Part I

Electrostatics in solvation

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More Information

1 Dielectric constant and fluctuation formulae for molecular dynamics

The dielectric constant ϵ of a material describes the collective response of its constituent molecules to electric fields, which is of fundamental importance in the study of electromagnetic phenomena in materials. In this chapter, we will present the statistical molecular theory for the dielectric constant. First, a brief review on the classical electrostatic theory of charges and dipoles is given. Then we present the classical Clausius–Mossotti theory for non-polar dielectrics, i.e., materials that do not have molecular dipole moments in the absence of external fields, and the Onsager theory for dipolar dielectrics, specifically for dipolar liquids. Finally, we discuss the statistical molecular theory for the dielectric constant and dielectric formula in terms of dipole moment fluctuations; the latter can be obtained over molecular trajectories in molecular dynamics simulations of the dielectric materials.

1.1 Electrostatics of charges and dipoles

In this section, we review the basics of electrostatics of charges and dipoles. The Coulombic force of a point charge q at $\mathbf{r}'$ exerting on a test charge Q at $\mathbf{r}$ is given by

$$\mathbf{F}(\mathbf{r}) = \frac{1}{4\pi\epsilon_0}\frac{Qq(\mathbf{r}-\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|^3}, \tag{1.1}$$

with the vacuum dielectric constant $\epsilon_0 = 8.854 \times 10^{-12} \ \ \mathrm{C}^2/(\mathrm{N}\cdot\mathrm{m}^2)$ set in the SI base units for force (N), distance (m), and charge (C). The force can also be expressed in terms of the electric field $\mathbf{E}(\mathbf{r})$ generated by the source charge q as

$$\mathbf{F}(\mathbf{r}) = Q\mathbf{E}(\mathbf{r}), \tag{1.2}$$

and the electric field $\mathbf{E}(\mathbf{r})$ can be written in terms of a scalar electrostatic potential $\Phi(\mathbf{r})$ as

$$\mathbf{E}(\mathbf{r}) = -\nabla\Phi(\mathbf{r}), \tag{1.3}$$

where

$$\Phi(\mathbf{r}) = \frac{1}{4\pi\epsilon_0}\frac{q}{|\mathbf{r}-\mathbf{r}'|}. \tag{1.4}$$

Meanwhile, the potential energy W for the test charge Q in the electrostatic potential field $\Phi(\mathbf{r})$ is simply

$$W = Q\Phi(\mathbf{r}). \tag{1.5}$$

It can be shown easily that the potential $\Phi(\mathbf{r})$ satisfies the following Poisson equation with a Dirac δ source:

$$-\nabla^2\Phi(\mathbf{r}) = q\frac{\delta(\mathbf{r}-\mathbf{r}')}{\epsilon_0}. \tag{1.6}$$

Molecules of many materials (such as dipolar liquids) possess permanent dipole moments (defined below) due to different mass centers for the positive nuclear charges and the negative electron charges. The dipole moments will experience change under external fields, i.e., polarization, which plays a fundamental role in the study of the electrical and optical properties of materials. Moreover, under the influence of an external field, even non-polar molecules can obtain induced dipole moments because of the displacement of the mass centers of the positive and the negative charges.

The electric dipole moment for a pair of opposite charges of magnitude q is defined as the magnitude of the charges times the distance d between the charges. The potential of such a dipole is given by

$$\Phi(\mathbf{r}) = \frac{1}{4\pi\epsilon_0}\left(\frac{q}{|\mathbf{r}-\frac{\mathbf{d}}{2}|} - \frac{q}{|\mathbf{r}+\frac{\mathbf{d}}{2}|}\right), \tag{1.7}$$

where $\mathbf{d}$ is the directional vector pointing from the negative charge to the positive charge. We define the dipole moment vector $\mathbf{p}$ as

$$\mathbf{p} = q\mathbf{d} \quad (\mathrm{C}\cdot\mathrm{m}). \tag{1.8}$$

In a far-field region, i.e., $|\mathbf{r}| \gg d$, we have

$$\Phi(\mathbf{r}) \approx \frac{1}{4\pi\epsilon_0}\frac{qd\cos\theta}{r^2} = \frac{1}{4\pi\epsilon_0}\frac{\mathbf{p}\cdot\mathbf{r}}{r^3}, \tag{1.9}$$

where θ is the angle between $\mathbf{p}$ and $\mathbf{r}$. The electric field due to the dipole $\mathbf{p}$ is then

$$\mathbf{E}(\mathbf{r}) = -\nabla\Phi(\mathbf{r}) = \frac{1}{4\pi\epsilon_0}\left(\frac{3\mathbf{p}\cdot\mathbf{r}}{r^5}\mathbf{r} - \frac{\mathbf{p}}{r^3}\right), \tag{1.10}$$

which also defines a dipole–dipole tensor $\overline{\mathbf{T}}(\mathbf{r})$ for $\mathbf{r} = (r_1, r_2, r_3)$:

$$T_{\alpha\beta}(\mathbf{r}) = \frac{1}{4\pi\epsilon_0}\frac{1}{r^3}\left(\frac{3r_\alpha r_\beta}{r^2} - \delta_{\alpha\beta}\right), \qquad \alpha, \beta = 1, 2, 3, \tag{1.11}$$

where $\delta_{\alpha\beta}$ is the Kronecker delta.

An ideal point dipole can be obtained by letting the separation distance d tend to zero while holding the product $qd = \mu$ unchanged. The ideal point dipole can be represented by a dipole moment *density* through the Dirac δ function with an orientation along the unit direction $\hat{\mathbf{d}} = \mathbf{d}/|\mathbf{d}|$:

$$\widetilde{\mathbf{p}} = \mu\delta(\mathbf{r})\hat{\mathbf{d}}, \tag{1.12}$$

the spatial integration of which will give the total dipole moment $\mu\hat{\mathbf{d}}$.

For an individual atom or molecule of a dipole moment $\mathbf{p}$, we assume the following linear relation between the induced dipole moment $\Delta\mathbf{p}(\mathbf{r})$ (i.e., $\mathbf{p} \to \mathbf{p} + \Delta\mathbf{p}(\mathbf{r})$) and an external field $\mathbf{E}(\mathbf{r})$:

$$\Delta\mathbf{p}(\mathbf{r}) = \alpha\mathbf{E}(\mathbf{r}), \tag{1.13}$$

where α (cm^3) is the atomic or molecular polarizability. For example, $\alpha/4\pi\epsilon_0 = 0.667$ for H, 0.205 for He, and 24.1 for Na (in units of 10^{-30}m^3), respectively (Griffiths, 1999).

For later use, we consider the potential energy W of a general finite-sized dipole moment $\mathbf{p} = q_1\mathbf{r}_1 + q_2\mathbf{r}_2$, $q_1 + q_2 = 0$, under an external electric field $\mathbf{E}^{\text{ext}} = -\nabla\Phi$. Using (1.5), we have

$$\begin{aligned} W &= q_1\Phi(\mathbf{r}_1) + q_2\Phi(\mathbf{r}_2) \simeq q_1[\Phi(\mathbf{0}) + \nabla\Phi(\mathbf{0})\cdot\mathbf{r}_1] + q_2[\Phi(\mathbf{0}) + \nabla\Phi(\mathbf{0})\cdot\mathbf{r}_2] \\ &= \mathbf{p}\cdot\nabla\Phi(\mathbf{0}). \end{aligned}$$

Therefore, we obtain

$$W = -\mathbf{p}\cdot\mathbf{E}^{\text{ext}}. \tag{1.14}$$

1.2 Polarization P and displacement flux D

The collective response of the constituent molecules of a material to an external electric field can be described by a phenomenological quantity, the susceptibility χ of a dielectric material, which measures the displacement (translation or rotation) of permanent dipole moments in polar molecules or the creation of induced dipole moments in non-polar molecules. This process is the so-called *polarization process*. The susceptibility χ and the dielectric constant ϵ are macroscopic quantities; the former links the Maxwell total electric field $\mathbf{E}(\mathbf{r})$ inside the material and the polarization density $\mathbf{P}(\mathbf{r})$ per unit volume by

$$\mathbf{P}(\mathbf{r}) = \epsilon_0\chi\mathbf{E}(\mathbf{r}), \tag{1.15}$$

where both $\mathbf{E}(\mathbf{r})$ and $\mathbf{P}(\mathbf{r})$ are averaged quantities over a scale larger than the molecular size but smaller than the overall macroscopic scale of the dielectric material under investigation. Specifically, over a physical region V_c around a location $\mathbf{r}$, we define the polarization density function $\mathbf{P}(\mathbf{r})$ through

$$\mathbf{P}(\mathbf{r})|V_c| = \sum_{i\in V_c}\mathbf{p}_i, \tag{1.16}$$

where $|V_c|$ represents the volume of the region V_c, and $\mathbf{p}_i$ is the dipole moment of the ith molecule inside V_c. Therefore, a complete understanding of the dielectric constant can be traced back to the response of each individual molecule under the influence of the external electric field.

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Excerpt
More Information

1.2.1 Bound charges induced by polarization

For a given polarization density $\mathbf{P}(\mathbf{r})$ within a volume V, and by the linear superposition principle and the far-field approximation of (1.9), the potential $\Phi(\mathbf{r})$ for $\mathbf{r} \notin V$ is

$$\Phi(\mathbf{r}) = \frac{1}{4\pi\epsilon_0} \int_V \frac{\mathbf{P}(\mathbf{r}') \cdot (\mathbf{r} - \mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|^3} \, \mathrm{d}\mathbf{r}', \tag{1.17}$$

which can be rewritten as

$$\begin{aligned} \Phi(\mathbf{r}) &= \frac{1}{4\pi\epsilon_0} \int_V \mathbf{P}(\mathbf{r}') \cdot \nabla' \left(\frac{1}{|\mathbf{r} - \mathbf{r}'|} \right) \mathrm{d}\mathbf{r}' \\ &= \frac{1}{4\pi\epsilon_0} \left[\int_V \nabla' \cdot \frac{\mathbf{P}(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} \, \mathrm{d}\mathbf{r}' - \int_V \frac{1}{|\mathbf{r} - \mathbf{r}'|} \nabla' \cdot \mathbf{P}(\mathbf{r}') \mathrm{d}\mathbf{r}' \right] \\ &= \frac{1}{4\pi\epsilon_0} \left[\int_S \frac{\mathbf{P}(\mathbf{r}') \cdot \mathbf{n}}{|\mathbf{r} - \mathbf{r}'|} \, \mathrm{d}s' - \int_V \frac{1}{|\mathbf{r} - \mathbf{r}'|} \nabla' \cdot \mathbf{P}(\mathbf{r}') \mathrm{d}\mathbf{r}' \right], \end{aligned} \tag{1.18}$$

where ∇' denotes differentiation with respect to $\mathbf{r}'$, $S = \partial V$ is the surface of the volume V, and $\mathbf{n}$ represents the outward unit normal vector to the surface. From the last equation, we can conclude that the potential $\Phi(\mathbf{r})$ due to the polarization density $\mathbf{P}(\mathbf{r})$ can be identified as those created by a surface bound charge σ_b on the surface S,

$$\sigma_b(\mathbf{r}) = \mathbf{P}(\mathbf{r}) \cdot \mathbf{n}, \tag{1.19}$$

and a volume bound charge ρ_b inside the volume V,

$$\rho_b(\mathbf{r}) = -\nabla \cdot \mathbf{P}(\mathbf{r}). \tag{1.20}$$

Namely, we have

$$\Phi(\mathbf{r}) = \frac{1}{4\pi\epsilon_0} \int_S \frac{\sigma_b(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} \, \mathrm{d}s' + \frac{1}{4\pi\epsilon_0} \int_V \frac{\rho_b(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} \, \mathrm{d}\mathbf{r}'. \tag{1.21}$$

It should be noted that the volume bound charge ρ_b and the surface bound charge σ_b cancel each other to reflect the overall charge neutrality of the dielectric, namely,

$$\int_V \rho_b(\mathbf{r}')\mathrm{d}\mathbf{r}' = -\int_V \nabla' \cdot \mathbf{P}(\mathbf{r}')\mathrm{d}\mathbf{r}' = -\int_S \mathbf{P}(\mathbf{r}') \cdot \mathbf{n} \, \mathrm{d}s' = -\int_S \sigma_b(\mathbf{r}')\mathrm{d}s'. \tag{1.22}$$

Accounting for the volume bound charge, the Gauss law for the electric field now becomes

$$\nabla \cdot \epsilon_0 \mathbf{E}(\mathbf{r}) = q(\mathbf{r}) + \rho_b(\mathbf{r}), \tag{1.23}$$

where $q(\mathbf{r})$ is the free charge inside the material (in contrast to the charge $\rho_b(\mathbf{r})$ induced by polarization, which is bound to nuclear sites). Using the definition of the volume bound polarization charge $\rho_b(\mathbf{r})$ (1.20), we have

$$\nabla \cdot (\epsilon_0 \mathbf{E}(\mathbf{r}) + \mathbf{P}(\mathbf{r})) = q(\mathbf{r}). \tag{1.24}$$

Introducing a displacement flux $\mathbf{D}(\mathbf{r})$ to account for the polarization effect due to the "displacement" of the dipoles in the dielectric material,

$$\mathbf{D}(\mathbf{r}) = \epsilon_0 \mathbf{E}(\mathbf{r}) + \mathbf{P}(\mathbf{r}) = \epsilon_0(1+\chi)\mathbf{E}(\mathbf{r}) = \epsilon \mathbf{E}(\mathbf{r}), \tag{1.25}$$

where the material dielectric constant ϵ is defined by

$$\epsilon = \epsilon_0(1+\chi), \tag{1.26}$$

we arrive at the Gauss law inside the dielectric material:

$$\nabla \cdot \mathbf{D}(\mathbf{r}) = q(\mathbf{r}). \tag{1.27}$$

For convenience, we also define a relative dielectric constant ϵ_r with respect to that of the vacuum ϵ_0 by

$$\epsilon_r = \frac{\epsilon}{\epsilon_0} = 1 + \chi. \tag{1.28}$$

1.2.2 Electric field $\mathbf{E}_{\text{pol}}(\mathbf{r})$ of a polarization density $\mathbf{P}(\mathbf{r})$

The macroscopic electric polarization field from the potential (1.17) is

$$\mathbf{E}_{\text{pol}}(\mathbf{r}) = -\nabla\Phi(\mathbf{r}) = -\frac{1}{4\pi\varepsilon_0}\nabla\int_V \frac{\mathbf{P}(\mathbf{r}')\cdot(\mathbf{r}-\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|^3}\,\mathrm{d}\mathbf{r}', \qquad \mathbf{r} \notin V. \tag{1.29}$$

For a field point $\mathbf{r} \notin V$, the integrand in (1.29) is a smooth function; thus we can move the gradient operator inside the integral to obtain

$$\mathbf{E}_{\text{pol}}(\mathbf{r}) = \int_V \overline{\mathbf{T}}(\mathbf{r}-\mathbf{r}')\mathbf{P}(\mathbf{r}')\mathrm{d}\mathbf{r}', \qquad \mathbf{r} \notin V, \tag{1.30}$$

where the dipole–dipole tensor $\overline{\mathbf{T}}$ is defined in (1.11).

For a field point $\mathbf{r}$ inside V, however, the integrand for the potential $\Phi(\mathbf{r})$ in (1.29) will be singular, and more so for the dipole tensor in the expression (1.30) for the electric field $\mathbf{E}_{\text{pol}}(\mathbf{r})$. Nonetheless, we will show in the following that (1.29) still holds even for $\mathbf{r} \in V$; however, (1.30) will be interpreted as a Cauchy principal value integral with an additional term in (1.43).

For a field point $\mathbf{r} \in V$, the polarization field $\mathbf{E}_{\text{pol}}(\mathbf{r})$ from the molecular polarization $\mathbf{p}_i$ can be split into two parts as follows:

$$\mathbf{E}_{\text{pol}}(\mathbf{r}) = \mathbf{E}_{\text{out}}(\mathbf{r}) + \mathbf{E}_{\text{in}}(\mathbf{r}), \tag{1.31}$$

where $\mathbf{E}_{\text{out}}(\mathbf{r})$ and $\mathbf{E}_{\text{in}}(\mathbf{r})$ are the field generated by the dipoles $\mathbf{p}_i$ outside and inside, respectively, a sphere Ω_R of radius R centered at $\mathbf{r}$. Using a far-field approximation similar to (1.17), we have

$$\mathbf{E}_{\text{out}}(\mathbf{r}) = -\nabla\Phi_{\text{out}}(\mathbf{r}), \tag{1.32}$$

where

$$\Phi_{\text{out}}(\mathbf{r}) = \frac{1}{4\pi\epsilon_0}\int_{V/\Omega_R} \frac{\mathbf{P}(\mathbf{r}')\cdot(\mathbf{r}-\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|^3}\,\mathrm{d}\mathbf{r}'. \tag{1.33}$$

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Excerpt
More Information

Meanwhile, to be consistent with the fact that the Maxwell electric field is an averaging quantity, $\mathbf{E}_{\text{in}}(\mathbf{r})$ is defined as the average field generated by all dipoles $\mathbf{p}_i$ inside the sphere Ω_R. Each of these dipoles $\mathbf{p}_i$, represented by two point charges $q_i\delta(\mathbf{r}-\mathbf{r}_i-\mathbf{d}_i/2)$ and $-q_i\delta(\mathbf{r}-\mathbf{r}_i+\mathbf{d}_i/2)$, with $\mathbf{p}_i = q_i\mathbf{d}_i$, will generate a microscopic electric field $\mathbf{e}_i(\mathbf{r})$, given by

$$\mathbf{e}_i(\mathbf{r}) = \frac{1}{4\pi\epsilon_0}\left(\frac{q_i(\mathbf{r}-\mathbf{r}_i-\mathbf{d}_i/2)}{|\mathbf{r}-\mathbf{r}_i-\mathbf{d}_i/2|^3} - \frac{q_i(\mathbf{r}-\mathbf{r}_i+\mathbf{d}_i/2)}{|\mathbf{r}-\mathbf{r}_i+\mathbf{d}_i/2|^3}\right), \tag{1.34}$$

which will contribute to the macroscopic electric field $\mathbf{E}_{\text{in}}(\mathbf{r})$ through its average value over the region Ω_R. Using the result (1.140) in Appendix A (Section 1.5.1), we can compute this average field quantity as

$$\mathbf{E}_{\text{in}}(\mathbf{r}) = \sum_i \bar{\mathbf{e}}_i(\mathbf{r}) = -\frac{1}{4\pi\epsilon_0}\frac{1}{R^3}\sum_i \mathbf{p}_i = -\frac{1}{3\epsilon_0}\mathbf{P}(\mathbf{r}), \tag{1.35}$$

where the last equality follows from

$$\sum_i \mathbf{p}_i = |\Omega_R|\mathbf{P}(\mathbf{r}) = \frac{4}{3}\pi R^3\mathbf{P}(\mathbf{r}). \tag{1.36}$$

Therefore, from (1.31), for a field point $\mathbf{r}\in V$, the polarization field $\mathbf{E}_{\text{pol}}(\mathbf{r})$ can be expressed as

$$\mathbf{E}_{\text{pol}}(\mathbf{r}) = -\frac{1}{4\pi\epsilon_0}\nabla\int_{V/\Omega_R}\frac{\mathbf{P}(\mathbf{r}')\cdot(\mathbf{r}-\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|^3}\,\mathrm{d}\mathbf{r}' - \frac{1}{3\epsilon_0}\mathbf{P}(\mathbf{r}). \tag{1.37}$$

On the other hand, if we assume that the polarization density $\mathbf{P}(\mathbf{r})$ is uniform inside the sphere Ω_R, then from (1.146) in Appendix B (Section 1.5.2), we know that a uniform electric field is created inside the sphere given by

$$-\frac{1}{3\epsilon_0}\mathbf{P}(\mathbf{r}) = -\frac{1}{4\pi\epsilon_0}\nabla\int_{\Omega_R}\frac{\mathbf{P}(\mathbf{r}')\cdot(\mathbf{r}-\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|^3}\,\mathrm{d}\mathbf{r}'. \tag{1.38}$$

As a result, we have

$$\begin{aligned}\mathbf{E}_{\text{pol}}(\mathbf{r}) &= -\frac{1}{4\pi\epsilon_0}\nabla\int_{V/\Omega_R}\frac{\mathbf{P}(\mathbf{r}')\cdot(\mathbf{r}-\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|^3}\,\mathrm{d}\mathbf{r}' - \frac{1}{4\pi\epsilon_0}\nabla\int_{\Omega_R}\frac{\mathbf{P}(\mathbf{r}')\cdot(\mathbf{r}-\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|^3}\,\mathrm{d}\mathbf{r}' \\ &= -\nabla\Phi(\mathbf{r}),\end{aligned} \tag{1.39}$$

where

$$\Phi(\mathbf{r}) = \frac{1}{4\pi\epsilon_0}\int_V\frac{\mathbf{P}(\mathbf{r}')\cdot(\mathbf{r}-\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|^3}\,\mathrm{d}\mathbf{r}'. \tag{1.40}$$

Therefore, for a material with a *locally uniform polarization density* (i.e., no interior material interfaces), the macroscopic electric polarization field $\mathbf{E}_{\text{pol}}(\mathbf{r})$ can be computed by (1.39), namely, as the negative of the gradient of the potential (1.40) in the whole space $\mathbb{R}^3$.

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More Information

1.2.3 Singular integral expressions of $\mathbf{E}_{\text{pol}}(\mathbf{r})$ inside dielectrics

For the electric field inside a dielectric with polarization density $\mathbf{P}$, we can extend (1.30) to the case of $\mathbf{r} \in V$ using Cauchy principal integrals. First we define a de-singularized dipole tensor with $\delta > 0$ by

$$\overline{\mathbf{T}}_\delta(\mathbf{r}-\mathbf{r}') = \begin{cases} 0, & \text{if } |\mathbf{r}-\mathbf{r}'| \le \delta, \\ \overline{\mathbf{T}}(\mathbf{r}-\mathbf{r}'), & \text{if } |\mathbf{r}-\mathbf{r}'| > \delta. \end{cases} \tag{1.41}$$

Then, we have from (1.37) that

$$\begin{aligned} \mathbf{E}_{\text{pol}}(\mathbf{r}) &= -\frac{1}{4\pi\epsilon_0}\nabla\int_{V/\Omega_\delta}\frac{\mathbf{P}(\mathbf{r}')\cdot(\mathbf{r}-\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|^3}\,\mathrm{d}\mathbf{r}' - \frac{1}{3\epsilon_0}\mathbf{P}(\mathbf{r}) \\ &= \int_V \overline{\mathbf{T}}_\delta(\mathbf{r}-\mathbf{r}')\mathbf{P}(\mathbf{r}')\mathrm{d}\mathbf{r}' - \frac{1}{3\epsilon_0}\mathbf{P}(\mathbf{r}). \end{aligned} \tag{1.42}$$

Now, letting $\delta \to 0$, the first term becomes the Cauchy principal value (p.v.) of the singular integral, and we thus have

$$\mathbf{E}_{\text{pol}}(\mathbf{r}) = \text{p.v.}\int_V \overline{\mathbf{T}}(\mathbf{r}-\mathbf{r}')\mathbf{P}(\mathbf{r}')\mathrm{d}\mathbf{r}' - \frac{1}{3\epsilon_0}\mathbf{P}(\mathbf{r}). \tag{1.43}$$

More discussion on the Cauchy principal value of singular integrals can be found in Section 3.1.1.

1.3 Clausius–Mossotti and Onsager formulae for dielectric constant

1.3.1 Clausius–Mossotti formula for non-polar dielectrics

In this section, we derive a relation between the polarization density $\mathbf{P}(\mathbf{r})$ and the Maxwell electric field $\mathbf{E}(\mathbf{r})$ inside dielectrics. First, from the definition of the polarization density (1.16), the polarization is the combined polarization of all individual molecules, which will be under the effect of a local field $\mathbf{E}_{\text{local}}(\mathbf{r})$ at molecule sites. This local field $\mathbf{E}_{\text{local}}(\mathbf{r})$ is the Lorentz field and should be distinguished from the macroscopic Maxwell field $\mathbf{E}(\mathbf{r})$. Thus, the polarization density $\mathbf{P}(\mathbf{r})$ can be expressed in terms of the polarization of all individual molecules in a linear sum as

$$\mathbf{P}(\mathbf{r}) = \sum_i N_i\alpha_i(\mathbf{E}_{\text{local}}(\mathbf{r}))_i, \tag{1.44}$$

where α_i is the polarizability of the ith type particle (molecule) and N_i is the number density of the ith type particle (per unit volume), respectively.

From (1.10), the microscopic local Lorentz field on each individual molecule is defined as (Kantorovich, 2004)

$$\begin{aligned}\mathbf{E}_{\text{local}}(\mathbf{r}) &= \mathbf{E}'(\mathbf{r}) + \frac{1}{4\pi\epsilon_0}\sum_{j\in V}\left[\frac{3\mathbf{p}_j\cdot(\mathbf{r}-\mathbf{r}_j)}{|\mathbf{r}-\mathbf{r}_j|^5}(\mathbf{r}-\mathbf{r}_j) - \frac{\mathbf{p}_j}{|\mathbf{r}-\mathbf{r}_j|^3}\right] \\ &= \mathbf{E}'(\mathbf{r}) - \frac{1}{4\pi\epsilon_0}\sum_{j\in V}\nabla\frac{\mathbf{p}_j\cdot(\mathbf{r}-\mathbf{r}_j)}{|\mathbf{r}-\mathbf{r}_j|^3}, \end{aligned} \tag{1.45}$$

where $\mathbf{E}'(\mathbf{r})$ denotes the external electric field when the dielectric material is absent, and $\mathbf{p}_j$ is the dipole moment of the molecule at $\mathbf{r}_j$.

We split the summation in (1.45) into two groups of dipoles: those dipoles inside a sphere Ω_R around $\mathbf{r}$ and the rest in the exterior of the sphere $\Omega_R^c = V\backslash\Omega_R$. Then, we have

$$\begin{aligned}\mathbf{E}_{\text{local}}(\mathbf{r}) &= \mathbf{E}'(\mathbf{r}) - \frac{1}{4\pi\epsilon_0}\nabla\left(\sum_{j\in\Omega_R} + \sum_{j\in\Omega_R^c}\right)\frac{\mathbf{p}_j\cdot(\mathbf{r}-\mathbf{r}_j)}{|\mathbf{r}-\mathbf{r}_j|^3} \\ &= \mathbf{E}'(\mathbf{r}) - \frac{1}{4\pi\epsilon_0}\left[\nabla\sum_{j\in\Omega_R}\frac{\mathbf{p}_j\cdot(\mathbf{r}-\mathbf{r}_j)}{|\mathbf{r}-\mathbf{r}_j|^3} + \nabla\int_{\Omega_R^c}\frac{\mathbf{P}(\mathbf{r}')\cdot(\mathbf{r}-\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|^3}\,\mathrm{d}\mathbf{r}'\right], \end{aligned} \tag{1.46}$$

where a far-field approximation has been used in replacing $\mathbf{p}_j$ by $\mathbf{P}(\mathbf{r}')$ for the summation over Ω_R^c. It should be noted that a more appropriate expression for the field of the dipole $\mathbf{p}_j$ inside Ω_R should be (1.34), however, it would not affect the discussion and conclusion below.

Meanwhile, the Maxwell electric field $\mathbf{E}(\mathbf{r})$, being the sum of the external field $\mathbf{E}'(\mathbf{r})$ and the field generated by the polarizations $\mathbf{E}_{\text{pol}}(\mathbf{r})$ in (1.37), can be expressed as

$$\mathbf{E}(\mathbf{r}) = \mathbf{E}'(\mathbf{r}) - \frac{1}{4\pi\epsilon_0}\nabla\int_{\Omega_R^c}\frac{\mathbf{P}(\mathbf{r}')\cdot(\mathbf{r}-\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|^3}\,\mathrm{d}\mathbf{r}' - \frac{1}{3\epsilon_0}\mathbf{P}(\mathbf{r}). \tag{1.47}$$

Subtracting (1.47) from (1.46), we have

$$\mathbf{E}_{\text{local}}(\mathbf{r}) - \mathbf{E}(\mathbf{r}) = -\frac{1}{4\pi\epsilon_0}\nabla\sum_{j\in\Omega_R}\frac{\mathbf{p}_j\cdot(\mathbf{r}-\mathbf{r}_j)}{|\mathbf{r}-\mathbf{r}_j|^3} + \frac{1}{3\epsilon_0}\mathbf{P}(\mathbf{r}).$$

The summation over $j \in \Omega_R$ will vanish if we assume a cubic lattice for the material (Böttcher, 1973, p. 168) and a constant polarization $\mathbf{p}_j$ inside Ω_R. Therefore, we have

$$\mathbf{E}_{\text{local}}(\mathbf{r}) = \mathbf{E}(\mathbf{r}) + \frac{1}{3\epsilon_0}\mathbf{P}(\mathbf{r}), \tag{1.48}$$

which is defined as the *Lorentz local field* (Kittel, 2004, p. 388) acting on an individual molecule. From (1.146) and (1.144), it can be seen that the field correction $\mathbf{P}(\mathbf{r})/(3\epsilon_0)$ over the Maxwell field $\mathbf{E}(\mathbf{r})$ in the Lorentz local field $\mathbf{E}_{\text{local}}(\mathbf{r})$ is caused by the surface bound polarization charge on the boundary of the region

Ω_R (zero volume bound charge due to the assumption of a uniform polarization inside).

Next, using the ansatz of a linear relation (1.15) between the polarization and the Maxwell field, (1.48) becomes

$$\mathbf{E}_{\mathrm{local}}(\mathbf{r}) = \mathbf{E}(\mathbf{r}) + \frac{\chi}{3}\mathbf{E}(\mathbf{r}) = \left(1 + \frac{\chi}{3}\right)\mathbf{E}(\mathbf{r}). \tag{1.49}$$

Substituting (1.49) into the right-hand side of (1.44) and using (1.15) for its left-hand side, we have

$$\epsilon_0 \chi \mathbf{E}(\mathbf{r}) = \sum_i N_i \alpha_i \left(1 + \frac{\chi}{3}\right)\mathbf{E}(\mathbf{r}),$$

and, after eliminating the field $\mathbf{E}(\mathbf{r})$, we get

$$\frac{\chi}{3+\chi}\,\epsilon_0 = \frac{1}{3}\sum_i N_i \alpha_i, \tag{1.50}$$

which gives the well-known Clausius–Mossotti formula by using (1.28) (Mossotti, 1850; Clausius, 1879; Böttcher, 1973):

$$\frac{\epsilon_r - 1}{\epsilon_r + 2}\,\epsilon_0 = \frac{1}{3}\sum_i N_i \alpha_i. \tag{1.51}$$

1.3.2 Onsager dielectric theory for dipolar liquids

In the Onsager dielectric theory for a material with permanent molecular dipole moments, the polarization of the material is considered to come from two different sources, i.e.,

$$\mathbf{P} = \mathbf{P}_\alpha + \mathbf{P}_\mu, \tag{1.52}$$

where $\mathbf{P}_\alpha$ is the induced polarization from the translation of the atom's electron/nuclear charges and $\mathbf{P}_\mu$ is the dipole polarization by the orientation change of permanent dipoles, respectively. If α_i is the atomistic polarizability of the ith type particle, then

$$\mathbf{P}_\alpha = \left(\sum_i N_i \alpha_i\right)\mathbf{E}_{\mathrm{local}} \tag{1.53}$$

and

$$\mathbf{P}_\mu = \sum_i N_i \overline{\boldsymbol{\mu}}_i, \tag{1.54}$$

where $\overline{\boldsymbol{\mu}}_i$ is the permanent dipole vector obtained through Gibbs-averaging over all orientations under the effect of a directing field $\mathbf{E}_d$; the latter is only part of the local field $\mathbf{E}_{\mathrm{local}}(\mathbf{r})$ acting on the molecules.

In deriving the Onsager theory, we will take a different approach from the procedure used in deriving (1.48), where a virtual sphere Ω_R of uniform polarization