1 Onsager reaction field

In order to correctly derive a charge–dipole interaction in a reaction field, I will follow the approach used by Onsager [1] for a reaction field of a dipole in a cavity of radius a. The initial hypotheses are:

- The dipole is rigid and its shape do not influence the electrostatic potential
- The dipole moment is μ
- the dipole can be thought as a singularity in the center of the cavity
- the cavity is immersed in a uniform dielectric material, with dielectric constant ϵ_1

Figure 1: Onsager system [1]:a rigid single-point dipole in a cavity (yellow) or radius a, immersed in a uniform dielectric (blue) ϵ_1.

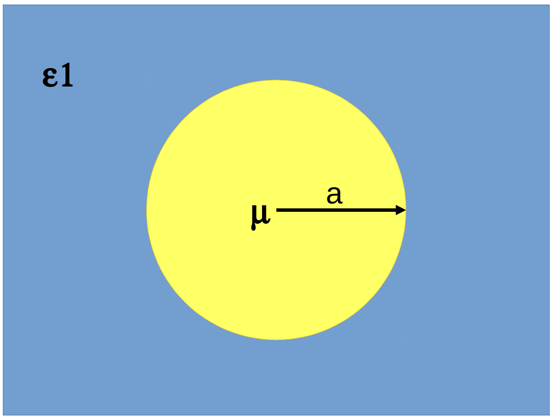

Fig. 1 shows the system under study. The total electrostatic potential $\psi(\mathbf{r})$, as a function of the vector position $\mathbf{r}$, must satisfy the Laplace equation all around the system:

$$\Delta\psi(\mathbf{r}) = 0 \tag{1}$$

Passing to polar coordinates, eq. 1 can be solved with the technique of separation of variables :

$$\psi(\mathbf{r},\theta) = R(\mathbf{r})\Theta(\theta) \tag{2}$$

where $R(\mathbf{r})$ is a function depending on the coordinates only and $\Theta(\theta)$ depends on the rotational degree of freedom θ. A known solution for $R(\mathbf{r})$ and $\Theta(\theta)$ is based on the use of spherical harmonics, giving a final potential $\psi(\mathbf{r},\theta)$:

$$\psi(\mathbf{r},\theta) = \sum_{l=0}^{\infty}\left(A_l\mathbf{r}^l + \frac{B_l}{\mathbf{r}^{l+1}}\right)P_l(\cos\theta) \tag{3}$$

where the sum is extended to all the lth-term, A_l and B_l are constants to be determined with the boundary conditions and P_l is the lth Legendre polynomial. From this general solution, we can express the electrostatic potential $\psi(\mathbf{r},\theta)$ as a sum of internal cavity potential $\psi_{\text{in}}(\mathbf{r},\theta)$ and dielectric medium potential $\psi_{\text{out}}(\mathbf{r},\theta)$, which must satisfy the following conditions:

$$\begin{cases} \lim_{\mathrm{r}\to 0}\psi_{\text{in}}(\mathbf{r},\theta) & = \frac{\mu\cos\theta}{4\pi\epsilon_0 r^2} \\ \\ \lim_{\mathrm{r}\to\infty}\psi_{\text{out}}(\mathbf{r},\theta) & = 0 \end{cases} \tag{4}$$

where μ is the dipole moment and $\frac{\mu\cos\theta}{4\pi\epsilon_0 r^2}$is the dipole electrostatic potential, where ϵ_0 is the vacuum permittivity. Thus, $\psi_{\text{in}}(\mathbf{r},\theta)$ and $\psi_{\text{out}}(\mathbf{r},\theta)$ can be expressed as a general solution from eq. 3 as:

$$\begin{gathered} \psi_{\text{in}}(\mathbf{r},\theta) = \frac{\mu\cos\theta}{4\pi\epsilon_0 r^2} + \sum_{l=0}^{\infty} A_l r^l P_l(\cos\theta) \\ \\ \psi_{\text{out}}(\mathbf{r},\theta) = \sum_{l=0}^{\infty}\frac{B_l}{r^{l+1}}P_l(\cos\theta) \end{gathered} \tag{5}$$

Futhermore, the following conditions hold at the boundary of the spherical cavity surface:

- The potential is continuous across the boundary:

$$\psi_{\text{in}}(a) = \psi_{\text{out}}(a) \tag{6}$$

- The normal component of the dielectric displacement across the surface is continuous:

$$\frac{\partial\psi_{\text{in}}}{\partial\mathbf{r}} = \epsilon_1\frac{\partial\psi_{\text{out}}}{\partial\mathbf{r}} \tag{7}$$

where position and angular dependency was omitted for ease of notation. Now, from eq. 6 a set of equations can be obtained:

$$\begin{cases} \frac{\mu\cos\theta}{4\pi\epsilon_0 a^2} + A_1 a^1 \cos\theta = \frac{B_1}{a^2}\cos\theta & \text{if } l = 1 \\ \\ A_l a^l = \frac{B_l}{a^{l+1}} & \text{if } l \neq 1 \end{cases} \tag{8}$$

which can be solved as:

$$\begin{cases} B_1 & = \frac{\mu}{4\pi\epsilon_0} + A_1 a^3 \\ \\ B_l & = (a^{2l+1}) A_l \end{cases} \tag{9}$$

Thus, from the conditions 7, the electric displacement is:

$$\begin{cases} -\frac{\mu}{2\pi\epsilon_0 a^3} + A_1 & = -\frac{2\epsilon_1}{a^3} B_1 \\ \\ A_l l a^{l-1} & = -\epsilon_1 (l+1) \frac{B_l}{a^{l+2}} \end{cases} \tag{10}$$

Substituting eq. 9 into eq. 10 :

$$\begin{cases} A_1 & = \frac{\mu}{2\pi\epsilon_0 a^3} \left(\frac{1-\epsilon_1}{1+2\epsilon_1} \right) \\ \\ A_l & = B_l = 0 \end{cases} \tag{11}$$

From this solution it is possible to express B_1 :

$$B_1 = \frac{\mu}{4\pi\epsilon_0} \left(\frac{3}{1+2\epsilon_0} \right) \tag{12}$$

From eq. 11 and 12 the final electrostatic potential can be expressed as:

$$\begin{aligned} \psi_{\text{in}}(\mathbf{r},\theta) &= \frac{\mu\cos\theta}{4\pi\epsilon_0 r^2} \left\{ 1 + 2\frac{r^3}{a^3} \left(\frac{1-\epsilon_1}{1+2\epsilon_1} \right) \right\} \\ \psi_{\text{out}}(\mathbf{r},\theta) &= \frac{\mu\cos\theta}{4\pi\epsilon_0 r^2} \left(\frac{3}{1+2\epsilon_1} \right) \end{aligned} \tag{13}$$

giving $\psi(\mathbf{r},\theta)$:

$$\psi(\mathbf{r},\theta) = \frac{\mu\cos\theta}{4\pi\epsilon_0 r^2} \left\{ 1 + 2\frac{r^3}{a^3} \left(\frac{1-\epsilon_1}{1+2\epsilon_1} \right) + \left(\frac{3}{1+2\epsilon_1} \right) \right\} \tag{14}$$

2 Reaction field for a charge-dipole interaction

In this case in the cavity a charge q_c and a dipole μ are present. The charge–dipole electrostatic potential can be expressed as:

$$V(\mathbf{r},\theta) = -\frac{q_c \mu \cos\theta}{4\pi\epsilon_0 r^2} \tag{15}$$

Recalling eq. 5, the total electrostatic potential $\psi(\mathbf{r},\theta)$ can be expressed as:

$$\begin{aligned} \psi_{\text{in}}(\mathbf{r},\theta) &= -\frac{q_c \mu \cos\theta}{4\pi\epsilon_0 r^2} + \sum_{l=0}^{\infty} A_l r^l P_l(\cos\theta) \\ \psi_{\text{out}}(\mathbf{r},\theta) &= \sum_{l=0}^{\infty} \frac{B_l}{r^{l+1}} P_l(\cos\theta) \end{aligned} \tag{16}$$

which satisfies the following conditions:

$$\begin{cases} \lim_{\mathrm{r}\to 0} \psi_{\text{in}}(\mathbf{r},\theta) & = -\frac{q_c \mu \cos\theta}{4\pi\epsilon_1 r^2} \\ \\ \lim_{\mathrm{r}\to \infty} \psi_{\text{out}}(\mathbf{r},\theta) & = 0 \end{cases} \tag{17}$$

Again, for eq. 16 the boundary conditions expressed in 6 and 7 must hold. Applying the condition 6 the following equations are obtained:

$$\begin{cases} -\frac{q_c \mu \cos\theta}{4\pi\epsilon_0 a^2} + A_1 a^1 \cos\theta = \frac{B_1}{a^2}\cos\theta & \text{if } l = 1 \\ \\ A_l a^l = \frac{B_l}{a^{l+1}} & \text{if } l \neq 1 \end{cases} \tag{18}$$

which can be solved as:

$$\begin{cases} B_1 & = -\frac{q_c \mu}{4\pi\epsilon_0} + A_1 a^3 \\ \\ B_l & = (a^{2l+1}) A_l \end{cases} \tag{19}$$

From condition 7 a new set of equations can be solved:

$$\begin{cases} \frac{q_c \mu}{2\pi\epsilon_0 a^3} + A_1 & = -2\epsilon_1 \frac{B_1}{a^3} \\ \\ \epsilon_1 A_l l a^{l-1} & = -\epsilon_2 (l+1) \frac{B_l}{a^{l+2}} \end{cases} \tag{20}$$

Eq. 20 brings to the solution for A_1, B_1 and A_l and B_l :

$$\begin{cases} A_1 & = \frac{q_c \mu}{4\pi\epsilon_0 a^3} \left(\frac{\epsilon_1 - 1}{1+2\epsilon_1}\right) \\ \\ B_1 & = \frac{q_c \mu}{2\pi\epsilon_0} \left(-\frac{1}{2} + \frac{\epsilon_1 - 1}{1+2\epsilon_1}\right) \\ \\ A_l = B_l & = 0 \end{cases} \tag{21}$$

Combining equations 21 into eq. 16, ψ_{in} and ψ_{out} can be expressed as:

$$\begin{aligned} \psi_{\text{in}}(\mathbf{r}, \theta) &= -\frac{q_c \mu \cos\theta}{4\pi\epsilon_0} \left(-\frac{1}{r^2} + 2\frac{r}{a^3}\left(\frac{\epsilon_1 - 1}{1+2\epsilon_1}\right)\right) \\ \psi_{\text{out}}(\mathbf{r}, \theta) &= -\frac{q_c \mu \cos\theta}{4\pi\epsilon_0 r^2} \left(\frac{3}{1+2\epsilon_1}\right) \end{aligned} \tag{22}$$

Finally, the total electrostatic potential $\psi(\mathrm{r}, \theta)$ is:

$$\psi(\mathbf{r}, \theta) = -\frac{q_c \mu \cos\theta}{4\pi\epsilon_0} \left(\frac{1}{r^2} - \frac{2r}{a^3}\frac{\epsilon_1 - 1}{1+2\epsilon_1} + \frac{1}{r^2}\frac{3}{1+2\epsilon_1}\right) \tag{23}$$

3 Derivation of a rotationally-averaged charge-dipole reaction field potential

Considering a charge-dipole system, the system's potential energy is influenced by the dipole rotations, described by an angle θ. In particular, these rotations are about the dipole center and relative to the interacting charge q_c. To work out a single optimal value for the electrostatic potential charge-dipole interactions, a rotationally-averaged potential $\psi(\mathbf{r}, \theta)\rangle$ can be computed by employing the Boltzmann average, starting from the charge-dipole interaction, given in eq. 23:

$$\langle\psi(\mathbf{r}, \theta)\rangle = \frac{\int_0^\pi C\cos\theta e^{-\frac{C\cos\theta}{k_B T}} \sin\theta d\theta}{\int_0^\pi e^{-\frac{C\cos\theta}{k_B T}} \sin\theta d\theta} \tag{24}$$

where $C = -\frac{q_c \mu}{4\pi\epsilon_0}\left(\frac{1}{r^2} - \frac{2r}{a^3}\frac{\epsilon_1 - 1}{1+2\epsilon_1} + \frac{1}{r^2}\frac{3}{1+2\epsilon_1}\right)$ and $\sin\theta d\theta$ is the polar angular variable of integration. The term $e^{-\cos\theta}$ cannot be carried out analytically, but it can be rewritten in terms of Taylor expansion as:

$$e^{-\cos\theta} \sim 1 - \cos\theta \tag{25}$$

So the integral in eq. 24 simplifies as :

$$\langle\psi(\mathbf{r}, \theta)\rangle = \frac{\int_0^\pi C\cos\theta\sin\theta - C\cos\theta\sin\theta\frac{C\cos\theta}{k_B T} d\theta}{\int_0^\pi \sin\theta - \sin\theta\frac{C\cos\theta}{k_B T} d\theta} \tag{26}$$

Now, computing each multiplication and carrying out all the terms not depending on θ, 4 integrals are obtained and can be solved. In particular, $\int_0^\pi \cos\theta \sin\theta d\theta = 0$ since $\cos\theta \sin\theta$ is a symmetric function in $[0..\pi]$ and $\int_0^\pi \cos^2\theta \sin\theta d\theta$ can be computed by substitution, namely $\sin\theta = t$.

Plugging each solved integral in eq. 26, the final rotationally-averaged charged dipole reaction field integration is obtained:

$$\langle\psi(\mathbf{r})\rangle = -\frac{C^2}{3k_\mathrm{B}T} \tag{27}$$

The C term can be written as:

$$C = -\frac{q_\mathrm{c}\mu}{4\pi\epsilon_0 r^2}\left(1 - 2\frac{r^3}{a^3}\left(\frac{\epsilon_1 - 1}{1+2\epsilon_1}\right) + \left(\frac{3}{1+2\epsilon_1}\right)\right) = A\left(1 - 2\frac{r^3}{a^3}\left(\epsilon'\right) + \left(\epsilon''\right)\right) \tag{28}$$

where $A = -\frac{q_\mathrm{c}\mu}{4\pi\epsilon_0 r^2}$, $\epsilon' = \frac{\epsilon_1 - 1}{1+2\epsilon_1}$ and $\epsilon'' = \frac{3}{1+2\epsilon_1}$. Computing C^2 gives:

$$C^2 = A^2\left(1 + 4\frac{r^6}{a^6}\epsilon'^2 + \epsilon''^2 - 4\frac{r^3}{a^3}\epsilon' + 2\epsilon'' - 4\frac{r^3}{a^3}\epsilon'\epsilon''\right) = A^2\left(\left(\epsilon''+1\right)^2 + 4\frac{r^3}{a^3}\left(\frac{r^3}{a^3}\epsilon'^2 - \epsilon' - \epsilon'\epsilon''\right)\right) \tag{29}$$

The term $4\frac{r^3}{a^3}\left(\frac{r^3}{a^3}\epsilon'^2 - \epsilon' - \epsilon'\epsilon''\right)$ can be solved as $4\frac{r^3}{a^3}\epsilon'\left(\epsilon'\left(\frac{r^3}{a^3} - 2\right) - 2\epsilon''\right)$. Thus, C^2 can be written as:

$$C^2 = \left(\frac{q_\mathrm{c}\mu}{4\pi\epsilon_0 r^2}\right)^2\left(4(\epsilon'+\epsilon'')^2 + 4\frac{r^3}{a^3}\epsilon'\left(\epsilon'\left(\frac{r^3}{a^3} - 2\right) - 2\epsilon''\right)\right) \tag{30}$$

Finally, the rotationally-averaged charge dipole reaction field potential is:

$$\langle\psi(\mathbf{r})\rangle = -\frac{1}{3k_\mathrm{B}T}\left(\frac{q_\mathrm{c}\mu}{4\pi\epsilon_0 r^2}\right)^2\left\{4(\epsilon'+\epsilon'')^2 + 4\frac{r^3}{a^3}\epsilon'\left[\epsilon'\left(\frac{r^3}{a^3} - 2\right) - 2\epsilon''\right]\right\} \tag{31}$$

References

[1] Lars Onsager. Electric moments of molecules in liquids. *Journal of the American Chemical Society*, 58(8):1486–1493, 1936. Paper of Onsager, first original derivation of a reaction field.