3.5: Appendix(A) - The Onsager Problem

An interesting variant of the problem of a sphere in a uniform field has been discussed by Onsager in connection with the calculation of the dielectric constant of a material from its atomic polarizability; L.Onsager, J.Amer.Chem.Soc.58, 1486-1493 (1936). When an isolated atom is placed in a uniform external electric field it develops a dipole moment, p_a, that is proportional to the applied field E_0;

$$\mathrm{p_a}=\alpha\epsilon_0\mathrm{E}_0,$$

where the polarizability α has the dimensions of a volume, and can in principle be calculated using quantum mechanics. In a solid or a liquid the atom is not isolated, but its electric moment is influenced by the electric fields due to its neighbours. As a crude approximation one may imagine that the atom plus its associated electric moment is located at the center of a spherical cavity of radius R cut out of an otherwise homogeneous dielectric material characterized by a dielectric constant ϵ, see Figure (3.4.18). Far from the cavity the electric field is E_0 and directed along the z-axis corresponding to the potential function

$$\mathrm{V}=-\mathrm{E}_0\mathrm{z}=-\mathrm{E}_0\mathrm{r}\cos\theta,$$

where r and θ are spherical polar co-ordinates. The problem is to determine the field inside the cavity that acts to polarize the atom. The externally applied electric field is derived from a potential function whose angular dependence is proportional to cos (θ); one is therefore motivated to seek a solution of this problem that corresponds to the use of the terms proportional to cos (θ) in the expansion for the potential, Equation (3.2.19). Inside the cavity the potential near r=0 must be dominated by the dipole potential

$$\frac{\mathrm{p_a}}{4\pi\epsilon_0}\frac{\cos\theta}{\mathrm{r}^2}.$$

One is therefore led to try

Inside: r < R

$$\mathrm{V_i}(\mathrm{r},\theta)=\left(\frac{\mathrm{p_a}\cos\theta}{4\pi\epsilon_0}\right)\frac{1}{\mathrm{r}^2}-A\mathrm{r}\cos\theta. \tag{3.5.1}$$

and

Outside: r > R

$$\mathrm{V_o}(\mathrm{r},\theta)=-\mathrm{E}_0\mathrm{r}\cos\theta+\frac{b\cos\theta}{\mathrm{r}^2}. \tag{3.5.2}$$

The requirements that the potential function and the normal components of $\vec{D}$ be continuous across the surface of the sphere, r=R, lead to the two equations

$$\begin{aligned}A+\frac{b}{\mathrm{R}^3}&=\left(\frac{\mathrm{p_a}}{4\pi\epsilon_0}\right)\frac{1}{\mathrm{R}^3}+\mathrm{E}_0\\-A+\frac{2\epsilon_r b}{\mathrm{R}^3}&=\left(\frac{2\mathrm{p_a}}{4\pi\epsilon_0}\right)\frac{1}{\mathrm{R}^3}-\epsilon_r\mathrm{E}_0,\end{aligned}$$

where $\epsilon_r=\epsilon/\epsilon_0$. From these two equations one finds

$$A=\left(\frac{3\epsilon_r}{2\epsilon_r+1}\right)\mathrm{E}_0+\left(\frac{\epsilon_r-1}{2\epsilon_r+1}\right)\frac{2\mathrm{p_a}}{4\pi\epsilon_0\mathrm{R}^3}, \tag{3.5.3}$$

and

$$\frac{b}{\mathrm{R}^3}=\left(\frac{1-\epsilon_r}{2\epsilon_r+1}\right)\mathrm{E}_0+\left(\frac{3}{2\epsilon_r+1}\right)\frac{\mathrm{p_a}}{4\pi\epsilon_0\mathrm{R}^3}. \tag{3.5.4}$$

But A is just the value of the uniform field inside the cavity that is responsible for the induced dipole moment on the atom, therefore from the definition of the polarizability one has

$$\mathrm{p_a}=\alpha\epsilon_0 A. \tag{3.5.5}$$

This value can be substituted into Equation (3.5.3) for the constant A to obtain

$$A=\left(\frac{3\epsilon_r}{2\epsilon_r+1}\right)\mathrm{E}_0+\left(\frac{\epsilon_r-1}{2\epsilon_r+1}\right)\frac{2\alpha A}{4\pi\mathrm{R}^3}. \tag{3.5.6}$$

Eqn.(3.5.6) can be solved for A in terms of the applied electric field E_0, and this result can be used in Equation (3.5.5) to calculate the atomic dipole moment $\mathrm{p_a}$:

$$\mathrm{p_a}=\left(\frac{3\epsilon_r\epsilon_0}{2\epsilon_r+1-\left(\frac{2\alpha}{4\pi\mathrm{R}^3}\right)(\epsilon_r-1)}\right)\alpha\mathrm{E}_0. \tag{3.5.7}$$

But the dipole moment per atom can be used to calculate the dipole moment per unit volume, $\vec{P}$:

$$|\overrightarrow{\mathrm{P}}|=\mathrm{P}=\mathrm{Np_a}, \tag{3.5.8}$$

where N is the number of atoms per unit volume. From the definition

$$\mathrm{D}=\epsilon_0\mathrm{E}_0+\mathrm{P}$$

one has

$$\mathrm{P}=(\epsilon_r-1)\,\epsilon_0\mathrm{E}_0. \tag{3.5.9}$$

(Notice that one can drop the vector signs on D, E_0, and P because all of these vectors are parallel with the z-axis). Using Equations (3.5.9,3.5.8, and 3.5.7) one can obtain a relation between the relative dielectric constant, ϵ_r and the polarizability α:

$$\epsilon_r-1=\left(\frac{3\epsilon_r}{2\epsilon_r+1-(\epsilon_r-1)\left(\frac{\alpha}{2\pi R^3}\right)}\right)\mathrm{N}\alpha.$$

The latter expression can be solved to obtain the polarizability in terms of the relative dielectric constant, ϵ_r:

$$\alpha=\frac{(2\epsilon_r+1)}{\left(\epsilon_r-1+\left(\frac{3\epsilon_r}{\epsilon_r-1}\right)2\pi\mathrm{NR}^3\right)}2\pi\mathrm{R}^3. \tag{3.5.10}$$

Eqn.(3.5.10) can be used to calculate the atomic polarizability from measured values of the relative dielectric constant, ϵ_r. These values of α can then be compared with values calculated from atomic theory.
