14 for the point dipole located at the origin gives considerably smaller values than Eq. 15 does above the r_A/a value of 0.2. The use of Eq. 14 is, therefore, inappropriate for the case where the point dipole is considerably shifted from the center of the spherical cavity.

Table 1. Values of $(1+u)$

r_A/a	Values of $(1+u)$					
	$\varepsilon_r=2$	$\varepsilon_r=10$	$\varepsilon_r=20$	$\varepsilon_r=30$	$\varepsilon_r=50$	$\varepsilon_r=80$
0	1	1	1	1	1	1
0.05	1.000	1.000	1.000	1.000	1.000	1.000
0.10	1.001	1.001	1.001	1.001	1.001	1.001
0.15	1.001	1.001	1.001	1.001	1.001	1.001
0.20	1.002	1.002	1.002	1.002	1.002	1.002
0.25	1.004	1.004	1.004	1.004	1.004	1.004
0.30	1.007	1.008	1.008	1.008	1.008	1.008
0.35	1.014	1.015	1.015	1.015	1.015	1.015
0.40	1.024	1.026	1.026	1.026	1.026	1.026
0.45	1.039	1.042	1.042	1.042	1.043	1.043
0.50	1.061	1.065	1.066	1.066	1.066	1.066
0.55	1.091	1.098	1.099	1.100	1.100	1.100
0.60	1.135	1.145	1.147	1.147	1.148	1.148

Table 2. Values of $(1+v)$

r_A/a	Values of $(1+v)$					
	$\varepsilon_r=2$	$\varepsilon_r=10$	$\varepsilon_r=20$	$\varepsilon_r=30$	$\varepsilon_r=50$	$\varepsilon_r=80$
0	1	1	1	1	1	1
0.05	1.002	1.003	1.003	1.003	1.003	1.003
0.10	1.010	1.010	1.010	1.010	1.010	1.010
0.15	1.022	1.023	1.023	1.023	1.023	1.023
0.20	1.039	1.041	1.041	1.041	1.041	1.042
0.25	1.063	1.066	1.066	1.066	1.066	1.067
0.30	1.093	1.097	1.098	1.098	1.099	1.099
0.35	1.130	1.137	1.138	1.139	1.139	1.139
0.40	1.178	1.187	1.189	1.189	1.190	1.189
0.45	1.236	1.249	1.251	1.252	1.253	1.253
0.50	1.310	1.327	1.330	1.331	1.331	1.331
0.55	1.402	1.425	1.429	1.430	1.431	1.429
0.60	1.520	1.551	1.556	1.558	1.557	1.558

From the reaction field for an eccentric point-dipole ($\boldsymbol{\mu}$) directed along the positive z-axis in the spherical cavity,[2)] the energy of the dipole in its reaction field is easily obtained as

$$E = -\frac{(\varepsilon_r - 1)\mu^2}{2} \sum_{n=0}^{\infty} \frac{n^2(n+1)}{(n+1)\varepsilon_r + n} \times \frac{s^{2(n-1)}}{a^{2n+1}}, \qquad (17)$$

where s is the distance from the origin to the eccentric point dipole on the z-axis. In order to compare the energy of Eq. 17 with that of Eq. 15, we should take $s = r_A/2$, because s is the position of the point dipole. Putting $s = r_A/2$ into Eq. 17, we have:

$$E = -\frac{\varepsilon_r - 1}{2\varepsilon_r + 1} \times \frac{\mu^2}{a^3} \times (1 + w), \qquad (18)$$

where

$$w = \frac{(2\varepsilon_r + 1)}{8} \left(\frac{r_A}{a}\right)^2 \sum_{n=2}^{\infty} \frac{n^2(n+1)}{2^{2(n-2)}\{(n+1)\varepsilon_r + n\}} \times \left(\frac{r_A}{a}\right)^{2(n-2)}. \qquad (19)$$

The w value also indicates the degree of difference in the E values between the eccentric point dipole and the point dipole located at the origin. The values of $(1+w)$ for several values of r_A/a and ε_r are listed in Table 3. The $2s$ value of the first column in Table 3 directly corresponds to the r_A/a value of Table 2: For example, the $2s/a$ value of 0.60 in Table 3 gives the $(1+w)$ value for the s/a value of 0.30. This $(1+w)$ value corresponds the $(1+v)$ value for the r_A/a of 0.60 in Table 2. Table 3 shows that the $(1+w)$ value also considerably increases with the increasing value of r_A/a from unity and slightly depends on the ε_r value, as in the case of the $(1+v)$ value. In the comparison of Table 3 with Table 2, the $(1+w)$ value is nearly equal to the corresponidng $(1+v)$ value within the r_A/a value of 0.5. It is, therefore, appropriate to apply Eq. 18 except for the case where the point dipole is shifted extremely far from the center of the spherical cavity.

Discussion

From Eq. 8, we can write the reaction field $\boldsymbol{R}$ in the cavity as

$$\boldsymbol{R} = -\text{grad}\ \phi^{R}(r). \qquad (20)$$

Table 3. Values of (1+w)

	Values of (1+w)					
$2s/a=r_A/a$	$\varepsilon_r=2$	$\varepsilon_r=10$	$\varepsilon_r=20$	$\varepsilon_r=30$	$\varepsilon_r=50$	$\varepsilon_r=80$
0	1	1	1	1	1	1
0.05	1.002	1.003	1.003	1.003	1.003	1.003
0.10	1.010	1.010	1.010	1.010	1.010	1.010
0.15	1.021	1.023	1.023	1.023	1.023	1.023
0.20	1.038	1.040	1.041	1.041	1.041	1.041
0.25	1.061	1.064	1.064	1.064	1.065	1.065
0.30	1.089	1.094	1.094	1.094	1.094	1.095
0.35	1.123	1.129	1.130	1.131	1.131	1.131
0.40	1.164	1.173	1.174	1.174	1.175	1.175
0.45	1.213	1.224	1.226	1.227	1.227	1.227
0.50	1.270	1.285	1.287	1.288	1.288	1.288
0.55	1.337	1.356	1.359	1.360	1.360	1.361
0.60	1.416	1.439	1.442	1.444	1.445	1.445

On the z-axis, the components of $\boldsymbol{R}$ in the x- and y-direction will be zero due to the symmetry.2) Thus, we have for the component of $\boldsymbol{R}(z)$ on the z-axis:

$$\begin{aligned}\boldsymbol{R}(z) &= -\frac{\mathrm{d}}{\mathrm{d}z}\{-\sum_{n=0}^{\infty}\frac{(n+1)(\varepsilon_r-1)}{(n+1)\varepsilon_r+n} \\ &\quad\times\frac{q\{(-1)^n r_B^n - r_A^n\}z^n}{a^{2n+1}}\times \mathrm{P}_n(1)\}\boldsymbol{k} \\ &= \boldsymbol{k}\sum_{n=0}^{\infty}\frac{n(n+1)(\varepsilon_r-1)}{(n+1)\varepsilon_r+n}\times\frac{q\{(-1)^n r_B^n - r_A^n\}}{a^{2n+1}}\times z^{n-1}.\end{aligned} \tag{21}$$

Here $\boldsymbol{k}$ is the unit vector in the direction of the z-axis. In order to compare with the reaction field given by Huis et al.,3) we write the following equation by putting $r_A=r_B=d$ into Eq. 21:

$$\boldsymbol{R}(z) = -\frac{2(\varepsilon_r-1)}{2\varepsilon_r+1}\times\frac{\boldsymbol{\mu}}{a^3}-\frac{12(\varepsilon_r-1)}{4\varepsilon_r+3}\times\frac{\boldsymbol{\mu}d^2z^2}{a^7}-\cdots. \tag{22}$$

If $z=0$ in Eq. 22, we obtain the reaction field at the origin due to the non-ideal dipole. This reaction field, similarly to Eq. 1, is independent of the position of the dipole, as in the case of the eccentric point dipole.2)

For the special case of $r_A=r_B$ ($t=1$) described above, Huis et al.3) presented the expression of $\boldsymbol{R}(z)$ up to the second order as follows:

$$\boldsymbol{R}(z) = \frac{2(\varepsilon_r-1)}{2\varepsilon_r+1}\times\frac{\boldsymbol{\mu}}{a^3}+\frac{6(\varepsilon_r-1)}{4\varepsilon_r+3}\times\frac{\boldsymbol{\mu}d^2(3z^2-r^2)}{a^7}. \tag{23}$$

The details of their calculation were not described in their paper.3) The difference of sign between Eqs. 22 and 23 is due to the difference in defining the direction of μ. Huis et al. chose the direction of $\boldsymbol{\mu}$ from $-q$ to $+q$ contrary to our case. In Eq. 23, the value of r^2 on the z-axis can be replaced by z^2, because $r^2=x^2+y^2+z^2$. Then, Eq. 23 is equal to Eq. 22. However, Huis et al.3) presented only the second-order expression for $\boldsymbol{R}(z)$ for the special case of $r_A=r_B$ ($t=1$).

Moreover, some consideration is needed in order to derive the E value by using the reaction field of Eq. 21 in this case of the non-ideal dipole. Remembering the expression of $\boldsymbol{\mu}=(-q)\boldsymbol{r}_A+q\boldsymbol{r}_B=\boldsymbol{k}(-q)(r_A+r_B)$ in this case, we should write as follows for the E value:

$$E = -\frac{1}{2}(-q)\int_B^A R(z)\mathrm{d}z = \frac{1}{2}\{(-q)\phi^R(\mathrm{A})+(+q)\phi^R(\mathrm{B})\}, \tag{24}$$

because the reaction field acts on the line from B to A on the z-axis in this case. Then, Eq. 24 is identical with Eq. 9. Otherwise, we cannot find the expression of Eq. 9 by using the reaction field of Eq. 21.

References

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