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LECTURE NOTES 13

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Continuum Theory of Disordered Systems

Centre of Excellence for
Advanced Materials and Structures

WARSAW 2004

AMAS LECTURE NOTES

Production of this volume has been partially supported by the European Commission

Published and distributed by
Institute of Fundamental Technological Research
Świętokrzyska 21, 00-049 Warszawa, Poland

ISSN 1642-0578

Papier offset. kl. III, 70 g, B1
Ark. wyd.: 7,1; ark. druk.: 6
Skład w systemie LaTeX: T.G. Zieliński
Oddano do druku i druk ukończono: IV 2004
Druk i oprawa: Drukarnia Braci Grodzickich, Piaseczno, ul. Geodetów 47a

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Chapter 1

Introduction

In this series of lectures we shall consider the average behavior of fields in systems consisting of a large number of particles embedded in a homogeneous medium. The medium can also be the vacuum. Examples of the fields considered are: the classical electric or magnetic field, the displacement field in an elastic solid, the number density of a different species of solute particles diffusing in the disordered system. The embedded particles will be regarded as fixed in space, but the theory can be extended to fluid suspensions, where the particles are free to move. The above examples belong to classical physics, but the theory can also be extended to quantum mechanics. In that case the field would be the wave function of an electron or neutron, and the embedded particles act as scatterers in the Schrödinger equation for electron or neutron.

In all cases we are interested in the average behavior of the field on a macroscopic level. We consider only disordered systems of embedded particles. The statistical average is performed over an ensemble of particle configurations. The ensemble is taken from statistical physics and is assumed to be known. According to ergodic theory the ensemble average is equivalent to a spatial average. The theory is easier to formulate on the basis of ensemble averaging.

The field equation is always assumed to be linear. Ensemble averaging of the linear equation shows that the average field satisfies a linear macroscopic equation. This equation must be complemented with a constitutive equation describing the influence of the embedded particles. The difficulty of the problem lies in the derivation of the constitutive equation [1, 2, 3, 4]. This equation contains the macroscopic material properties of the system.

In the framework of statistical physics we must:

- derive the macroscopic equation(s),
- derive a scheme for the calculation of transport coefficients or material properties occurring in the constitutive equation(s).

Example

Consider a system of N spheres, radius a, dielectric constant ε_2, embedded in a homogeneous matrix of dielectric constant ε_1, with volume V in the form of an ellipsoid (see Fig. 1.1). The spheres are distributed approximately uniformly with number density $n = N/V$. Their volume fraction is therefore $\phi = \frac{4\pi}{3}na^3$.

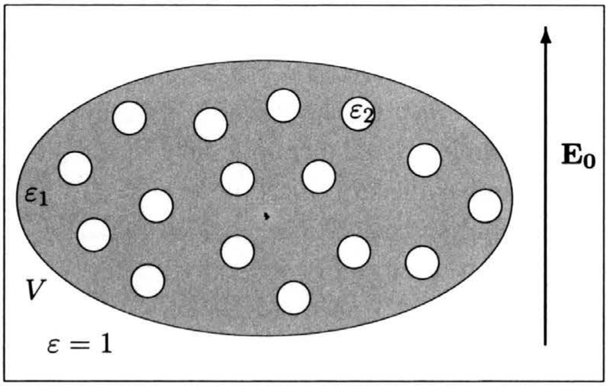

FIGURE 1.1. Ellipsoidal composite in uniform applied electric field.

If a constant external field $\boldsymbol{E}_0$ is applied to this system, then on the microscopic level for each configuration of centers $(\boldsymbol{R}_1, \dots, \boldsymbol{R}_N)$ a complicated field $\boldsymbol{E}(\boldsymbol{R}_1, \dots, \boldsymbol{R}_N; \boldsymbol{r})$ is generated. On the microscopic level this field satisfies Maxwell's electrostatic equations

$$\nabla \cdot \varepsilon \boldsymbol{E} = 0, \qquad \nabla \times \boldsymbol{E} = 0, \tag{1.1}$$

where $\varepsilon(\boldsymbol{R}_1, \dots, \boldsymbol{R}_N; \boldsymbol{r})$ is the local dielectric constant, given by

$$\begin{aligned} \varepsilon(\boldsymbol{R}_1, \dots, \boldsymbol{R}_N; \boldsymbol{r}) &= 1 \quad \text{for } \boldsymbol{r} \text{ not in } V, \\ &= \varepsilon_1 \quad \text{for } \boldsymbol{r} \text{ in } V \text{ in the matrix}, \\ &= \varepsilon_2 \quad \text{for } \boldsymbol{r} \text{ in } V \text{ in the spheres}. \end{aligned} \tag{1.2}$$

We assume that the probability distribution of configurations $W(\boldsymbol{R}_1, \ldots, \boldsymbol{R}_N)$ is known.

The average value of the field is given by

$$< \boldsymbol{E}(\boldsymbol{r}) > = \int \boldsymbol{E}(\boldsymbol{R}_1, \ldots, \boldsymbol{R}_N; \boldsymbol{r})\, d\boldsymbol{R}_1 \ldots d\boldsymbol{R}_N. \tag{1.3}$$

We abbreviate

$$\mathbf{X} \equiv (\boldsymbol{R}_1, \ldots, \boldsymbol{R}_N) \tag{1.4}$$

and write

$$\boldsymbol{E}(\mathbf{X}; \boldsymbol{r}), \qquad \varepsilon(\mathbf{X}; \boldsymbol{r}). \tag{1.5}$$

Then

$$< \boldsymbol{E}(\boldsymbol{r}) > = \int \boldsymbol{E}(\mathbf{X}; \boldsymbol{r}) W(\mathbf{X})\, dX. \tag{1.6}$$

$W(\mathbf{X})$ does not depend on $\boldsymbol{r}$. Therefore the microscopic equations can simply be averaged by interchange of $\int \ldots W d\mathbf{X}$ and ∇. This is the great advantage of ensemble averaging, in contrast to spatial averaging over volume elements.

The average equations read

$$\nabla \cdot < \varepsilon \boldsymbol{E} > = 0, \qquad \nabla \times < \boldsymbol{E} > = 0. \tag{1.7}$$

One defines

$$\boldsymbol{D} = \varepsilon \boldsymbol{E}, \tag{1.8}$$

so that also

$$< \boldsymbol{D} > = < \varepsilon \boldsymbol{E} > . \tag{1.9}$$

In the macroscopic Maxwell theory the material is described by an effective dielectric constant $\varepsilon_{\text{eff}}(\boldsymbol{r})$ with

$$\begin{aligned} \varepsilon_{\text{eff}}(\boldsymbol{r}) = 1 & \qquad\qquad\qquad \text{for } \boldsymbol{r} \notin \text{V}, \\ = \varepsilon_{\text{eff}} & \quad \text{(constant)} \quad \text{for } \boldsymbol{r} \in \text{V}, \\ & \quad \text{(for the assumed uniform distribution).} \end{aligned} \tag{1.10}$$

How does one show this and how can ε_{eff} be calculated?

Somewhat more generally one considers an external charge density $\rho_0(\boldsymbol{r})$. This is supposed to be an arbitrary function of $\boldsymbol{r}$.

Here "external" means that $\rho_0(\boldsymbol{r})$ does not depend on $\mathbf{X}$.

Then the microscopic equations read

$$\nabla \cdot \varepsilon \boldsymbol{E} = 4\pi\rho_0, \qquad \nabla \times \boldsymbol{E} = 0, \tag{1.11}$$

or equivalently

$$\boldsymbol{D} = \varepsilon \boldsymbol{E}, \qquad \nabla \cdot \boldsymbol{D} = 4\pi\rho_0, \qquad \nabla \times \boldsymbol{E} = 0. \tag{1.12}$$

The averaged equations read

$$\nabla \cdot < \epsilon \boldsymbol{E} > = 4\pi\rho_0, \qquad \nabla \times < \boldsymbol{E} > = 0, \tag{1.13}$$

or equivalently

$$< \boldsymbol{D} > = < \epsilon \boldsymbol{E} >, \qquad \nabla \cdot < \boldsymbol{D} > = 4\pi\rho_0, \qquad \nabla \times < \boldsymbol{E} > = 0. \tag{1.14}$$

The macroscopic equations are not complete. They must be completed by a constitutive equation, i.e. a relation between $< \boldsymbol{D} >$ and $< \boldsymbol{E} >$.

It is advantageous to introduce a microscopic polarization $\boldsymbol{P}(\boldsymbol{r})$ via

$$\begin{aligned} \boldsymbol{D} &= \varepsilon_1 \boldsymbol{E} + 4\pi \boldsymbol{P} && \text{for } \boldsymbol{r} \in \mathrm{V} \\ \boldsymbol{D} &= \boldsymbol{E} && \text{for } \boldsymbol{r} \notin \mathrm{V}. \end{aligned} \tag{1.15}$$

$\boldsymbol{P}(\boldsymbol{r})$ differs from zero only inside the particles. Macroscopically one has

$$< \boldsymbol{D} > = \varepsilon_1 < \boldsymbol{E} > + 4\pi < \boldsymbol{P} > \quad \text{for } \boldsymbol{r} \in V. \tag{1.16}$$

On account of the linearity of the problem the constitutive equation can be written generally as

$$< \boldsymbol{P}(\boldsymbol{r}) > = \int \boldsymbol{X}(\boldsymbol{r}, \boldsymbol{r}') \cdot < \boldsymbol{E}(\boldsymbol{r}') > d\boldsymbol{r}' \tag{1.17}$$

with an integral kernel that is determined by the nature of the particles and their statistical distribution. It is suggested by macroscopic Maxwell theory that the integral kernel has short range, i.e. one expects that $\boldsymbol{X}(\boldsymbol{r}, \boldsymbol{r}')$ decays to zero for distances $|\boldsymbol{r} - \boldsymbol{r}'|$ larger than say the mean distance between particles. It is the task of theory to show this and to find an effective way of calculating the kernel $\boldsymbol{X}(\boldsymbol{r}, \boldsymbol{r}')$.

In a region where $< \boldsymbol{E}(\boldsymbol{r}) >$ changes slowly one can approximate

$$< \boldsymbol{P}(\boldsymbol{r}) > \approx \left[\int \boldsymbol{X}(\boldsymbol{r}, \boldsymbol{r}') d\boldsymbol{r}' \right] \cdot < \boldsymbol{E}(\boldsymbol{r}) > \tag{1.18}$$

or

$$< \boldsymbol{P}(\boldsymbol{r}) > \approx \boldsymbol{\chi}_{\text{eff}}(\boldsymbol{r}) \cdot < \boldsymbol{E}(\boldsymbol{r}) > \tag{1.19}$$

with susceptibility tensor

$$\boldsymbol{\chi}_{\text{eff}}(\boldsymbol{r}) = \int \boldsymbol{X}(\boldsymbol{r}, \boldsymbol{r}')d\boldsymbol{r}'. \tag{1.20}$$

Correspondingly

$$\boldsymbol{\varepsilon}_{\text{eff}}(\boldsymbol{r}) = \varepsilon_1 \mathbf{1} + 4\pi \boldsymbol{\chi}_{\text{eff}}(\boldsymbol{r}). \tag{1.21}$$

If the distribution is isotropic one has simply

$$\varepsilon_{\text{eff}}(\boldsymbol{r}) = \varepsilon_1 + 4\pi \chi_{\text{eff}}(\boldsymbol{r}) \tag{1.22}$$

with scalars ε_{eff} and χ_{eff}.

Before we develop the theory any further we note that the equations can be mapped onto several other problems.

Electrical conductivity

Microscopically:

$$\begin{aligned} &\boldsymbol{j} = \sigma \boldsymbol{E}, \\ &\nabla \cdot \boldsymbol{j} = 4\pi\rho_0, \qquad \nabla \times \boldsymbol{E} = 0, \end{aligned} \tag{1.23}$$

with

$$\sigma(\mathbf{X}, \boldsymbol{r}), \qquad W(\mathbf{X}). \tag{1.24}$$

Macroscopically:

$$\begin{aligned} <\boldsymbol{j}> &= <\sigma \boldsymbol{E}>, \qquad & \nabla \cdot <\boldsymbol{j}> = 4\pi\rho_0, \\ &\approx \sigma_{\text{eff}} <\boldsymbol{E}>, \qquad & \nabla \times <\boldsymbol{E}> = 0. \end{aligned} \tag{1.25}$$

Heat conduction

Microscopically:

$$\begin{aligned} &\boldsymbol{j} = -\lambda \nabla T, \\ &\nabla \cdot \boldsymbol{j} = 4\pi\rho_0, \qquad \nabla \times \nabla T = 0. \end{aligned} \tag{1.26}$$

Macroscopically:

$$\begin{aligned} &<\boldsymbol{j}> = -<\lambda \nabla T> \approx -\lambda_{\text{eff}} <\nabla T> = -\lambda_{\text{eff}} \nabla <T>, \\ &\nabla \cdot <\boldsymbol{j}> = 4\pi\rho_0, \qquad \nabla \times \nabla <T> = 0. \end{aligned} \tag{1.27}$$

Stationary diffusion of solute particles

Microscopically:

$$\begin{aligned} \boldsymbol{j} &= -D\nabla n, \\ \nabla \cdot \boldsymbol{j} &= 4\pi\rho_0, \qquad \nabla \times \nabla n = 0. \end{aligned} \tag{1.28}$$

Macroscopically:

$$\begin{aligned} &< \boldsymbol{j} > = - < D\nabla n > \approx -D_{\text{eff}} < \nabla n > = -D_{\text{eff}}\nabla < n >, \\ &\nabla \cdot < \boldsymbol{j} > = 4\pi\rho_0, \qquad \nabla \times \nabla < n > = 0. \end{aligned} \tag{1.29}$$

Chapter 2

Simple approximations and bounds in electrostatics

The effective transport coefficients are often quite well described by simple approximations. We consider again the master example of the effective dielectric constant ε_{eff}.

It is clear that for a sufficiently dilute system ε_{eff} can be calculated from a one-body problem. Consider a situation, for which $\boldsymbol{E}_0$ is uniform in the ellipsoid V. Every particle is polarized by the applied field $\boldsymbol{E}_0$, i.e., it obtains a dipole moment

$$\boldsymbol{p} = \alpha_1 \boldsymbol{E}_0, \tag{2.1}$$

where α_1 is the dipole polarizability.

The dipole itself generates a field that acts on the other particles, but if the system is sufficiently dilute, this can be neglected.

The local polarization is then

$$< \boldsymbol{P} > \approx n\alpha_1 \boldsymbol{E}_0, \tag{2.2}$$

and since we neglect the influence of the dipoles one has also

$$< \boldsymbol{E} > \approx \boldsymbol{E}_0, \tag{2.3}$$

so that

$$< \boldsymbol{P} > \approx n\alpha_1 < \boldsymbol{E} >, \qquad \chi_{\text{eff}} \approx n\alpha_1, \qquad \varepsilon_{\text{eff}} \approx \varepsilon_1 + 4\pi n\alpha_1. \tag{2.4}$$

This expression is correct to the first order in n.

For a sphere with dielectric constant ϵ_2 embedded in a medium with dielectric constant ϵ_1 the dipole polarizability α_1 can be calculated from a simple Maxwell problem.

We introduce a potential ψ, such that $\boldsymbol{E} = -\nabla\psi$. Then one has

$$\begin{aligned} [\psi] &= 0 \quad \text{for } r = a, \\ \left[\varepsilon \frac{\partial \psi}{\partial r}\right] &= 0 \quad \text{for } r = a. \end{aligned} \tag{2.5}$$

Choose z-axis parallel to $\boldsymbol{E}_0$.

Ansatz:

$$\psi(\boldsymbol{r}) = \begin{cases} A\, r \cos\theta & \text{for } r < a, \\ B \frac{\cos\theta}{r^2} - E_0 r \cos\theta & \text{for } r > a. \end{cases} \tag{2.6}$$

The continuity conditions at the boundary $r = a$ are

$$\begin{aligned} [\psi]: &\quad A\, a = \frac{B}{a^2} - E_0 a, \\ \left[\varepsilon \frac{\partial \psi}{\partial r}\right]: &\quad \varepsilon_2\, A = -2\varepsilon_1 \frac{B}{a^3} - \varepsilon_1\, E_0. \end{aligned} \tag{2.7}$$

or

$$\begin{aligned} a^3 A - B &= -E_0 a^3, \\ \varepsilon_2 a^3 A + 2\varepsilon_1 B &= -\varepsilon_1 E_0 a^3. \end{aligned} \tag{2.8}$$

The solution is

$$A = \frac{-3\varepsilon_1}{\varepsilon_2 + 2\varepsilon_1}\, E_0, \qquad B = \frac{\varepsilon_2 - \varepsilon_1}{\varepsilon_2 + 2\varepsilon_1}\, a^3 E_0. \tag{2.9}$$

The sphere is uniformly polarized. The dipole moment generates a potential $\frac{\boldsymbol{p}\cdot\boldsymbol{r}}{\varepsilon_1 r^3}$ for $r > a$. We read off

$$\boldsymbol{p} = \alpha_1 \boldsymbol{E}_0 \qquad \text{with} \qquad \alpha_1 = \varepsilon_1 \frac{\varepsilon_2 - \varepsilon_1}{\varepsilon_2 + 2\varepsilon_1}\, a^3. \tag{2.10}$$

The polarization in the sphere is

$$\boldsymbol{P} = \frac{3}{4\pi a^3}\, \boldsymbol{p} = \frac{3\varepsilon_1}{4\pi}\, \frac{\varepsilon_2 - \varepsilon_1}{\varepsilon_2 + 2\varepsilon_1}\, \boldsymbol{E}_0, \quad r < a. \tag{2.11}$$

The field in the sphere is

$$\boldsymbol{E} = \frac{3\epsilon_1}{\epsilon_2 + 2\epsilon_1}\, \boldsymbol{E}_0 = \boldsymbol{E}_0 + \frac{\epsilon_1 - \epsilon_2}{\epsilon_2 + 2\epsilon_1}\, \boldsymbol{E}_0 = \boldsymbol{E}_0 - \frac{4\pi}{3\epsilon_1}\, \boldsymbol{P}, \qquad r < a. \tag{2.12}$$

The contribution $-\frac{4\pi}{3\varepsilon_1}\boldsymbol{P}$ is called the depolarization field. The field outside the sphere is a dipole field

$$\boldsymbol{E} = \frac{-\mathbf{1} + \hat{\boldsymbol{r}}\hat{\boldsymbol{r}}}{\varepsilon_1 r^3} \cdot \boldsymbol{p}, \qquad r > a. \tag{2.13}$$

The dipole field acts on other spheres and induces there dipole moments, as well multipole moments of higher order. In principle one deals with a complicated many-body problem. In simple approximations one attempts to reproduce the field in the neighborhood of a selected particle approximately correctly.

A very early theory is due to Mossotti (1846) [6]. It was formulated independently also by Clausius (1879) [7] and Lorentz (1879) [8, 9, 10].

In a region where the macroscopic polarization $< \boldsymbol{P} >$ and the macroscopic Maxwell field $< \boldsymbol{E} >$ are uniform one imagines a large sphere drawn about the center of a selected particle with radius R_c sufficiently large such that $\frac{4\pi}{3}\, n\, R_c^3 \gg 1$ (see Fig. 2.1).

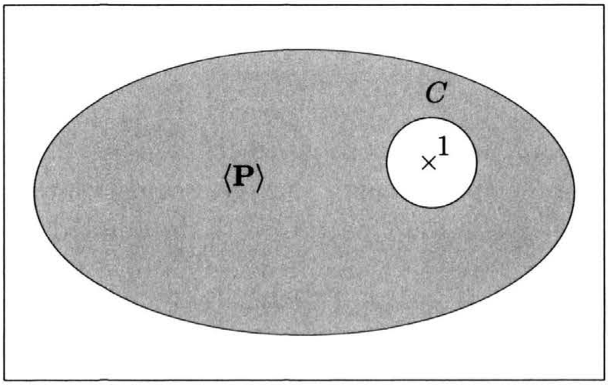

FIGURE 2.1. Geometry in derivation of Lorentz local field.

The particles outside the sphere C are approximated by a continuum. The field that is generated by the continuum outside C must be of the form

$$\boldsymbol{E}_L = < \boldsymbol{E} > + \frac{4\pi}{3\epsilon_1} < \boldsymbol{P} > \qquad \text{(Lorentz-field)}, \tag{2.14}$$

since the depolarization field of the sphere C with polarization $< \boldsymbol{P} >$ added to this must yield $< \boldsymbol{E} >$.

The Lorentz-field $\boldsymbol{E}_L$ is a good approximation for the field acting on the central particle. For an isotropic arrangement of identical dipoles in its immediate neighborhood the total field acting on the central dipole vanishes on account of the identity $\int(-\mathbf{1}+3\hat{\boldsymbol{r}}\hat{\boldsymbol{r}})d\Omega = 0$. The same is true for a cubic lattice. Hence the central dipole moment is approximately

$$<\boldsymbol{p}>\approx \alpha_1 \boldsymbol{E}_L \tag{2.15}$$

or

$$<\boldsymbol{P}>\approx n\alpha_1 \boldsymbol{E}_L, \qquad <\boldsymbol{P}>\approx n\alpha_1 \left[<\boldsymbol{E}> + \frac{4\pi}{3\epsilon_1} <\boldsymbol{P}>\right]. \tag{2.16}$$

Solving for $<\boldsymbol{P}>$ we get

$$<\boldsymbol{P}> = \frac{n\alpha_1}{1-\frac{4\pi}{3\epsilon_1}n\alpha_1} <\boldsymbol{E}>. \tag{2.17}$$

This leads to

$$\chi_{\text{eff}} \approx \frac{n\alpha_1}{1-\frac{4\pi}{3\varepsilon_1}n\alpha_1}, \qquad \varepsilon_{\text{eff}} \approx \varepsilon_1 + \frac{4\pi n\alpha_1}{1-\frac{4\pi}{3\varepsilon_1}n\alpha_1}. \tag{2.18}$$

The last expression can also be written as

$$\frac{\varepsilon_{\text{eff}}-\varepsilon_1}{\varepsilon_{\text{eff}}+2\varepsilon_1} = \frac{4\pi}{3\varepsilon_1}n\alpha_1 \qquad \text{(Clausius–Mossotti)}. \tag{2.19}$$

This is the famous Clausius–Mossotti formula. It is exact for a cubic lattice of dipoles and a very good approximation for isotropic disordered systems. The error made in the above argument is the assumption that the dipoles in the immediate environment are identical with the selected one. In fact there are correlation effects causing a small correction to ε_{eff}. An approximation to that effect was first calculated by Kirkwood and independently by Yvon in 1936. We shall study the correction in Chapter 4.

Another interesting derivation leading to the same result is due to Maxwell [11]. He assumed that the spheres are distributed approximately uniformly over a large sphere of radius R_0, volume $\Omega = \frac{4\pi}{3}R_0^3$ embedded in an infinite medium of dielectric constant ε_1. The average number density is therefore $n = N/\Omega$. The whole system is subject to a uniform applied field $\boldsymbol{E}_0$. According to Maxwell theory the total induced dipole moment is

$$\overline{\boldsymbol{M}}_S = \varepsilon_1 \frac{\varepsilon_{\text{eff}}-\varepsilon_1}{\varepsilon_{\text{eff}}+2\varepsilon_1} R_0^3 \boldsymbol{E}_0, \tag{2.20}$$

where the prefactor is the polarizability of the macroscopic sphere in the medium ε_1. Maxwell now argues that the total dipole moment must equal approximately $N\alpha_1\boldsymbol{E}_0$. This leads precisely to the Clausius–Mossotti formula, given by Eq. (2.19). Maxwell's derivation is suspect, since clearly dipolar interactions are neglected in the second argument.

We consider also the *shell model*, probably the first example of a self-consistent theory. In this model one considers a selected sphere with dielectric constant ε_2, radius a embedded in a medium with dielectric constant ε_{eff}, to be calculated, such that the sphere is surrounded by a shell of width $b - a$ and dielectric constant ε_1 (see Fig. 2.2). One imagines this configuration to be subject to the average field $< \boldsymbol{E} >$ and requires that the external dipole moment vanishes, i.e. for $r > b$ the field is precisely $< \boldsymbol{E} >$. The radius b is chosen such that one has the correct volume fractions for the two dielectric constants ε_1 and ε_2, namely

$$\frac{a^3}{b^3} = \phi, \tag{2.21}$$

or

$$b = \left(\frac{3}{4\pi n}\right)^{1/3}. \tag{2.22}$$

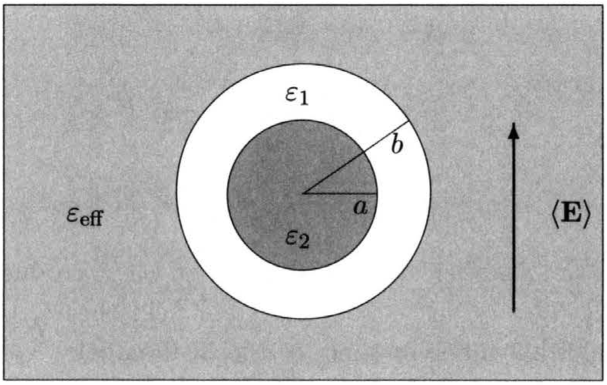

FIGURE 2.2. Shell model.

We calculate first the total induced dipole moment of the configuration and then put it equal to zero.

Ansatz:

$$\psi(\boldsymbol{r}) = \begin{cases} A\, r \cos\theta & \text{for } r < a, \\ B\, r \cos\theta + C\frac{\cos\theta}{r^2} & \text{for } a < r < b, \\ \frac{D\cos\theta}{r^2} - < E > r\cos\theta & \text{for } b < r. \end{cases} \tag{2.23}$$

$$\begin{array}{rc}
{}_a: & Aa = Ba + \dfrac{C}{a^2}, \\[2ex]
[\varepsilon \dfrac{\partial \psi}{\partial r}]_a: & \varepsilon_2 A = \varepsilon_1 B - 2\epsilon_1 \dfrac{C}{a^3}, \\[2ex]
[\psi]_b: & Bb + \dfrac{C}{b^2} = \dfrac{D}{b^2} - < E > b, \\[2ex]
[\varepsilon \dfrac{\partial \psi}{\partial r}]_b: & \varepsilon_1 B - 2\varepsilon_1 \dfrac{C}{b^3} = -2\varepsilon_{\text{eff}} \dfrac{D}{b^3} - \varepsilon_{\text{eff}} < E > .
\end{array} \tag{2.24}$$

Solving these equations for A, B, C, D and putting $D = 0$ we find

$$\varepsilon_{\text{eff}} = \varepsilon_1 + \frac{3\phi\beta}{1 - \phi\beta}\varepsilon_1 \quad \text{with} \quad \beta = \frac{\varepsilon_2 - \varepsilon_1}{\varepsilon_2 + 2\varepsilon_1} = \frac{\alpha_1}{\varepsilon_1 a^3}. \tag{2.25}$$

Equivalently

$$\frac{\varepsilon_{\text{eff}} - \varepsilon_1}{\varepsilon_{\text{eff}} + 2\varepsilon_1} = \phi\beta. \tag{2.26}$$

This is just the Clausius–Mossotti formula.
The values of the coefficients A, B, C are

$$A = \frac{-3\varepsilon_1}{\varepsilon_2(1 - \phi) + \varepsilon_1(2 + \phi)} < E >, \tag{2.27}$$

$$B = -\frac{\varepsilon_2 + 2\varepsilon_1}{\varepsilon_2(1 - \phi) + \varepsilon_1(2 + \phi)} < E >, \tag{2.28}$$

$$C = \frac{\varepsilon_2 - \varepsilon_1}{\varepsilon_2(1 - \phi) + \varepsilon_1(2 + \phi)} a^3 < E > . \tag{2.29}$$

We consider yet another approximation that was introduced in 1935 by Bruggeman [12]. This is also a self-consistent field theory, but the chosen geometry is somewhat different than for the shell model.

Bruggeman imagines the system as a mixtures of spheres with dielectric constant ε_2, radius a and little spheres with dielectric constant ε_1 and many different radii $\{a_{l1}\}$, all embedded in a medium with dielectric constant ε_{eff}.

For the spheres with ε_2 one has

$$\beta_2^* = \frac{\varepsilon_2 - \varepsilon_{\text{eff}}}{\varepsilon_2 + 2\varepsilon_{\text{eff}}}, \tag{2.30}$$

whilst for the spheres with ϵ_1 one gets

$$\beta_1^* = \frac{\varepsilon_1 - \varepsilon_{\text{eff}}}{\varepsilon_1 + 2\varepsilon_{\text{eff}}}. \tag{2.31}$$

Now Bruggeman requires that on average the additional polarization be equal to zero:

$$\overline{\boldsymbol{P}^*} = \left[\sum_l n_{l1}\alpha^*_{l1} + n_2\alpha^*_2\right] < \boldsymbol{E} > = 0, \tag{2.32}$$

where in the first term in brackets we sum over all possible radii. Now

$$\sum_l n_{l1}\alpha^*_{l1} = \sum_l n_{l1}\varepsilon_{\text{eff}}\frac{\varepsilon_1 - \varepsilon_{\text{eff}}}{\varepsilon_1 + 2\varepsilon_{\text{eff}}}\, a^3_{l1} = \frac{3}{4\pi}(1-\phi)\varepsilon_{\text{eff}}\beta^*_1. \tag{2.33}$$

The condition is therefore

$$(1-\phi)\beta^*_1 + \phi\beta^*_2 = 0, \tag{2.34}$$

or explicitly

$$(1-\phi)\frac{\varepsilon_1 - \varepsilon_{\text{eff}}}{\varepsilon_1 + 2\varepsilon_{\text{eff}}} + \phi\frac{\varepsilon_2 - \varepsilon_{\text{eff}}}{\varepsilon_2 + 2\varepsilon_{\text{eff}}} = 0. \tag{2.35}$$

This is a quadratic equation for ε_{eff}

$$2\varepsilon^2_{\text{eff}} + \left[(\varepsilon_2 - 2\varepsilon_1)\phi_1 + (\varepsilon_1 - 2\varepsilon_2)\phi_2\right]\varepsilon_{\text{eff}} - \varepsilon_1\varepsilon_2 = 0, \tag{2.36}$$

where we have put $\phi_1 = 1-\phi$, $\phi_2 = \phi$.

One needs the solution with $\varepsilon_{\text{eff}} = \varepsilon_1$ for $\phi_2 = 0$ and $\varepsilon_{\text{eff}} = \varepsilon_2$ for $\phi_1 = 0$. This is

$$\begin{aligned}
\varepsilon_{\text{eff}} &= \frac{1}{4}\left[\,(2\varepsilon_1 - \varepsilon_2)\phi_1 + (2\varepsilon_2 - \varepsilon_1)\phi_2\,\right] \\
&\quad + \frac{1}{4}\sqrt{\left[\,(2\varepsilon_1 - \varepsilon_2)\phi_1 + (2\varepsilon_2 - \varepsilon_1)\phi_2\,\right]^2 + 8\varepsilon_1\varepsilon_2} \\
&= \frac{1}{4}\left[2\varepsilon_1 - \varepsilon_2 + 3(\varepsilon_2 - \varepsilon_1)\phi\right] \\
&\quad + \frac{1}{4}\sqrt{(2\varepsilon_1 + \varepsilon_2)^2 + 6(2\varepsilon_1 - \varepsilon_2)(\varepsilon_2 - \varepsilon_1)\phi + 9(\varepsilon_2 - \varepsilon_1)^2\phi^2}.
\end{aligned} \tag{2.37}$$

The Bruggeman-formula is symmetrical in (ε_1, ϕ_1) and (ε_2, ϕ_2) in contrast to the Clausius–Mossotti formula. Hence it is thought to be more suitable for media where both components occur geometrically in equivalent fashion.

The formula becomes particularly interesting when rewritten for the electrical conductivity

$$(1-\phi)\frac{\sigma_1 - \sigma_{\text{eff}}}{\sigma_1 + 2\sigma_{\text{eff}}} + \phi\frac{\sigma_2 - \sigma_{\text{eff}}}{\sigma_2 + 2\sigma_{\text{eff}}} = 0. \tag{2.38}$$

If we now assume that material 2 is an ideal conductor, $\sigma_2 = \infty$, we obtain

$$(1-\phi)\frac{\sigma_1 - \sigma_{\text{eff}}}{\sigma_1 + 2\sigma_{\text{eff}}} + \phi = 0 \quad \text{or} \quad \sigma_{\text{eff}} = \frac{\sigma_1}{1-3\phi}, \tag{2.39}$$

i.e. σ_{eff} diverges to $\phi \to \frac{1}{3}$. This is regarded as a percolation transition.

Note that for $\sigma_2 = \infty$ the CM-formula becomes ($\beta \to 1$)

$$\sigma_{\text{eff}} = \sigma_1 + \frac{3\phi}{1-\phi}\sigma_1 \qquad \text{(CM)}, \tag{2.40}$$

i.e. according to this expression σ_{eff} diverges at $\phi = 1$.

For small ϕ both formulae yield $\varepsilon_{\text{eff}} \approx \varepsilon_1[1 + 3\phi\beta]$. For $\phi = 1$, $\varepsilon_{\text{eff}} = \varepsilon_2$ according to both formulae.

The different behavior shows that the nature of the microgeometry can have a large influence on the effective property, if the difference between the two media is large.

For $\phi = \frac{1}{3}$ the Bruggeman formula yields

$$\varepsilon_{Br} = \frac{\varepsilon_1}{4}\left[1 + \sqrt{8\frac{\varepsilon_2}{\varepsilon_1} + 1}\right] \sim \varepsilon_1\sqrt{\frac{\varepsilon_2}{2\varepsilon_1}} \qquad \text{for } \frac{\varepsilon_2}{\varepsilon_1} \to \infty, \tag{2.41}$$

whereas the Clausius–Mossotti formula leads to

$$\varepsilon_{CM} = \varepsilon_1\left[1 + \frac{3\beta}{3-\beta}\right] \to \frac{5}{2}\varepsilon_1 \qquad \text{as } \frac{\varepsilon_2}{\varepsilon_1} \to \infty. \tag{2.42}$$

Somewhat more generally Bruggeman's approximation can be formulated as

$$\sum_j n_j \alpha_j^* = 0. \tag{2.43}$$

The sum runs over all species of particles such that the entire space is filled:

$$\frac{4\pi}{3}\sum_j n_j\, a_j^3 = \sum_j \phi_j = 1. \tag{2.44}$$

For the calculation of the polarizabilities α_j^* the particles need not be uniform, just spherically symmetric.

In the above formulation the theory is strongly related to the so-called "coherent potential approximation" (CPA) [13]. To formulate the equation for ε_{eff} it suffices to calculate the one-particle susceptibilities in the effective medium.

It is clear that the effective dielectric constant ε_{eff} depends on the microgeometry. For a general isotropic two-phase medium with dielectric constants ε_1, ε_2 distributed with volume fractions ϕ_1, $\phi_2 = 1 - \phi_1$ in some prescribed fashion, e.g. a polydisperse suspension of spheres ε_2 with definite distribution of sphere ratios embedded in medium ε_1, the effective dielectric constant will be some function $\varepsilon_{\text{eff}}(\varepsilon_1, \varepsilon_2, \phi_2)$.

For small difference $\varepsilon_2 - \varepsilon_1$ this function can be expanded in the difference, and we shall argue that the first three terms of the expansion are

$$\varepsilon_{\text{eff}} = \varepsilon_1 \big[1 + \frac{\varepsilon_2 - \varepsilon_1}{\varepsilon_1}\phi_2 + \frac{1}{3}\big(\frac{\varepsilon_2 - \varepsilon_1}{\varepsilon_1}\big)^2 \phi_2^2\big] + O\big(\big(\frac{\varepsilon_2 - \varepsilon_1}{\varepsilon_1}\big)^3\big). \tag{2.45}$$

The local dielectric constant for the given microgeometry is given by

$$\varepsilon(\boldsymbol{r}) = \varepsilon_1 \theta_1(\boldsymbol{r}) + \varepsilon_2 \theta_2(\boldsymbol{r}) \tag{2.46}$$

with step functions

$$\begin{aligned} &\theta_1(\boldsymbol{r}) = 1, \quad \theta_2(\boldsymbol{r}) = 0 \quad \text{if } \boldsymbol{r} \in \text{phase } 1, \\ &\theta_2(\boldsymbol{r}) = 0, \quad \theta_2(\boldsymbol{r}) = 1 \quad \text{if } \boldsymbol{r} \in \text{phase } 2. \end{aligned} \tag{2.47}$$

Hence

$$\varepsilon(\boldsymbol{r}) = \varepsilon_1 + (\varepsilon_2 - \varepsilon_1)\theta_2(\boldsymbol{r}). \tag{2.48}$$

The average polarization at some field point $\boldsymbol{r}$ is given by

$$< \boldsymbol{P} >= \phi_2(\varepsilon_2 - \varepsilon_1)\boldsymbol{E}_{\text{loc2}}, \tag{2.49}$$

where $\boldsymbol{E}_{\text{loc2}}$ is the mean local field acting at the point $\boldsymbol{r}$ on condition that it is in phase 2. By Lorentz' argument this is given by

$$\boldsymbol{E}_{\text{loc2}} =< \boldsymbol{E} > + \frac{4\pi}{3\varepsilon_1} < \boldsymbol{P} > + O\big(\big(\frac{\varepsilon_2 - \varepsilon_1}{\varepsilon_1}\big)^2\big). \tag{2.50}$$

The polarization inside the Lorentz sphere yields no correction to the mean acting local field to the first order in $(\varepsilon_2 - \varepsilon_1)/\varepsilon_1$, since to this order it acts directly on the central point with the Green function $\boldsymbol{G}_0(\boldsymbol{r} - \boldsymbol{r}')$ given by

$$\boldsymbol{G}_0(\boldsymbol{r}) = \frac{-\boldsymbol{1} + 3\hat{\boldsymbol{r}}\hat{\boldsymbol{r}}}{\varepsilon_1 r^3}, \tag{2.51}$$

and for an isotropic distribution of phase 2 the resulting field vanishes by angular averaging. The central point $\boldsymbol{r}$ in medium 2 is assumed to be surrounded by an infinitesimal sphere of radius δ, and only points $\boldsymbol{r}'$ outside this little sphere contribute. From Eqs. (2.49), (2.50) and the definitions (1.19) and (1.22) one derives Eq. (2.45). Thus the first three terms of the expansion (2.45) are independent of the microgeometry. It is easily checked that both the Clausius–Mossotti formula for a suspension of uniform spheres, and the Bruggeman formula agree with this statement.

One can derive some general properties for the dependence $\varepsilon_{\text{eff}}(\varepsilon_1, \varepsilon_2, \phi_2)$. We assume that phase 2 is distributed approximately uniformly over a large sphere of radius R_0, volume $\Omega = \frac{4\pi}{3} R_0^3$ embedded in an infinite medium of dielectric constant ε_1. The whole system is subject to a uniform applied field $\boldsymbol{E}_0$. According to Maxwell theory the total induced dipole moment is given by Eq. (2.20), and the energy density of the material is $< \boldsymbol{D} > \cdot < \boldsymbol{E} > /(8\pi)$. We can compare the latter with the microscopic expression for the energy to obtain

$$\varepsilon_{\text{eff}} < \boldsymbol{E} >^2 = \frac{1}{\Omega} \int\limits_{\Omega} \boldsymbol{D} \cdot \boldsymbol{E} \, d\boldsymbol{r}. \tag{2.52}$$

We investigate how ε_{eff} varies with ε_2 when keeping the microgeometry and ε_1 fixed. It is convenient to vary the applied field $\boldsymbol{E}_0$ in such a way that $< \boldsymbol{E} >$ inside the sample remains fixed. It follows from Eq. (2.7) that the average potential at the surface then also remains fixed, since $< \psi > |_S = -R_0 < \boldsymbol{E} > \cdot \boldsymbol{e}_z$. Under the variation the energy density changes by

$$\frac{1}{8\pi}(\varepsilon_{\text{eff}} + \delta\varepsilon_{\text{eff}}) < \boldsymbol{E} >^2 = \frac{1}{8\pi\Omega} \int\limits_{\Omega} (\varepsilon + \delta\varepsilon)(\boldsymbol{E} + \delta\boldsymbol{E})^2 \, d\boldsymbol{r}. \tag{2.53}$$

Hence for small deviations we have

$$\delta\varepsilon_{\text{eff}} < \boldsymbol{E} >^2 = \frac{1}{\Omega} \int\limits_{\Omega} [\boldsymbol{E}^2(\boldsymbol{r})\delta\varepsilon(\boldsymbol{r}) + 2\varepsilon(\boldsymbol{r})\boldsymbol{E}(\boldsymbol{r}) \cdot \delta\boldsymbol{E}(\boldsymbol{r})] \, d\boldsymbol{r}. \tag{2.54}$$

The last term vanishes on average, since

$$\int\limits_{\Omega} \varepsilon(\boldsymbol{r})\boldsymbol{E}(\boldsymbol{r}) \cdot \delta\boldsymbol{E}(\boldsymbol{r}) \, d\boldsymbol{r} = \int\limits_{\Omega} \nabla \cdot (\varepsilon\boldsymbol{E})\delta\psi(\boldsymbol{r}) \, d\boldsymbol{r} - \int\limits_{S} \varepsilon(\boldsymbol{r})\boldsymbol{E}(\boldsymbol{r}) \cdot \hat{\boldsymbol{r}}\delta\psi \, dS. \tag{2.55}$$

The first integral on the right vanishes, since $\nabla \cdot (\varepsilon\boldsymbol{E}) = 0$, and the second vanishes after taking the ensemble average, since $\delta < \psi > |_S = 0$. We find therefore

$$\delta\varepsilon_{\text{eff}} = \frac{1}{< \boldsymbol{E} >^2 \Omega} \int\limits_{\Omega} \boldsymbol{E}^2(\boldsymbol{r})\delta\varepsilon(\boldsymbol{r}) \, d\boldsymbol{r}, \tag{2.56}$$

or, using symmetry in $\varepsilon_1, \varepsilon_2$,

$$\frac{\partial \varepsilon_{\text{eff}}}{\partial \varepsilon_i} = \frac{1}{<\boldsymbol{E}>^2 \, \Omega} \int\limits_{\Omega} \boldsymbol{E}^2(\boldsymbol{r}) \theta_i(\boldsymbol{r}) \, d\boldsymbol{r} = \frac{<\theta_i \boldsymbol{E}^2>}{<\boldsymbol{E}>^2} \qquad i = 1, 2. \tag{2.57}$$

This last identity is due to Bergman [14]. It shows that ε_{eff} increases with ε_2 at fixed ε_1, and vice versa.

Next we derive an inequality due to Matheron [3, 15]. By Schwarz's inequality and since $\theta_i^2(\boldsymbol{r}) = \theta_i(\boldsymbol{r})$ we have

$$\Big| \int\limits_{\Omega} \theta_i(\boldsymbol{r}) \boldsymbol{E}(\boldsymbol{r}) \, d\boldsymbol{r} \Big|^2 \leq \int\limits_{\Omega} \theta_i(\boldsymbol{r}) \, d\boldsymbol{r} \int\limits_{\Omega} \theta_i(\boldsymbol{r}) \, |\boldsymbol{E}(\boldsymbol{r})|^2 \, d\boldsymbol{r}, \tag{2.58}$$

or

$$\frac{\partial \varepsilon_{\text{eff}}}{\partial \varepsilon_i} \geq \frac{1}{\phi_i <\boldsymbol{E}>^2} | <\theta_i \boldsymbol{E}> |^2. \tag{2.59}$$

We can write

$$\theta_1(\boldsymbol{r}) = \frac{\varepsilon_2 - \varepsilon(\boldsymbol{r})}{\varepsilon_2 - \varepsilon_1}, \qquad \theta_2(\boldsymbol{r}) = \frac{\varepsilon(\boldsymbol{r}) - \varepsilon_1}{\varepsilon_2 - \varepsilon_1}. \tag{2.60}$$

Substituting this we find

$$<\theta_1 \boldsymbol{E}> = \frac{\varepsilon_2 - \varepsilon_{\text{eff}}}{\varepsilon_2 - \varepsilon_1} <\boldsymbol{E}>, \qquad <\theta_2 \boldsymbol{E}> = \frac{\varepsilon_{\text{eff}} - \varepsilon_1}{\varepsilon_2 - \varepsilon_1} <\boldsymbol{E}>, \tag{2.61}$$

so that

$$\frac{\partial \varepsilon_{\text{eff}}}{\partial \varepsilon_1} \geq \frac{1}{\phi_1} \Big(\frac{\varepsilon_2 - \varepsilon_{\text{eff}}}{\varepsilon_2 - \varepsilon_1} \Big)^2, \qquad \frac{\partial \varepsilon_{\text{eff}}}{\partial \varepsilon_2} \geq \frac{1}{\phi_2} \Big(\frac{\varepsilon_{\text{eff}} - \varepsilon_1}{\varepsilon_2 - \varepsilon_1} \Big)^2 \tag{2.62}$$

(Matheron inequalities [15]).

Note next that ε_{eff} is a homogeneous function of first degree in ε_1, ε_2, i.e. $\varepsilon_{\text{eff}}(\lambda\varepsilon_1, \lambda\varepsilon_1) = \lambda\varepsilon_{\text{eff}}(\varepsilon_1, \varepsilon_1)$ for all positive λ. Hence

$$\varepsilon_{\text{eff}} = \varepsilon_1 \frac{\partial \varepsilon_{\text{eff}}}{\partial \varepsilon_1} + \varepsilon_2 \frac{\partial \varepsilon_{\text{eff}}}{\partial \varepsilon_2} \geq \frac{\varepsilon_1}{\phi_1} \Big(\frac{\varepsilon_2 - \varepsilon_{\text{eff}}}{\varepsilon_2 - \varepsilon_1} \Big)^2 + \frac{\varepsilon_2}{\phi_2} \Big(\frac{\varepsilon_{\text{eff}} - \varepsilon_1}{\varepsilon_2 - \varepsilon_1} \Big)^2. \tag{2.63}$$

This can be cast in the form

$$(\varepsilon_V - \varepsilon_{\text{eff}})(\varepsilon_{\text{eff}} - \varepsilon_R) \geq 0, \tag{2.64}$$

where

$$\varepsilon_V = \phi_1 \varepsilon_1 + \phi_2 \varepsilon_2 = <\varepsilon> \tag{2.65}$$

is the Voigt approximation, and

$$\varepsilon_R = \frac{1}{\phi_1 \frac{1}{\varepsilon_1} + \phi_2 \frac{1}{\varepsilon_2}} = < \frac{1}{\varepsilon} >^{-1} \tag{2.66}$$

is the Reuss approximation. The inequality (2.62) becomes

$$\varepsilon_R < \varepsilon_{\text{eff}} < \varepsilon_V . \tag{2.67}$$

These are the so-called Wiener bounds.

One can derive better bounds if the composite is known to be isotropic. We assume without loss of generality $\varepsilon_2 > \varepsilon_1$.

Following Matheron [15] consider the function

$$F_2(\varepsilon_2) = \frac{1}{\varepsilon_1 - \varepsilon_{\text{eff}}} + \frac{1}{\phi_2(\varepsilon_2 - \varepsilon_1)} \tag{2.68}$$

for fixed ε_1. Then by the second inequality in Eq. (2.62)

$$\frac{\partial F_2}{\partial \varepsilon_2} = \frac{1}{(\varepsilon_1 - \varepsilon_{\text{eff}})^2} \Big[\frac{\partial \varepsilon_{\text{eff}}}{\partial \varepsilon_2} - \frac{1}{\phi_2} \Big(\frac{\varepsilon_{\text{eff}} - \varepsilon_1}{\varepsilon_2 - \varepsilon_1} \Big)^2 \Big] \geq 0. \tag{2.69}$$

Therefore $F_2(\varepsilon_2)$ is an increasing function of ε_2, and consequently

$$F_2(\varepsilon_2) \geq F_{20}, \qquad F_{20} = \lim_{\varepsilon_2 \to \varepsilon_1 +} F_2(\varepsilon_2). \tag{2.70}$$

From Eq. (2.45) one finds

$$F_{20} = -\frac{\phi_1}{3\phi_2 \varepsilon_1}, \tag{2.71}$$

so that

$$\frac{1}{\varepsilon_1 - \varepsilon_{\text{eff}}} + \frac{1}{\phi_2(\varepsilon_2 - \varepsilon_1)} \geq -\frac{\phi_1}{3\phi_2 \varepsilon_1}. \tag{2.72}$$

This can be cast in the form

$$\varepsilon_{\text{eff}} \geq \varepsilon_1 \Big(1 + \frac{3\phi_2 \beta_2}{1 - \phi_2 \beta_2}\Big) \tag{2.73}$$

with $\beta_2 = (\varepsilon_2 - \varepsilon_1)/(\varepsilon_2 + 2\varepsilon_1)$. The right hand side is just the Clausius–Mossotti expression for uniform spheres ε_2 embedded at volume fraction ϕ_2 in the medium ε_1.

Next consider the function

$$F_1(\varepsilon_1) = \frac{1}{\varepsilon_{\text{eff}} - \varepsilon_2} + \frac{1}{\phi_1(\varepsilon_2 - \varepsilon_1)} \tag{2.74}$$

for fixed ε_2. Then by the first inequality in Eq. (2.62)

$$\frac{\partial F_1}{\partial \varepsilon_1} = \frac{-1}{(\varepsilon_{\text{eff}} - \varepsilon_2)^2}\Big[\frac{\partial \varepsilon_{\text{eff}}}{\partial \varepsilon_1} - \frac{1}{\phi_1}\Big(\frac{\varepsilon_2 - \varepsilon_{\text{eff}}}{\varepsilon_2 - \varepsilon_1}\Big)^2\Big] \leq 0. \tag{2.75}$$

Therefore $F_1(\varepsilon_1)$ is a decreasing function of ε_1, and consequently

$$F_1(\varepsilon_1) \geq F_{10}, \qquad F_{10} = \lim_{\varepsilon_1 \to \varepsilon_2 -} F_1(\varepsilon_1). \tag{2.76}$$

From Eq. (2.45) with interchanged subscripts one finds

$$F_{10} = \frac{\phi_2}{3\phi_1\varepsilon_2}, \tag{2.77}$$

so that

$$\frac{1}{\varepsilon_{\text{eff}} - \varepsilon_2} + \frac{1}{\phi_1(\varepsilon_2 - \varepsilon_1)} \geq \frac{\phi_2}{3\phi_1\varepsilon_2}. \tag{2.78}$$

This can be cast in the form

$$\varepsilon_{\text{eff}} \leq \varepsilon_2\Big(1 + \frac{3\phi_1\beta_1}{1 - \phi_1\beta_1}\Big) \tag{2.79}$$

with $\beta_1 = (\varepsilon_1 - \varepsilon_2)/(\varepsilon_1 + 2\varepsilon_2)$. The right hand side is just the Clausius–Mossotti expression for uniform spheres ε_1 embedded at volume fraction ϕ_1 in the medium ε_2.

The two bounds just derived are due to Hashin and Shtrikman [16]. We can write

$$\varepsilon^L_{\text{HS}} \leq \varepsilon_{\text{eff}} \leq \varepsilon^U_{\text{HS}} \tag{2.80}$$

with lower and upper Hashin–Shtrikman bounds given by

$$\varepsilon^L_{\text{HS}} = \varepsilon_1\Big(1 + \frac{3\phi_2\beta_2}{1 - \phi_2\beta_2}\Big), \qquad \varepsilon^U_{\text{HS}} = \varepsilon_2\Big(1 + \frac{3\phi_1\beta_1}{1 - \phi_1\beta_1}\Big). \tag{2.81}$$

It is clear that for $\varepsilon_2 < \varepsilon_1$ the two expressions must be interchanged. It is easily checked, that the Hashin–Shtrikman bounds are sharper than the Wiener bounds. An additional property, isotropy, has been used in their derivation. Hashin and Shtrikman showed also that materials can be constructed for which the lower or upper bound is achieved. The construction is based on the shell model studied above (Eq. (2.26)). The shell arrangement was chosen such that it has no influence outside if it is embedded in the effective medium. Therefore one can replace more and more of the effective medium with shell arrangements of different sizes, but with the same ratio of radii, without

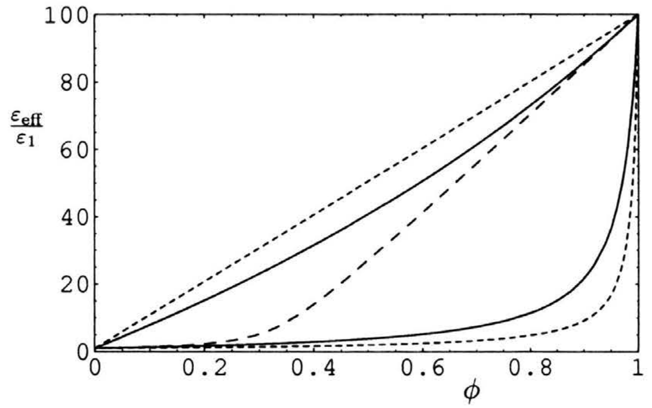

FIGURE 2.3. Comparison of Wiener bounds (short dashes) and Hashin–Shtrikman bounds (drawn curves) with Bruggeman's expression Eq. (2.42) (long dashes) for the ratio $\varepsilon_{\text{eff}}/\varepsilon_1$ as a function of $\phi = \phi_2$ for $\varepsilon_2/\varepsilon_1 = 100$.

affecting the value of the effective dielectric constant. Eventually the whole volume is filled with shell arrangements, and one has a two-phase medium with effective dielectric constant given by the Clausius–Mossotti formula.

Finally, it is of interest to compare the Wiener bounds and the Hashin–Shtrikman bounds numerically with the Bruggeman formula for a large ratio $\varepsilon_2/\varepsilon_1$, e.g. for $\varepsilon_2/\varepsilon_1 = 100$. In Fig. 2.3 we plot the various curves for $\varepsilon_{\text{eff}}/\varepsilon_1$ for ratio $\varepsilon_2/\varepsilon_1 = 100$ vs. volume fraction $\phi = \phi_2$.

Chapter 3

Mean field approximation to the effective elastic moduli of a suspension of spheres

The calculation of the effective elastic properties of a solid composite is an important problem of material science. In this Chapter we study a solid suspension consisting of spheres with a spherically symmetric elastic profile embedded in a uniform and isotropic matrix [17]. We derive mean field expressions for the effective shear and bulk moduli of the suspension by a method analogous to that used by Lorentz for the derivation of the Clausius–Mossotti formula in the theory of dielectrics. For the special case of uniform spheres the mean field expressions reduce to the Hashin–Shtrikman bounds [18], except when the shear modulus of the spheres is larger and the bulk modulus is smaller than that of the matrix, or vice versa.

We consider N identical spherical particles of radius a , centered at $\boldsymbol{R}_1, \ldots, \boldsymbol{R}_N$, and embedded in an isotropic elastic medium with uniform shear modulus μ_1 and bulk modulus κ_1. The inclusions are assumed to have a spherically symmetric shear modulus $\mu_2(s)$ and bulk modulus $\kappa_2(s)$, so that the elastic moduli in the inclusions are given by

$$\begin{gathered}\mu(\boldsymbol{r}) = \mu_2\left(|\boldsymbol{r} - \boldsymbol{R}_j|\right), \qquad \kappa(\boldsymbol{r}) = \kappa_2\left(|\boldsymbol{r} - \boldsymbol{R}_j|\right) \\ \text{for } |\boldsymbol{r} - \boldsymbol{R}_j| \leq a, \quad j = 1, \ldots, N.\end{gathered} \tag{3.1}$$

The linear equation of elastic equilibrium for the displacement field $\boldsymbol{u}(\boldsymbol{r})$ can be written as

$$\nabla \cdot \boldsymbol{\sigma} = -\boldsymbol{F}_0, \tag{3.2}$$

where $\boldsymbol{\sigma}(\boldsymbol{r})$ is the stress tensor and $\boldsymbol{F}_0(\boldsymbol{r})$ is an applied force density. The stress tensor is given by the local constitutive equation

$$\boldsymbol{\sigma} = 2\mu(\nabla\boldsymbol{u})^0 + \kappa(\nabla\cdot\boldsymbol{u})\mathbf{1}, \tag{3.3}$$

where $\mu(\boldsymbol{r})$ is the local shear modulus, $\kappa(\boldsymbol{r})$ is the local bulk modulus, and $(\nabla\boldsymbol{u})^0$ is the symmetric traceless part of the strain tensor defined by

$$\left((\nabla\boldsymbol{u})^0\right)_{\alpha\beta} = \frac{1}{2}\left(\partial_\alpha u_\beta + \partial_\beta u_\alpha\right) - \frac{1}{3}\left(\nabla\cdot\boldsymbol{u}\right)\delta_{\alpha\beta}. \tag{3.4}$$

The last term in Eq. (3.3) corresponds to the local pressure

$$p = -\kappa\nabla\cdot\boldsymbol{u}. \tag{3.5}$$

We define the difference functions

$$\tilde{\mu}(\boldsymbol{r}) = \mu(\boldsymbol{r}) - \mu_1, \qquad \tilde{\kappa}(\boldsymbol{r}) = \kappa(\boldsymbol{r}) - \kappa_1, \tag{3.6}$$

which vanish outside the inclusions, and introduce the stress s induced by the inclusions as

$$\mathsf{s} = 2\tilde{\mu}(\nabla\boldsymbol{u})^0 + \tilde{\kappa}\left(\nabla\cdot\boldsymbol{u}\right)\mathbf{1}. \tag{3.7}$$

The equilibrium equation (3.2) may then be rewritten as

$$\mu_1\nabla^2\boldsymbol{u} + \left(\frac{1}{3}\mu_1 + \kappa_1\right)\nabla\nabla\cdot\boldsymbol{u} = -\boldsymbol{F}_0 - \boldsymbol{F}, \tag{3.8}$$

with the induced force density $\boldsymbol{F}(\boldsymbol{r})$ given by

$$\boldsymbol{F}(\boldsymbol{r}) = \sum_{j=1}^{N}\boldsymbol{F}_j(\boldsymbol{r}) \tag{3.9}$$

where

$$\boldsymbol{F}_j(\boldsymbol{r}) = \theta\left(a - |\boldsymbol{r} - \boldsymbol{R}_j|\right)\nabla\cdot\mathsf{s} \tag{3.10}$$

is the contribution from the jth inclusion. Here $\theta(r)$ is the Heaviside step function. It follows from Eq. (3.2) that $\boldsymbol{F}$ is the divergence of a tensor field. We may interpret Eq. (3.8) as the equilibrium equation for a uniform medium with moduli μ_1, κ_1 on which the force density $\boldsymbol{F}_0 + \boldsymbol{F}$ acts locally.

The formal solution to Eq. (3.8) is given by

$$\boldsymbol{u}(\boldsymbol{r}) = \boldsymbol{u}_0(\boldsymbol{r}) + \int \boldsymbol{G}_0(\boldsymbol{r},\boldsymbol{r}')\cdot\boldsymbol{F}(\boldsymbol{r}')d\boldsymbol{r}', \tag{3.11}$$

where $\boldsymbol{u}_0(\boldsymbol{r})$ is the solution in the absence of inclusions, and $\boldsymbol{G}_0(\boldsymbol{r},\boldsymbol{r}')$ is the Green's function. For an infinite and unbounded medium the Green's function is translationally invariant, so that

$$\boldsymbol{G}_0(\boldsymbol{r},\boldsymbol{r}') = \boldsymbol{G}_0(\boldsymbol{r}-\boldsymbol{r}'). \tag{3.12}$$

By Fourier transformation one finds the explicit expression [19]

$$\boldsymbol{G}_0(\boldsymbol{r}) = \frac{1}{8\pi\mu_1}\left[\frac{\xi+1}{\xi+4}\frac{\mathbf{1}+\hat{\boldsymbol{r}}\hat{\boldsymbol{r}}}{r} + \frac{6}{\xi+4}\frac{\mathbf{1}}{r}\right], \tag{3.13}$$

where ξ is the ratio

$$\xi = 3\kappa_1/\mu_1. \tag{3.14}$$

The first term in Eq. (3.13) is proportional to the Oseen tensor known from low Reynolds number hydrodynamics [20].

By substitution of the formal solution (3.11) into Eqs. (3.7) and (3.10) one obtains a self-consistent equation for the induced force density $\boldsymbol{F}$. The force density exerted by inclusion j on the medium is given by

$$\boldsymbol{F}_j(\boldsymbol{r}) = \int \boldsymbol{M}\left(j;\boldsymbol{r},\boldsymbol{r}'\right)\cdot \boldsymbol{u}_j^a(\boldsymbol{r}')d\boldsymbol{r}', \tag{3.15}$$

where the integral kernel $\boldsymbol{M}(j;\boldsymbol{r},\boldsymbol{r}')$ describes the response of sphere j to an incident field, and $\boldsymbol{u}_j^a(\boldsymbol{r})$ is the displacement field acting on sphere j. The latter is given by

$$\boldsymbol{u}_j^a(\boldsymbol{r}) = \boldsymbol{u}_0(\boldsymbol{r}) + \sum_{k\neq j}\boldsymbol{u}_k(\boldsymbol{r}), \tag{3.16}$$

where $\boldsymbol{u}_k(\boldsymbol{r})$ in turn is given by

$$\boldsymbol{u}_k(\boldsymbol{r}) = \int \boldsymbol{G}_0(\boldsymbol{r},\boldsymbol{r}')\cdot \boldsymbol{F}_k(\boldsymbol{r}')d\boldsymbol{r}'. \tag{3.17}$$

The above equations may be solved by iteration and hence the induced force density $\boldsymbol{F}(\boldsymbol{r})$ can be found from the displacement field $\boldsymbol{u}_0(\boldsymbol{r})$ for any configuration of particles.

For any configuration $(\boldsymbol{R}_1,\ldots,\boldsymbol{R}_N)$ and for any applied force density $\boldsymbol{F}_0(\boldsymbol{r})$ the above equations provide a formal solution for the displacement field and for the induced force density. Assuming the probability distribution of configurations to be known one can perform an average over the positions of the spheres. This leads to a macroscopic equation for the average displacement field and to a constitutive equation for the average force density.

From Eq. (3.8) we find the average equation

$$\mu_1 \nabla^2 \langle \boldsymbol{u} \rangle + \left(\frac{1}{3}\mu_1 + \kappa_1 \right) \nabla\nabla \cdot \langle \boldsymbol{u} \rangle = -\boldsymbol{F}_0 - \langle \boldsymbol{F} \rangle . \tag{3.18}$$

We have assumed that the applied force density $\boldsymbol{F}_0(\boldsymbol{r})$ is independent of the configuration of scatterers. The average induced force density $\langle \boldsymbol{F}(\boldsymbol{r}) \rangle$ may be expressed in terms of the average displacement field $\langle \boldsymbol{u}(\boldsymbol{r}) \rangle$ by means of a linear integral kernel which has a relatively short range. For a field $\langle \boldsymbol{u}(\boldsymbol{r}) \rangle$ of slow spatial variation the integral operator may be expressed with a local elastic tensor. For systems which on average are locally uniform and isotropic the average equation in the bulk of the medium takes the form

$$\mu_{\text{eff}} \nabla^2 \langle \boldsymbol{u} \rangle + \left(\frac{1}{3}\mu_{\text{eff}} + \kappa_{\text{eff}} \right) \nabla\nabla \cdot \langle \boldsymbol{u} \rangle = -\boldsymbol{F}_0, \tag{3.19}$$

with effective moduli μ_{eff} and κ_{eff}.

In the statistical mechanical derivation of Eq. (3.19) one considers a probability distribution $W(1,\ldots,N)$ for which the particle centers are localized inside a volume Ω and for which the average density becomes uniform in the thermodynamic limit $N \to \infty$, $\Omega \to \infty$ at constant $n = N/\Omega$. All higher order distribution functions must become translationally invariant and isotropic. The procedure leads to well-defined statistical expressions for the effective moduli μ_{eff} and κ_{eff}, which are independent of the shape of the volume Ω.

To lowest order in the density the effective moduli are given by [12, 21, 22]

$$\mu_{\text{eff}} = \mu_1 + [\mu]\phi\mu_1 + O\left(\phi^2\right), \quad \kappa_{\text{eff}} = \kappa_1 + [\kappa]\phi\kappa_1 + O\left(\phi^2\right), \tag{3.20}$$

where $\phi = 4\pi n a^3/3$ is the volume fraction, and the intrinsic moduli $[\mu]$ and $[\kappa]$ follow from the solution of a single particle problem [23]. The expressions (3.20) are useful only for very dilute suspensions. At higher volume fractions correction terms involving elastic interactions between inclusions must be considered.

We derive expressions for the effective moduli μ_{eff} and κ_{eff} in mean field approximation by following the approach first developed by Clausius [7], Mossotti [6], and Lorentz [8, 24] in the theory of dielectrics. In the case of dielectrics the average local electric field acting on a selected particle is expressed in terms of the average Maxwell field and the average polarization. In mean field approximation correlations between spheres, apart from the non-overlap condition, are neglected. As a result the expression for the effective dielectric constant depends only on the volume fraction occupied by spheres and contains no further details of the geometry of the microstructure. By following the same approach in the elastic case we shall find similar expressions for the effective elastic moduli.

We follow Lorentz's approach in the case of elastic suspensions. First of all we must find the equivalent of the polarization. The multipole moments of the force density of a selected sphere j are defined by [25]

$$\boldsymbol{\mu}_j^{(n)} = \frac{1}{(n-1)!} \int \boldsymbol{F}_j(\boldsymbol{r}) \, (\boldsymbol{r} - \boldsymbol{R}_j)^{n-1} \, d\boldsymbol{r} \tag{3.21}$$

where $\boldsymbol{a}^n$ indicates the direct tensor product of n vectors $\boldsymbol{a}$. The moment for $n = 1$ vanishes, since the inclusion can exert no force, and the moment for $n = 2$ is symmetric, since the inclusion can exert no torque. The corresponding force multipole density of order n is defined by

$$\mathsf{F}^{(n)} = \sum_{j=1}^{N} \boldsymbol{\mu}_j^{(n)} \delta\left(\boldsymbol{r} - \boldsymbol{R}_j\right). \tag{3.22}$$

The average induced force density may be effectively replaced by the multipole expansion

$$< \boldsymbol{F}(\boldsymbol{r}) > = \sum_{n=2}^{\infty} \quad (-1)^{n-1} \quad \nabla^{n-1} :< \mathsf{F}^{(n)}(\boldsymbol{r}) > . \tag{3.23}$$

In situations with slow spatial variation it is sufficient to consider only the dipolar term $< \mathsf{F}^{(2)}(\boldsymbol{r}) >$. This is the analogue of the electric polarization in the dielectric case. We separate the symmetric second rank tensor into two parts

$$< \mathsf{F}^{(2)} > = < (\mathsf{F}^{(2)})^0 > + \frac{1}{3} \mathbf{1} \mathrm{Tr} < \mathsf{F}^{(2)} > . \tag{3.24}$$

The average stress in the suspension may be approximated by

$$< \boldsymbol{\sigma} > = 2\mu_1 (\nabla < \boldsymbol{u} >)^0 - < (\mathsf{F}^{(2)})^0 > + \mathbf{1} \left(\kappa_1 \nabla \cdot < \boldsymbol{u} > - \frac{1}{3} \mathrm{Tr} < \mathsf{F}^{(2)} > \right). \tag{3.25}$$

Thus the first term in Eq. (3.24) contributes to the average shear stress, and the second term contributes to the average pressure.

Next we consider the response of an isolated inclusion centered at $\boldsymbol{R}$ to an almost uniform acting displacement field. The relevant moments are

$$(\boldsymbol{\mu}^{(2)})^0 = -\frac{8\pi a^3}{3} [\mu] \mu_1 (\nabla \boldsymbol{u})^0 \,|_{\boldsymbol{R}}, \qquad \mathrm{Tr}\, \boldsymbol{\mu}^{(2)} = -4\pi a^3 [\kappa] \kappa_1 \nabla \cdot \boldsymbol{u} \,|_{\boldsymbol{R}} . \tag{3.26}$$

At low density the acting field may be replaced by the average field. This leads to the low density expressions (3.20). At higher density one must consider corrections to the local field. Again we draw a large Lorentz sphere around the selected inclusion and calculate the contribution from the particles outside the sphere in continuum approximation. The influence of the average second rank force density $< \mathsf{F}^{(2)} >$ is mediated by the Green's function given in Eq. (3.13). The second term in this expression is just a Coulomb propagator. We consider first the part of the displacement field caused by this part of the propagator. Denoting the field by $\boldsymbol{u}_C(\boldsymbol{r})$ we obtain

$$< \boldsymbol{u}_C(\boldsymbol{r}) >= \frac{3}{4\pi\mu_1}\frac{1}{\xi+4} \int \frac{1}{|\boldsymbol{r}-\boldsymbol{r}'|} < \boldsymbol{F}(\boldsymbol{r}') > d\boldsymbol{r}'. \tag{3.27}$$

Substituting Eq. (3.23) and neglecting the higher order multipole densities we find

$$< \boldsymbol{u}_C(\boldsymbol{r}) >= \frac{3}{4\pi\mu_1}\frac{1}{\xi+4} \int \frac{-1}{|\boldsymbol{r}-\boldsymbol{r}'|} \nabla' \cdot < \mathsf{F}^{(2)}(\boldsymbol{r}') > d\boldsymbol{r}'. \tag{3.28}$$

This means that each of the cartesian components of $< \boldsymbol{u}_C(\boldsymbol{r}) >$ may be regarded as the electrostatic potential generated by a charge density given by the corresponding component of $-\nabla \cdot < \mathsf{F}^{(2)}(\boldsymbol{r}) >$. Recalling that in electrostatics $-\nabla \cdot \boldsymbol{P}$ acts like a charge density we can write down the Lorentz field corresponding to Eq. (3.28), namely

$$(\nabla \boldsymbol{u}_C)_L = \nabla < \boldsymbol{u}_C > - \frac{1}{\mu_1}\frac{1}{\xi+4} < \mathsf{F}^{(2)} > . \tag{3.29}$$

It will be convenient to separate this into the relevant tensor parts. The symmetric traceless part is

$$((\nabla \boldsymbol{u}_C))_L^0 =< (\nabla \boldsymbol{u}_C)^0 > - \frac{1}{\mu_1}\frac{1}{\xi+4} < (\mathsf{F}^{(2)})^0 >, \tag{3.30}$$

and the trace part is

$$\mathrm{Tr}\,(\nabla \boldsymbol{u}_C)_L =< \nabla \cdot \boldsymbol{u}_C > - \frac{1}{\mu_1}\frac{1}{\xi+4} \mathrm{Tr} < \mathsf{F}^{(2)} > . \tag{3.31}$$

Next we consider the displacement field caused by the first part of the Green's function in Eq. (3.13). We denote this Oseen part as $\boldsymbol{u}_{Os}(\boldsymbol{r})$ and obtain

$$< \boldsymbol{u}_{Os}(\boldsymbol{r}) >= \frac{\xi+1}{\xi+4} \int \mathsf{T}(\boldsymbol{r}-\boldsymbol{r}') \cdot < \boldsymbol{F}(\boldsymbol{r}') > d\boldsymbol{r}', \tag{3.32}$$

where the propagator is given by the Oseen tensor

$$\boldsymbol{T}(\boldsymbol{r}) = \frac{1}{8\pi\mu_1}\frac{\mathbf{1}+\hat{\boldsymbol{r}}\hat{\boldsymbol{r}}}{r}. \tag{3.33}$$

By comparison with Eq. (3.11) we have

$$< \boldsymbol{u} > = \boldsymbol{u}_0 + < \boldsymbol{u}_C > + < \boldsymbol{u}_{Os} > . \tag{3.34}$$

The Lorentz field corresponding to the Oseen propagator has been studied in the context of low Reynolds number hydrodynamics [25]. Neglecting again the higher order multipole densities we obtain from Eq. (6.4) of ref. [25] the Lorentz field

$$(\nabla \boldsymbol{u}_{Os})_L = \nabla < \boldsymbol{u}_{Os} > - \frac{1}{5\mu_1}\frac{\xi+1}{\xi+4}\left[< \mathsf{F}^{(2)} > - \frac{1}{3}\mathbf{1}\mathrm{Tr} < \mathsf{F}^{(2)} >\right]. \tag{3.35}$$

The symmetric traceless part of this equation is

$$((\nabla \boldsymbol{u}_{Os}))^0_L = < (\nabla \boldsymbol{u}_{Os})^0 > - \frac{1}{5\mu_1}\frac{\xi+1}{\xi+4} < (\mathsf{F}^{(2)})^0 > . \tag{3.36}$$

The trace part vanishes identically. We define the local pure strain in mean field approximation as

$$\mathsf{E}_L = (\nabla \boldsymbol{u}_0)^0 + ((\nabla \boldsymbol{u}_C))^0_L + ((\nabla \boldsymbol{u}_{Os}))^0_L. \tag{3.37}$$

Altogether we find from Eqs. (3.31), (3.34), and (3.36)

$$\mathsf{E}_L = (\nabla < \boldsymbol{u} >)^0 - \frac{1}{5\mu_1}\frac{\xi+6}{\xi+4} < (\mathsf{F}^{(2)})^0 > . \tag{3.38}$$

Similarly we define the local pressure in mean field approximation

$$P_L = -\kappa_1 \nabla \cdot \boldsymbol{u}_0 - \kappa_1 \mathrm{Tr}\,(\nabla \boldsymbol{u}_C)_L . \tag{3.39}$$

From Eqs. (3.31) and (3.34) we find

$$P_L = -\kappa_1 \nabla \cdot < \boldsymbol{u} > + \frac{1}{3}\frac{\xi}{\xi+4}\mathrm{Tr} < \mathsf{F}^{(2)} > . \tag{3.40}$$

The last equation is in agreement with Eq. (6.9) of Ref. [25].

Finally we calculate the average force dipole density by replacing the acting field in Eq. (3.26) by the local field in analogy to Eq. (2.15). For the symmetric traceless part this yields

$$< (\mathsf{F}^{(2)})^0 > = -2\phi[\mu]\mu_1 \mathsf{E}_L \tag{3.41}$$

and for the trace part

$$\mathrm{Tr} < \mathsf{F}^{(2)} > = 3\phi[\kappa]\kappa_1 P_L. \tag{3.42}$$

Substituting Eq. (3.38) into Eq. (3.41) and solving for the force density tensor we find

$$< (\mathsf{F}^{(2)})^0 > = -\frac{2[\mu]\phi\mu_1}{1-\frac{2}{5}\frac{\xi+6}{\xi+4}[\mu]\phi}(\nabla < \boldsymbol{u} >)^0. \tag{3.43}$$

Substituting Eq. (3.40) into Eq. (3.42) we find

$$\mathrm{Tr} < \mathsf{F}^{(2)} > = \frac{3[\kappa]\phi\kappa_1}{1-\frac{\xi}{\xi+4}[\kappa]\phi}\nabla\cdot < \boldsymbol{u} > . \tag{3.44}$$

These are the desired constitutive equations in mean field approximation. Substituting in Eq. (3.25) we find the effective shear modulus

$$\mu_{\text{eff}} = \mu_1 + \frac{[\mu]\phi}{1-\frac{2}{5}\frac{\xi+6}{\xi+4}[\mu]\phi}\mu_1 \tag{3.45}$$

and the effective bulk modulus

$$\kappa_{\text{eff}} = \kappa_1 + \frac{[\kappa]\phi}{1-\frac{\xi}{\xi+4}[\kappa]\phi}\kappa_1. \tag{3.46}$$

There is a clear resemblance with the CM formula (2.27) for the effective dielectric constant. In the incompressible limit, where κ_1 and ξ tend to infinity, the expression (3.45) for the effective shear modulus becomes

$$\mu_{\text{eff}} = \mu_1 + \frac{[\mu]\phi}{1-\frac{2}{5}[\mu]\phi}\mu_1 \qquad (\kappa_1 \to \infty), \tag{3.47}$$

which is closely similar to Saitô's expression for the effective shear viscosity of a fluid suspension of hard spheres [26]. Saitô's derivation was based on a local field argument similar to that of Lorentz for dielectric suspensions [25].

For uniform spheres the effective elastic moduli in mean field approximation, as given by Eqs. (3.45) and (3.46), were obtained earlier by Weng [27] on the basis of the Mori–Tanaka method [28]. The method is explained particularly clearly by Benveniste [29] and by Christensen [30]. There is no obvious relation with the concept of the effective local field. An expression for the effective elastic tensor of a system of uniform ellipsoids proposed by Markov [31] reduces to Eqs. (3.45) and (3.46) for the case of spheres. For this case Markov refers to an earlier result by Levin. The mean field expressions (3.45) and (3.46) are closely related to the so-called Hashin–Shtrikman bounds [18]. In this section we investigate the relation.

For a uniform sphere with shear modulus μ_2 and bulk modulus κ_2 the intrinsic shear modulus is given by [22, 23]

$$[\mu] = 5(\xi+4)\frac{\mu_2-\mu_1}{(2\xi+12)\mu_2+(3\xi+8)\mu_1}, \tag{3.48}$$

and the intrinsic bulk modulus is given by [18, 19]

$$[\kappa] = (\xi+4)\frac{\kappa_2-\kappa_1}{\xi\kappa_2+4\kappa_1}. \tag{3.49}$$

Following Walpole [32] the Hashin–Shtrikman upper and lower bounds can be presented in the following form. We introduce

$$\begin{aligned} \mu^{U*} &= \frac{3}{2}\left[\frac{1}{\mu^g}+\frac{10}{9\kappa^g+8\mu^g}\right]^{-1}, \quad & \mu^{L*} &= \frac{3}{2}\left[\frac{1}{\mu^l}+\frac{10}{9\kappa^l+8\kappa^l}\right]^{-1}, \\ \kappa^{U*} &= \frac{4}{3}\mu^g, & \kappa^{L*} &= \frac{4}{3}\mu^l, \end{aligned} \tag{3.50}$$

where

$$\begin{aligned} \mu^g &= \max(\mu_1,\mu_2), \quad \mu^l = \min(\mu_1,\mu_2), \\ \kappa^g &= \max(\kappa_1,\kappa_2), \quad \kappa^l = \min(\kappa_1,\kappa_2). \end{aligned} \tag{3.51}$$

Then the upper (U) and lower (L) bounds on μ_{eff}, κ_{eff} are

$$\mu_{\text{HS}}^{U(L)} = \mu_1+\phi\,(\mu_2-\mu_1)\left[1+\frac{(\mu_2-\mu_1)\,(1-\phi)}{\mu_1+\mu^{U(L)*}}\right]^{-1}, \tag{3.52}$$

$$\kappa_{\text{HS}}^{U(L)} = \kappa_1+\phi\,(\kappa_2-\kappa_1)\left[1+\frac{(\kappa_2-\kappa_1)\,(1-\phi)}{\kappa_1+\kappa^{U(L)*}}\right]^{-1}. \tag{3.53}$$

We consider first the bulk modulus. After some algebra one finds

$$\begin{aligned} \kappa_{\text{eff}} &= \kappa_{\text{HS}}^{L} \quad \text{for} \quad \mu_1<\mu_2, \\ \kappa_{\text{eff}} &= \kappa_{\text{HS}}^{U} \quad \text{for} \quad \mu_1>\mu_2. \end{aligned} \tag{3.54}$$

Thus the mean field approximation coincides with one of the Hashin–Shtrikman bounds. The same situation occurs for the effective dielectric constant. The situation is more complicated for the effective shear modulus. Here we find

$$\begin{aligned} \mu_{\text{eff}} &= \mu_{\text{HS}}^{L} \quad \text{for} \quad \mu_1<\mu_2, \quad \kappa_1<\kappa_2, \\ \mu_{\text{eff}} &= \mu_{\text{HS}}^{U} \quad \text{for} \quad \mu_1>\mu_2, \quad \kappa_1>\kappa_2. \end{aligned} \tag{3.55}$$

However, in mixed cases, where $\mu_1 < \mu_2$, $\kappa_1 > \kappa_2$, or $\mu_1 > \mu_2$, $\kappa_1 < \kappa_2$, the mean field approximation lies between the two Hashin–Shtrikman bounds.

For the special case $\mu_1 = \mu_2$ the upper and lower Hashin–Shtrikman bounds for the bulk modulus coincide, so that for that case the bounds give the exact value. It may be cast in the form

$$\frac{1}{3\kappa_{\text{eff}} + 4\mu} = \frac{1-\phi}{3\kappa_1 + 4\mu} + \frac{\phi}{3\kappa_2 + 4\mu}, \tag{3.56}$$

where $\mu = \mu_1 = \mu_2$. This remarkable result was first proven in greater generality by Hill [33].

Chapter 4

Microscopic theory of Kirkwood and Yvon

In order to improve on the simple approximations discussed above, one needs a more detailed microscopic theory.

We follow the historical development and consider as prime example a system of spheres in electrostatics. The spheres are assumed to be in vacuum, each with a polarizable point dipole of polarizability α_1 at its center.

We consider a definite configuration $\mathbf{X} = (\boldsymbol{R}_1, \ldots, \boldsymbol{R}_N)$. Then the dipole moment induced in the sphere centered at $\boldsymbol{R}_j$ is

$$\boldsymbol{p}_j = \alpha_1 \boldsymbol{E}'_j, \tag{4.1}$$

where $\boldsymbol{E}'_j$ is the field acting on sphere j. In a uniform external field $\boldsymbol{E}_0$

$$\boldsymbol{E}'_j = \boldsymbol{E}_0 + \sum_{k \neq j} \boldsymbol{T}_{jk} \cdot \boldsymbol{p}_k \tag{4.2}$$

with dipole tensor

$$\boldsymbol{T}_{jk} = \boldsymbol{T}(\boldsymbol{R}_j - \boldsymbol{R}_k), \qquad \boldsymbol{T}(\boldsymbol{r}) = \frac{-\mathbf{1} + 3\hat{\boldsymbol{r}}\hat{\boldsymbol{r}}}{r^3}. \tag{4.3}$$

One therefore obtains $3N$ coupled equations

$$\boldsymbol{p}_j = \alpha_1 \left[\boldsymbol{E}_0 + \sum_{k \neq j} \boldsymbol{T}_{jk} \cdot \boldsymbol{p}_k \right] \qquad j = 1, \ldots, N. \tag{4.4}$$

One solves these conveniently by introducing $3N$-dimensional vectors

$$\mathbf{p} = (\boldsymbol{p}_1, \ldots, \boldsymbol{p}_N) \qquad \mathbf{E}_0 = (\boldsymbol{E}_0, \ldots, \boldsymbol{E}_0). \tag{4.5}$$

Then in abbreviated form the equations read

$$\mathbf{p} = \alpha_1 \left[\mathbf{E}_0 + a^{-3}\mathbf{T} \cdot \mathbf{p}\right], \tag{4.6}$$

where the $3N \times 3N$-matrix $\mathbf{T}$ has dimensionless elements

$$T_{j\alpha,k\beta} = a^3 T_{jk,\alpha\beta} \tag{4.7}$$

($= 0$ for $j = k$). The formal solution of the above equation is

$$\mathbf{p} = a^3(z\mathbf{I} - \mathbf{T})^{-1} \cdot \mathbf{E}_0 \quad \text{with } z = a^3/\alpha_1. \tag{4.8}$$

We introduce three vectors $\boldsymbol{\lambda}$, so that $\boldsymbol{\lambda} = (\boldsymbol{e}_\lambda, \ldots, \boldsymbol{e}_\lambda)$, $\lambda = x, y, z$, where $\boldsymbol{e}_\lambda$ are the three Cartesian unit vectors. The total induced dipole moment $\boldsymbol{M} = \sum_{j=1}^{N} \boldsymbol{p}_j$ can be written as

$$\boldsymbol{M} = \sum_{\lambda} (\boldsymbol{\lambda} \cdot \mathbf{p}) \boldsymbol{e}_\lambda. \tag{4.9}$$

It is given by

$$\boldsymbol{M} = a^3 \boldsymbol{A}(\mathbf{X}) \cdot \boldsymbol{E}_0 \tag{4.10}$$

with the microscopic polarizability tensor $\boldsymbol{A}(\mathbf{X})$ with components

$$A^{\lambda\mu}(\mathbf{X}) = \boldsymbol{\lambda} \cdot (z\mathbf{I} - \mathbf{T})^{-1} \cdot \boldsymbol{\mu}. \tag{4.11}$$

We compare this result with macroscopic Maxwell theory.

We assume that the spheres are distributed approximately uniformly over a large sphere of radius R_0, volume $\Omega = \frac{4\pi}{3} R_0^3$. The average number density is therefore $n = N/\Omega$. According to the Maxwell theory the total induced dipole moment is

$$\overline{\boldsymbol{M}}_S = \frac{\varepsilon - 1}{\varepsilon + 2} R_0^3 \boldsymbol{E}_0, \tag{4.12}$$

where the prefactor is the polarizability of the macroscopic sphere in vacuum.

We define

$$A_S(\mathbf{X}) = \frac{1}{3} \operatorname{Tr} A(\mathbf{X}) \tag{4.13}$$

with the condition that the positions are distributed over the sphere R_0 as described above. We now identify $\overline{\boldsymbol{M}}_S$ with the ensemble average

$$< \boldsymbol{M}(\mathbf{X}) > = \int \boldsymbol{M}(\mathbf{X}) W(\mathbf{X}) d\mathbf{X} \tag{4.14}$$

over a probability distribution $W(\mathbf{X})$ that is assumed known. This yields

$$< \boldsymbol{M} > = a^3 < \boldsymbol{A}(\mathbf{X}) > \cdot \boldsymbol{E}_0. \tag{4.15}$$

By comparison with $< \overline{\boldsymbol{M}}_S >$ we obtain

$$\frac{\varepsilon - 1}{\varepsilon + 2} = \lim_{\substack{N\to\infty \\ \Omega\to\infty}} \frac{4\pi a^3}{3\Omega} < A_S(\mathbf{X}) >_N . \tag{4.16}$$

We now expand $A^{\lambda\mu}(\mathbf{X})$ in inverse powers of z up to z^{-3}

$$\begin{aligned} A^{\lambda\mu}(\mathbf{X}) &= \frac{1}{z}\boldsymbol{\lambda} \cdot \left(\mathbf{I} - z^{-1}\mathbf{T}\right)^{-1} \cdot \boldsymbol{\mu} \\ &= \frac{1}{z}\boldsymbol{\lambda} \cdot \left[\mathbf{I} + z^{-1}\mathbf{T} + z^{-2}\mathbf{T}^2\right] \cdot \boldsymbol{\mu} + O(z^{-4}) \\ &= \frac{N}{z}\delta_{\lambda\mu} + z^{-2}\boldsymbol{\lambda} \cdot \mathbf{T} \cdot \boldsymbol{\mu} + z^{-3}\boldsymbol{\lambda} \cdot \mathbf{T}^2 \cdot \boldsymbol{\mu} + O(z^{-4}), \end{aligned} \tag{4.17}$$

so that

$$A_S(\mathbf{X}) = \frac{N}{z} + \frac{1}{3z^2}\sum_{\lambda} \boldsymbol{\lambda} \cdot \mathbf{T} \cdot \boldsymbol{\lambda} + \frac{1}{3z^3}\sum_{\lambda} \boldsymbol{\lambda} \cdot \mathbf{T}^2 \cdot \boldsymbol{\lambda} + O(z^{-4}) \tag{4.18}$$

and

$$< A_S(\mathbf{X}) >_N = \frac{N}{z} + \frac{1}{3z^2}\sum_{\lambda} \boldsymbol{\lambda} \cdot < \mathbf{T} >_N \cdot \boldsymbol{\lambda} + \frac{1}{3z^3}\sum_{\lambda} \boldsymbol{\lambda} \cdot < \mathbf{T}^2 >_N \cdot \boldsymbol{\lambda} + O(z^{-4}). \tag{4.19}$$

The correction to the Clausius–Mossotti formula is written as

$$\frac{\epsilon - 1}{\epsilon + 2} = \frac{4\pi}{3} n\alpha_1 [1 + S]. \tag{4.20}$$

Up to order α_1^2 we find

$$S = \lim_{\substack{N\to\infty \\ \Omega\to\infty}} \frac{1}{3N}\left[z^{-1}\sum_{\lambda} \boldsymbol{\lambda} \cdot < \mathbf{T} >_N \cdot \boldsymbol{\lambda} + z^{-2}\sum_{\lambda} \boldsymbol{\lambda} \cdot < \mathbf{T}^2 >_N \cdot \boldsymbol{\lambda} + O(z^{-3})\right]. \tag{4.21}$$

The first term vanishes for a large sphere:

$$\boldsymbol{\lambda} \cdot < \mathbf{T} >_N \cdot \boldsymbol{\lambda} = 0. \tag{4.22}$$

One has

$$\begin{aligned} a^{-3}\boldsymbol{\lambda} \cdot < \mathbf{T} >_N \cdot \boldsymbol{\lambda} &= \sum_{j\neq k} \boldsymbol{e}_\lambda \cdot < \boldsymbol{T}_{jk} >_N \ \boldsymbol{e}_\lambda \\ &= N(N-1)\boldsymbol{e}_\lambda \cdot < \boldsymbol{T}_{jk} > \cdot \boldsymbol{e}_\lambda \approx N^2 \boldsymbol{e}_\lambda \cdot < \boldsymbol{T}_{12} > \cdot \boldsymbol{e}_\lambda. \end{aligned} \tag{4.23}$$

Now one can write

$$\boldsymbol{e}_\lambda \cdot < \boldsymbol{T}_{12} > \cdot \boldsymbol{e}_\lambda = \frac{1}{\Omega^2} \iint\limits_{\text{Sphere}} \boldsymbol{e}_\lambda \cdot \boldsymbol{T}(\boldsymbol{R}_1 - \boldsymbol{R}_2) \cdot \boldsymbol{e}_\lambda \, g(R_{12}) d\boldsymbol{R}_1 \, d\boldsymbol{R}_2, \quad (4.24)$$

where $g(R)$ is the radial distribution function. Therefore

$$a^{-3}\boldsymbol{\lambda} \cdot < \mathbf{T} >_N \cdot \boldsymbol{\lambda} = n^2 \iint\limits_{\text{Sphere}} \boldsymbol{e}_\lambda \cdot \boldsymbol{T}(\boldsymbol{R}_1 - \boldsymbol{R}_2) \cdot \boldsymbol{e}_\lambda \, g(R_{12}) d\boldsymbol{R}_1 \, d\boldsymbol{R}_2. \quad (4.25)$$

The function $g(R)$ vanishes for $R < 2a$. We write the integral as

$$\int\limits_{\Omega} d\boldsymbol{R}_1 \int\limits_{\Omega - v_1} d\boldsymbol{R}_2 \, \boldsymbol{e}_\lambda \cdot \boldsymbol{T}(\boldsymbol{R}_1 - \boldsymbol{R}_2) \cdot \boldsymbol{e}_\lambda \, g(R_{12}) \quad (4.26)$$

where v_1 represents a sphere of volume $\frac{32\pi}{3}a^3$ about the point $\boldsymbol{R}_1$ (see Fig. 4.1). The integral is transformed to

$$\begin{aligned} &\int\limits_{\Omega} d\boldsymbol{R}_1 \int\limits_{\Omega - v_1} d\boldsymbol{R}_2 \, \boldsymbol{e}_\lambda \cdot \boldsymbol{T}(\boldsymbol{R}_1 - \boldsymbol{R}_2) \cdot \boldsymbol{e}_\lambda [1 + g(R_{12}) - 1] \\ &\qquad = \int\limits_{\Omega} d\boldsymbol{R}_1 \int\limits_{\Omega - v_1} d\boldsymbol{R}_2 \, \boldsymbol{e}_\lambda \cdot \boldsymbol{T}(\boldsymbol{R}_1 - \boldsymbol{R}_2) \cdot \boldsymbol{e}_\lambda \\ &\qquad + \int\limits_{\Omega} d\boldsymbol{R}_1 \int\limits_{\infty - v_1} d\boldsymbol{R}_2 \, \boldsymbol{e}_\lambda \cdot \boldsymbol{T}(\boldsymbol{R}_1 - \boldsymbol{R}_2) \cdot \boldsymbol{e}_\lambda [g(R_{12}) - 1]. \end{aligned} \quad (4.27)$$

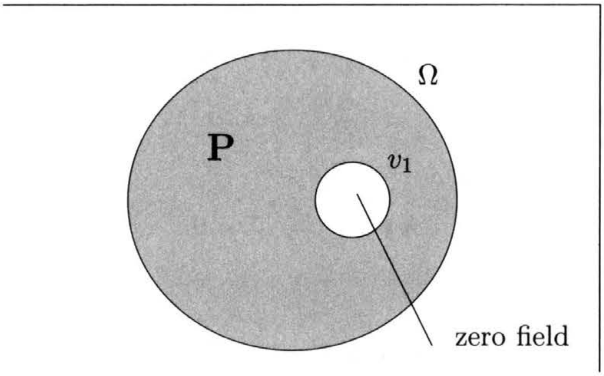

FIGURE 4.1. Geometry in the derivation of Kirkwood and Yvon.

In the second integral one has $\int_{\infty - v_1} d\boldsymbol{R}_2\, \boldsymbol{T}(\boldsymbol{R}_1 - \boldsymbol{R}_2)[g(R_{12}) - 1] = 0$ since $\int \boldsymbol{T}(\boldsymbol{r}) d\Omega = 0$ (here the integral is over all space outside the small sphere with volume v_1). In the first integral this argument cannot be used, because

$$\int_{\Omega - v_1} d\boldsymbol{R}_2\, \boldsymbol{T}(\boldsymbol{R}_1 - \boldsymbol{R}_2) \cdot \boldsymbol{e}_\lambda \tag{4.28}$$

does not converge absolutely, i.e. the result depends on the shape of the volume of integration Ω in the limit $\Omega \to \infty$. But we know from the Lorentz argument that the integral vanishes for a sphere.

We find therefore

$$S = S_2 + O(z^{-3}) \tag{4.29}$$

with

$$S_2 = \lim_{\substack{N\to\infty \\ \Omega\to\infty}} \frac{1}{3N} z^{-2} \sum_\lambda \boldsymbol{\lambda} \cdot < \mathbf{T}^2 >_N \cdot \boldsymbol{\lambda}. \tag{4.30}$$

One has

$$\begin{aligned} \sum_\lambda \boldsymbol{\lambda} \cdot < \mathbf{T}^2 >_N \cdot \boldsymbol{\lambda} &= a^6 \sum_\lambda \sum_{j=1}^{N} \sum_{k\neq j} \sum_{\neq k} \boldsymbol{e}_\lambda \cdot < \boldsymbol{T}_{jk} \cdot \boldsymbol{T}_{kl} > \cdot \boldsymbol{e}_\lambda \\ &= a^6 \operatorname{Tr} \sum_{j=1}^{N} \sum_{k\neq j} \sum_{l\neq k} < \boldsymbol{T}_{jk} \cdot \boldsymbol{T}_{kl} > = N(N-1) a^6 \operatorname{Tr} < \boldsymbol{T}_{12} \cdot \boldsymbol{T}_{21} > \\ &\quad + N(N-1)(N-2) a^6 \operatorname{Tr} < \boldsymbol{T}_{12} \cdot \boldsymbol{T}_{23} > . \end{aligned} \tag{4.31}$$

The first average is given by

$$\begin{aligned} < \boldsymbol{T}_{12} \cdot \boldsymbol{T}_{21} > &= \frac{1}{N(N-1)} \int_\Omega d\boldsymbol{R}_1 d\boldsymbol{R}_2\, n(1,2) \boldsymbol{T}_{12} \cdot \boldsymbol{T}_{21} \\ &\approx \frac{1}{\Omega} \int d\boldsymbol{R}\, g(R) \boldsymbol{T}(\boldsymbol{R}) \cdot \boldsymbol{T}(\boldsymbol{R}), \end{aligned} \tag{4.32}$$

where we have used $n(1,2) \approx n^2 g(R_{12})$ in the thermodynamic limit. The integral converges since $g(R) \to 1$, $\boldsymbol{T}(\boldsymbol{R}) \cdot \boldsymbol{T}(\boldsymbol{R}) \sim 1/R^6$.

In the second average one finds in the same way

$$\begin{aligned} < \boldsymbol{T}_{12} \cdot \boldsymbol{T}_{23} > &= \frac{1}{N(N-1)(N-2)} \int_{\text{Sphere}} d\boldsymbol{R}_1\, d\boldsymbol{R}_2\, d\boldsymbol{R}_3\, n(1,2,3) \boldsymbol{T}_{12} \cdot \boldsymbol{T}_{23} \\ &\approx \frac{1}{\Omega^3} \int_{\text{Sphere}} d\boldsymbol{R}_1\, d\boldsymbol{R}_2\, d\boldsymbol{R}_3\, g_3(1,2,3) \boldsymbol{T}_{12} \cdot \boldsymbol{T}_{23}. \end{aligned} \tag{4.33}$$

We change the last integral into an absolutely convergent one by subtracting a term that vanishes when integrated over a sphere

$$<\boldsymbol{T}_{12}\cdot\boldsymbol{T}_{23}>=\frac{1}{\Omega^3}\int_\Omega d\boldsymbol{R}_1\,d\boldsymbol{R}_2\,d\boldsymbol{R}_3\,[g_3(1,2,3)-g(1,2)g(2,3)]\boldsymbol{T}_{12}\cdot\boldsymbol{T}_{23}. \tag{4.34}$$

This integral is now absolutely convergent, and we need not specify that the large volume of integration is spherical. In total we obtain

$$S_2=\frac{1}{3}\,\alpha_1^2\left[n\int d\boldsymbol{R}\,g(R)\,\mathrm{Tr}\,\boldsymbol{T}(\boldsymbol{R})\cdot\boldsymbol{T}(\boldsymbol{R})\right.$$
$$\left.+\,n^2\int d\boldsymbol{R}_{12}\,d\boldsymbol{R}_{23}\,[g_3(1,2,3)-g(1,2)g(2,3)]\,\mathrm{Tr}\,\boldsymbol{T}(\boldsymbol{R}_{12})\cdot\boldsymbol{T}(\boldsymbol{R}_{23})\right] \tag{4.35}$$

with

$$\boldsymbol{R}_{12}=\boldsymbol{R}_2-\boldsymbol{R}_1,\qquad \boldsymbol{R}_{23}=\boldsymbol{R}_3-\boldsymbol{R}_2. \tag{4.36}$$

In diagrammatic representation we have

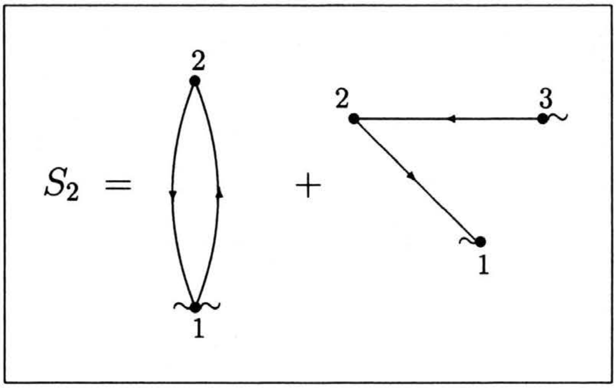

FIGURE 4.2. Diagrammatic representation of S_2.

The expression for S_2 is the famous result of Kirkwood [34] and Yvon [35].

Computer simulations [36] show that S_2 is a good approximation to the complete correction to the Clausius–Mossotti formula for values $0<\alpha_1<a^3$.

The integrands of both Kirkwood–Yvon integrals have relatively short range. The transport coefficient ε is local, i.e. its value is determined by properties in the immediate neighborhood of the field point considered.

The three-particle correlation function $g_3(1,2,3)$ is known only poorly. Often one uses Kirkwood's superposition-approximation

$$g(1,2,3) \approx g(1,2)g(2,3)g(3,1) \qquad \text{(SA)}. \tag{4.37}$$

This is sufficient up to volume fraction $\phi \approx 0.3$. For higher densities an approximation proposed by Blawzdziewicz, Cichocki and Szamel [37] yields satisfying results.

The coefficient S_2 can be found precisely from computer simulation, so that the results constitute a test for the quality of the function. The radial function $g(R)$ is quite well known for a system of hard spheres (Percus–Yevick approximation with Verlet–Weis correction).

In superposition approximation the second KY-integral can be calculated conveniently by Fourier transformation [38].

The result for S_2 can be simplified to

$$\begin{aligned} S_2 = \alpha_1^2 \Bigg[8\pi n \int_0^\infty \frac{g(R)}{R^4}\, dR + 2n^2 \int \big[g_3(\boldsymbol{R}_{12}, \boldsymbol{R}_{23}) - g(R_{12})g(R_{23}) \big] \\ \cdot \frac{1}{R_{12}^3 R_{23}^3}\, P_2(\hat{R}_{12} \cdot \hat{R}_{23})\, d\boldsymbol{R}_{12}\, d\boldsymbol{R}_{23} \Bigg]. \end{aligned} \tag{4.38}$$

In the first integral we have used

$$\operatorname{Tr} \boldsymbol{T}(\boldsymbol{R}) \cdot \boldsymbol{T}(\boldsymbol{R}) = \frac{-\mathbf{1} + 3\hat{\boldsymbol{R}}\hat{\boldsymbol{R}}}{R^3} \cdot \frac{-\mathbf{1} + 3\hat{\boldsymbol{R}}\hat{\boldsymbol{R}}}{R^3} = \operatorname{Tr} \frac{\mathbf{1} + 3\hat{\boldsymbol{R}}\hat{\boldsymbol{R}}}{R^6} = \frac{6}{R^6}. \tag{4.39}$$

In the second integral

$$\begin{aligned} &\operatorname{Tr} \frac{-\mathbf{1} + 3\hat{\boldsymbol{R}}_{12}\hat{\boldsymbol{R}}_{12}}{R_{12}^3} \cdot \frac{-\mathbf{1} + 3\hat{\boldsymbol{R}}_{23}\hat{\boldsymbol{R}}_{23}}{R_{23}^3} \\ &\quad = \frac{1}{R_{12}^3 R_{23}^3} \operatorname{Tr} \Big[\mathbf{1} - 3\hat{\boldsymbol{R}}_{12}\hat{\boldsymbol{R}}_{12} - 3\hat{\boldsymbol{R}}_{23}\hat{\boldsymbol{R}}_{23} + 9\hat{\boldsymbol{R}}_{12}\hat{\boldsymbol{R}}_{23}(\hat{\boldsymbol{R}}_{12} \cdot \hat{\boldsymbol{R}}_{23}) \Big] \\ &\quad = \frac{1}{R_{12}^3 R_{23}^3} \Big[-3 + 9(\hat{\boldsymbol{R}}_{12} \cdot \hat{\boldsymbol{R}}_{23})^2 \Big] = \frac{6}{R_{12}^3 R_{23}^3} P_2(\hat{\boldsymbol{R}}_{12} \cdot \hat{\boldsymbol{R}}_{23}). \end{aligned} \tag{4.40}$$

We write

$$S_2 = s_2\, z^{-2} = s_2 \frac{\alpha_1^2}{a^6}, \qquad z = a^3/\alpha_1. \tag{4.41}$$

The numerical values obtained from computer simulation for hard spheres are presented in Table 4.1. This shows that for a system of spheres the corrections

TABLE 4.1.

ϕ	0.1	0.2	0.3	0.4	0.5
s_2	0.0192	0.0276	0.0282	0.0235	0.0190

to the Clausius–Mossotti formula are quite small. On the other hand the index of refraction $n = \sqrt{\epsilon}$ can be measured very accurately.

We consider also the microscopic expression for the total energy. This consists of three contributions

$$U = U_{\text{field}} + U_{\text{Coulomb}} + U_{\text{Pol}}. \tag{4.42}$$

The energy of the dipoles in the external field is given by

$$U_{\text{field}} = -\sum_{j=1}^{N} \boldsymbol{p}_j \cdot \boldsymbol{E}_0 = -\mathsf{p} \cdot \mathsf{E}_0. \tag{4.43}$$

The Coulomb interaction energy of the dipoles is given by

$$U_{\text{Coulomb}} = -\frac{1}{2} \sum_{j \neq k} \boldsymbol{p}_j \cdot \boldsymbol{T}_{jk} \cdot \boldsymbol{p}_k = -\frac{1}{2a^3} \mathsf{p} \cdot \mathsf{T} \cdot \mathsf{p}. \tag{4.44}$$

The polarization energy is given by

$$U_{\text{Pol}} = \frac{1}{2} \sum_{j=1}^{N} \frac{\boldsymbol{p}_j^2}{\alpha_1} = \frac{1}{2\alpha_1} \mathsf{p} \cdot \mathsf{p}. \tag{4.45}$$

The sum of the last two contributions is just

$$U_{\text{Coulomb}} + U_{\text{Pol}} = \frac{1}{2a^3} \mathsf{p} \cdot (z\mathsf{I} - \mathsf{T}) \cdot \mathsf{p} = \frac{a^3}{2} \mathsf{E}_0 \cdot (z\mathsf{I} - \mathsf{T})^{-1} \cdot \mathsf{E}_0 = \frac{1}{2} \mathsf{p} \cdot \mathsf{E}_0. \tag{4.46}$$

The total energy is therefore

$$U = -\frac{1}{2} \mathsf{p} \cdot \mathsf{E}_0 = -\frac{a^3}{2} \mathsf{E}_0 \cdot (z\mathsf{I} - \mathsf{T})^{-1} \cdot \mathsf{E}_0. \tag{4.47}$$

This expression can be written as

$$U = -\frac{a^3}{2} \sum_{\lambda\mu} E_{0\lambda} A^{\lambda\mu}(\mathsf{X}) E_{0\mu} = -\frac{1}{2} a^3 \boldsymbol{E}_0 \cdot \boldsymbol{A}(\mathsf{X}) \cdot \boldsymbol{E}_0 = -\frac{1}{2} \boldsymbol{M}(\mathsf{X}) \cdot \boldsymbol{E}_0. \tag{4.48}$$

We shall return to these expressions later.

To conclude this chapter we note a simple scaling property. For a system with positions $\{\sigma \boldsymbol{R}_j\}$, sphere radius σa and polarizability $\sigma^3\alpha_1$ the microscopic polarizability tensor has the property

$$\boldsymbol{A}(\sigma \mathsf{X}, \sigma a, \sigma^3\alpha_1) = \boldsymbol{A}(\mathsf{X}, a, \alpha_1), \tag{4.49}$$

and therefore in the external field $\boldsymbol{E}_0$

$$U(\sigma \mathsf{X}, \sigma a, \alpha^3\alpha_1) = \sigma^3\, U(\mathsf{X}, a, \alpha_1). \tag{4.50}$$

The effective dielectric constant ε is independent of the scaling factor σ.

Chapter 5

Multiple scattering

The formal solution for the system of coupled dipoles in the Kirkwood–Yvon theory is closely related to the theory of multiple scattering. In this Chapter we derive the so-called multiple scattering expansion.

We consider a stationary wave equation for wave propagation in a system with many scattering centers. For simplicity we consider a scalar field $\psi(\boldsymbol{r})$. The stationary wave equation reads

$$\nabla^2\psi + k^2\psi - \sum_{j=1}^{N} V(j)\psi = 0. \tag{5.1}$$

In case this equation originates in a Schrödinger equation for a particle with mass m, one has $k^2 = \frac{2m}{\hbar^2}\,E$. Then $\psi(\boldsymbol{r})$ is the corresponding wavefunction for sound waves $k^2 = \omega^2/s^2$, with frequency ω and sound velocity s. The potential $V(j)$ describes the effect of the scattering center j. The potential $V(j) = V(\boldsymbol{r} - \boldsymbol{R}_j)$ is assumed to vanish for $|\boldsymbol{r} - \boldsymbol{R}_j| > a$.

We consider first scattering by a particle centered at the origin. The wave equation then reads

$$\nabla^2\psi + k^2\psi - V(1)\psi = 0. \tag{5.2}$$

We consider an incident wave $\psi_0(\boldsymbol{r})$ that is a solution of the homogeneous equation

$$\nabla^2\psi_0 + k^2\psi_0 = 0. \tag{5.3}$$

We wish to describe the effect of the potential on the wave. In scattering theory one usually considers an incident plane wave $\psi_0 = \exp(ikz)$ and then analyzes the outgoing spherical waves. For our purpose it is useful to consider instead the inhomogeneous equation

$$\nabla^2\psi + k^2\psi - V(1)\psi = s \tag{5.4}$$

and correspondingly

$$\nabla^2\psi_0 + k^2\psi_0 = s \tag{5.5}$$

with a source $s(\boldsymbol{r})$. The plane wave $\psi_0(\boldsymbol{r}) = \exp(ikz)$ may be regarded as a special case generated by a source at infinity.

This consideration allows a reformulation in integral form. Without perturbation $V(1)$ the wave generated by $s(\boldsymbol{r})$ is

$$\psi_0(\boldsymbol{r}) = \int G_0(\boldsymbol{r}-\boldsymbol{r}')s(\boldsymbol{r}')d\boldsymbol{r}' \tag{5.6}$$

with the Green function

$$G_0(\boldsymbol{r}) = -\frac{1}{4\pi}\frac{e^{ikr}}{r}. \tag{5.7}$$

With time-factor $\exp(-i\omega t)$ the choice of sign in the exponent corresponds to an outgoing spherical wave centered at each point of the source. Abbreviated

$$\psi_0 = G_0\, s \tag{5.8}$$

with linear operator G_0.

The formal solution of the equation with perturbation $V(1)$ is given by

$$\psi = G_0[s + V(1)\psi] \tag{5.9}$$

or

$$\psi = \psi_0 + G_0\, V(1)\psi. \tag{5.10}$$

By iteration one obtains

$$\psi = \psi_0 + G_0\, T(1)\psi_0 \tag{5.11}$$

with the T-operator

$$T(1) = V(1) + V(1)G_0\, V(1) + \cdots = V(1)[I - G_0\, V(1)]^{-1}. \tag{5.12}$$

The complete solution can be summarized as

$$\psi = G\, s, \tag{5.13}$$

with the Green function

$$G = G_0 + G_0 T(1) G_0. \tag{5.14}$$

By substitution of $T(1)$ one sees that

$$G = G_0 + G_0 V(1) G. \tag{5.15}$$

This is called the Dyson equation.

The equation defining $T(1)$ implies

$$T(1)\psi_0 = V(1)\psi. \tag{5.16}$$

From the solution ψ for arbitrary s one reads off the operator $T(1)$. The sum

$$T(1) = V(1) + V(1) G_0 V(1) + \cdots \tag{5.17}$$

sum corresponds to a perturbation expansion, but note that the construction of the T-operator does not rely on the expansion.

The above equations can be generalized to many scattering centers. Let the solution of the equation

$$\nabla^2\psi + k^2\psi - \sum_{j=1}^{N} V(j)\psi = s \tag{5.18}$$

be $\psi(1,\ldots,N)$. The N-particle T-operator $T(1,\ldots,N)$ is defined by

$$T(1,\ldots,N)\psi_0 = V\psi(1,\ldots,N) \tag{5.19}$$

with $V = \sum_{j=1}^{N} V(j)$. As above one obtains the formal expression

$$T(1,\ldots,N) = V[I - G_0 V]^{-1}. \tag{5.20}$$

Hence one can derive a perturbation expansion, but it is preferable to express $T(1,\ldots,N)$ as a sum of scattering events from the individual scattering centers. For clarity we write the one-particle T-operator for particle j as $M(j) \equiv T(j)$. We define two $N \times N$ operator-matrices. The scattering from the individual particles is expressed by the matrix

$$\mathcal{M} = \begin{pmatrix} M(1) & 0 & 0 & \cdots & 0 \\ 0 & M(2) & 0 & \cdots & 0 \\ 0 & 0 & M(3) & \cdots & 0 \\ \vdots & \vdots & \vdots & \ddots & \vdots \\ 0 & 0 & 0 & \cdots & M(N) \end{pmatrix}. \tag{5.21}$$

The propagation of the wave between particles is expressed by the matrix

$$\mathcal{G}_0 = \begin{pmatrix} 0 & G_0 & G_0 & \cdots & G_0 \\ G_0 & 0 & G_0 & \cdots & G_0 \\ G_0 & G_0 & 0 & \cdots & G_0 \\ \vdots & \vdots & \vdots & \ddots & \vdots \\ G_0 & G_0 & G_0 & \cdots & 0 \end{pmatrix}. \tag{5.22}$$

The sum of all scattering sequences is now given by

$$T(1,\ldots,N) = \sum_{jk} T_{jk}(1,\ldots,N) \tag{5.23}$$

with

$$T_{jk}(1,\ldots,N) = \left[\mathcal{M}(\mathsf{I} - \mathcal{G}_0\mathcal{M})^{-1}\right]_{jk}. \tag{5.24}$$

This equation can be read as a resummation of perturbation series for the individual particles.

More explicitly the T-operator is given by the multiple scattering expansion

$$\begin{aligned} T(1,\ldots,N) = \sum_{j=1}^{N} M(j) + \sum_{j=1}^{N}\sum_{k\neq j}^{N} M(j)G_0\,M(k) \\ + \sum_{l=2}^{\infty}\sum_{[j]}^{\prime} M(j_1)\left[\Pi_{i=2}^{l}\,G_0\,M(j_i)\right] G_0\,M(j_{l+1}). \end{aligned} \tag{5.25}$$

The last sum runs over all sequences $[j]$ of $l+1$ particle labels, with the condition that no two subsequent labels are the same.

The matrix expression for $T_{jk}(1,\ldots,N)$ can be compared with the formal solution

$$\mathsf{p} = a^3(z\mathsf{I} - \mathbf{T})^{-1}\cdot \mathsf{E}_0 \tag{5.26}$$

from the Kirkwood–Yvon theory.

In the next Chapter we consider average equations for a disordered system of many scattering centers.

Chapter 6

Averaging the multiple scattering expansion over configurations

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We consider again the equation

$$\nabla^2\psi + k^2\,\psi - \sum_{j=1}^{N} V(j)\psi = s. \tag{6.1}$$

We assume that the n scattering centers are distributed approximately uniformly in a volume Ω. The probability distribution $W(\mathsf{X})$ of configurations $\mathsf{X} = (\boldsymbol{R}_1, \ldots, \boldsymbol{R}_N)$ is assumed to be known. The source term $s(\boldsymbol{r})$ is independent of the configuration X.

The potential

$$V = \sum_{j=1}^{N} V(j) \tag{6.2}$$

causes multiple scattering.

We are interested in the average wave

$$< \psi(\boldsymbol{r}) > = \int \psi(\mathsf{X}, \boldsymbol{r}) W(\mathsf{X})\, d\mathsf{X}. \tag{6.3}$$

We know from the macroscopic phenomenological description that the influence of the medium can be described by an index of refraction (equivalently: optical potential, self-energy).

The average wave $< \psi(\boldsymbol{r}) >$ is called the *coherent wave*, since it is the result of constructive interference of many single scattering processes.

The coherent wave satisfies the average equation

$$\nabla^2 < \psi > + k^2 < \psi > - < V\psi > = s. \tag{6.4}$$

The relation between $< V\psi >$ and $< \psi >$ is linear. Hence one can write

$$< V\psi > = X < \psi > \tag{6.5}$$

with the linear operator $X \equiv X(\boldsymbol{r}, \boldsymbol{r}')$. It is the task of theory to show that $X(\boldsymbol{r}, \boldsymbol{r}')$ is an integral kernel of relatively short range. If that is true, the above equation yields a local relation, the so-called *constitutive equation.*

We know from the theory of multiple scattering

$$\psi(1, \ldots, N) = \psi_0 + G_0 T(1, \ldots, N)\psi_0 \tag{6.6}$$

where

$$T(1, \ldots, N)\psi_0 = V\,\psi(1, \ldots, N). \tag{6.7}$$

The average of these equations yields

$$< \psi > = \psi_0 + G_0 < T > \psi_0 \tag{6.8}$$

and

$$< T > \psi_0 = < V\psi > . \tag{6.9}$$

Elimination of ψ_0 yields

$$< V\psi > = < T > [1 + G_0 < T >]^{-1} < \psi > . \tag{6.10}$$

The operator X is therefore given by

$$X = < T > [1 + G_0 < T >]^{-1} . \tag{6.11}$$

Regarded as integral kernel $< T > (\boldsymbol{r}, \boldsymbol{r}')$ the average T-operator differs from zero even for points $\boldsymbol{r}$ and $\boldsymbol{r}'$ at large relative distance. The only requirement is that each point is located in a scatterer. On the contrary, one expects that the integral kernel $X(\boldsymbol{r}, \boldsymbol{r}')$ has relatively short range.

In $< T > (\boldsymbol{r}, \boldsymbol{r}')$ the points $\boldsymbol{r}$ and $\boldsymbol{r}'$ possibly are connected only by a single Green function G_0. Such loose connections are cancelled by the denominator $[1 + G_0 < T >]^{-1}$.

How this happens can be understood by a multiple scattering analysis. We write the equation

$$< V(\psi) > = < T > \psi_0 \tag{6.12}$$

as

$$< V\psi > = < T > \psi_0 = \int d1\; n(1)B(1)\psi_0 + \int d1\, d2\; n(1)n(2)A(1,2)\psi_0. \tag{6.13}$$

Here $n(1)$ is the one-particle density

$$n(1) = N \int d2 \cdots dN\, W(\mathsf{X}). \tag{6.14}$$

Clearly

$$\int d1\; n(1) = N. \tag{6.15}$$

The operator $B(1)$ is called the *bridge operator*. It describes all scattering sequences beginning and ending with the same scatterer.The operator $A(1,2)$ describes all scattering sequences beginning and ending with a different scatterer. It is natural to decompose this operator as

$$A(1,2) = B(1)H(1,2)B(2) \tag{6.16}$$

The operator $H(1,2)$ is called the *pair connector*. We further decompose this operator via an equation of Ornstein–Zernike type

$$H(1,2) = C(1,2) + \int d3\; n(3)C(1,3)B(3)H(3,2). \tag{6.17}$$

The operator $C(1,2)$ is the so-called *direct connector*. One of the contributions to $C(1,2)$ is given by direct propagation from 2 to 1 via the Green function G_0. We subtract this contribution and define the *short-range connector* $S(1,2)$ by

$$C(1,2) = G_0 + S(1,2). \tag{6.18}$$

Finally we define a corresponding *pair connector* $F(1,2)$ via the Ornstein–Zernike equation

$$F(1,2) = S(1,2) + \int d3\; n(3)S(1,3)B(3)F(3,2). \tag{6.19}$$

The operator $< T >$ can be written as

$$< T > = X[1 - G_0 X]^{-1}. \tag{6.20}$$

From the above chain of equations it follows that

$$X = \int d1\; n(1)B(1) + \int d1\, d2\; n(1)n(2)B(1)F(1,2)B(2). \tag{6.21}$$

It is clear from the construction that the operator X contains no single connections G_0 between uncorrelated particles.

The bridge operator $B(1)$ can be further decomposed as

$$B(1) = M(1)\,[1 - S(1)M(1)]^{-1}\,. \tag{6.22}$$

Here $M(1)$ is the single particle scattering operator. The operator $S(1)$ is called the *reaction field operator*. The basic elements of the theory that require further analysis are the operators $S(1)$ and $S(1,2)$.

The above analysis is taken from an article by Cichocki and Felderhof [39]. It modifies and generalizes an earlier theory for dielectrics formulated by Wertheim [40].

In the article mentioned above [39] it is shown that the operators $S(1)$ and $S(1,2)$ can be decomposed by cluster expansion

$$S(1) = \sum_{s=2}^{\infty} S_s(1), \qquad S(1,2) = \sum_{s=2}^{\infty} S_s(1,2), \tag{6.23}$$

where $S_s(1)$ and $S_s(1,2)$ are given as integrals of s-body scattering operators over certain s-body correlation functions.

We only indicate the first few terms of the above series explicitly. For $S_2(1)$ one finds

$$S_2(1) = \int d2\, n(2)k(1,2)N_{11}(1,2). \tag{6.24}$$

Here $k(1,2) = g(1,2)$ is the 2-particle correlation function and $N_{11}(1,2)$ is a nodal connector, defined from the 2-body scattering operator $T_{11}(1,2)$ via

$$T_{11}(1,2) = M(1)N_{11}(1,2)M(1). \tag{6.25}$$

The 3-particle contribution is already more complicated and given by

$$S_3(1) = \int d2\, d3\, n(2)n(3)\,[k(1,2,3)N_{11}(1,2,3) + k(1,2|1,3)N_{11}(1,2|1,3)]\,. \tag{6.26}$$

Here

$$k(1,2,3) = g(1,2,3), \tag{6.27}$$

and

$$\begin{aligned} k(1,2|1,3) &= g(1,2,3) - g(1,2)g(1,3), \\ N_{11}(1,2|1,3) &= N_{11}(1,2)M(1)N_{11}(1,3). \end{aligned} \tag{6.28}$$

In the last expression the label 1 occurs as nodal point. The connector $N_{11}(123)$ corresponds to the sum of scattering sequences $[1231]+[12321]+\cdots$, with the conditions that, reading from left to right, the first and last scatterer be 1, that the scattering sequence contain no nodal point, and that the label $1,2,3$ first occur in this sequence.

The 2-particle contribution to $S(1,2)$ is given by

$$S_2(1,2) = g(1,2)\,[N_{12}(1,2) - G_0] + (g(1,2)-1)G_0 \tag{6.29}$$

with

$$T_{12}(1,2) = M(1)N_{12}(1,2)M(2). \tag{6.30}$$

The 3-particle contribution to $S(1,2)$ is given by

$$\begin{aligned} S_3(1,2) = \int d3\; n(3)\,[&k(1,2,3)N_{12}(1,2,3) + k(1,2|2,3)N_{12}(1,2|2,3)\\ &+ k(1,2,3)N_{12}(1,3,2) + k(1,3|1,2)N_{12}(1,3|1,2)\\ &+ k(1,3|2,3)N_{12}(1,3|3,2)] \end{aligned} \tag{6.31}$$

with correlation functions

$$\begin{aligned} k(1,2|2,3) &= g(1,2,3) - g(1,2)g(2,3),\\ k(1,3|1,2) &= g(1,2,3) - g(1,3)g(1,2),\\ k(1,3|2,3) &= g(1,2,3) - g(1,3)g(2,3), \end{aligned} \tag{6.32}$$

and nodal connector given by

$$\begin{aligned} N_{12}(1,2|2,3) &= N_{12}(1,2)M(2)N_{22}(2,3),\\ N_{12}(1,3|1,2) &= N_{12}(1,3)M(1)N_{12}(1,2),\\ N_{12}(1,3|3,2) &= N_{13}(1,3)M(3)N_{32}(2,3). \end{aligned} \tag{6.33}$$

The nodal connector $N_{12}(1,2,3)$ corresponds to the sum of all scattering sequences $[12312] + [121312] + \cdots$ with the same conditions as for $N_{11}(1,2,3)$ with the only difference that now the first scatterer must be 1 and the second 2. The connector $N_{12}(1,3,2)$ corresponds to the sum of all scattering sequences $[13212] + [131232] + \cdots$, with the same conditions as before, with the difference that now the first scatterer must be 1 the second 2, and that the labels $1,3,2$ must first appear in this sequence.

We close this Chapter with some remarks.

1. The theory can easily be generalized to more complicated fields, e.g. a vector field, or tensor field, and to more complicated field equations.
2. The scatterers need not be spherical. The integration over particle coordinates can contain an integration over orientation angles, besides the integration over center of mass coordinates.
3. The theory is valid for arbitrary geometry. For example, wall effects can be taken into account by incorporating the influence of the wall into the Green function G_0 and the particle correlation functions.
4. In the three equations

$$\begin{aligned} <\psi> &= \psi_0 + G_0 <T> \psi_0, \\ <T> \psi_0 &= <V\psi>, \\ <V\psi> &= <T> [1 + G_0 <T>]^{-1} <\psi>, \end{aligned} \tag{6.34}$$

the value of the functions ψ_0 and $<\psi>$ is relevant only in the region where $<T>$ acts. Essentially this is the region Ω occupied by particles. In this region there is a unique relation $\psi_0 \leftrightarrow <\psi>$ between ψ_0 and $<\psi>$. The behavior of the functions ψ_0 and $<\psi>$ outside Ω is determined by the field equations.

5. "Unphysical" or "virtual" contributions occur, i.e. contributions from configurations that physically cannot be realized. This happens because in the expression

$$X = <T> [1 + G_0 <T>]^{-1} \tag{6.35}$$

one is forming the ratio of two averages. In the Ornstein–Zernike type formulation the only contribution of this nature is the second term in the expression

$$S_2(1,2) = g(1,2)[N_{12}(1,2) - G_0] + (g(1,2) - 1)G_0. \tag{6.36}$$

The second term differs from zero in the region where $g(1,2) = 0$, i.e. in the region where particles 1 and 2 overlap. As we shall see, this *virtual overlap contribution* is very important. The contribution is independent of the form of the correlation functions, and is determined only by the Green function and the shape and size of the overlap region. For spherical particles of radius a the overlap region is a sphere of radius $2a$.

Chapter 7

Susceptibility

In this Chapter we consider the constitutive equation in the neighborhood of a point, somewhere in the middle of the system, in the thermodynamic limit $N \to \infty$, $\Omega \to \infty$, $n = N/\Omega$ constant. The particles are assumed to fill the volume Ω uniformly, so that in the thermodynamic limit, n can be identified with the average particle density. One expects that in the limit the integral kernel $X(\boldsymbol{r} - \boldsymbol{r}')$ becomes translationally invariant and dependent only on the distance vector $\boldsymbol{r} - \boldsymbol{r}'$. We are interested in this translation-invariant operator. We follow an article by Felderhof and Cichocki [41].

From the deliberations of the last Chapter it follows that the operator X can be written as

$$X = \int d1\; n(1)\chi(1) \tag{7.1}$$

with the susceptibility operator $\chi(1)$ given by

$$\chi(1) = B(1) + \int d2\; n(2)B(1)F(1,2)B(2). \tag{7.2}$$

One expects that the corresponding integral kernel $\chi(1; \boldsymbol{r}, \boldsymbol{r}')$ is short range in the variables $\boldsymbol{r} - \boldsymbol{R}_1$ and $\boldsymbol{r}' - \boldsymbol{R}_1$, so that the action of the operator $\chi(1)$ is localized about the position $\boldsymbol{R}_1$.

On the other hand, if we write the average T-Operator $< T >$ in similar form

$$< T > = \int d1\; n(1)\tau(1) \tag{7.3}$$

with

$$\tau(1) = B(1) + \int d2\, n(2)B(1)H(1,2)B(2), \tag{7.4}$$

then the integral kernel $\tau(1; \boldsymbol{r}, \boldsymbol{r}')$ has long range. Both operators $\chi(1)$ and $\tau(1)$ are related by

$$\tau(1) = \chi(1) + \int d2\, n(2)\chi(1)G_{\text{av}}\chi(2), \tag{7.5}$$

where the average Green function G_{av} is given by the Dyson-equation

$$G_{\text{av}} = G_0 + G_0 X G_{\text{av}}. \tag{7.6}$$

The long-range properties of the operator $\tau(1)$ are directly related to those of the Green function G_{av}.

We shall consider matrix elements of the form

$$(\boldsymbol{q}|A|\boldsymbol{q}') = \int e^{-i\boldsymbol{q}\cdot\boldsymbol{r}}\, A(\boldsymbol{r}, \boldsymbol{r}')e^{i\boldsymbol{q}'\cdot\boldsymbol{r}'}\, d\boldsymbol{r}d\boldsymbol{r}'. \tag{7.7}$$

The susceptibility $\chi_\infty(\boldsymbol{q})$ of the infinite system is defined by

$$\lim_{\substack{N\to\infty \\ \Omega\to\infty}} (\boldsymbol{q}|X|\boldsymbol{q}') = 8\pi^3\chi_\infty(\boldsymbol{q})\delta(\boldsymbol{q} - \boldsymbol{q}'). \tag{7.8}$$

The delta-function is an expression of the translation-invariance of the system in the thermodynamic limit.

In the following we assume that the particles are spherical, so that a configuration X is characterized by the positions $(\boldsymbol{R}_1, \ldots, \boldsymbol{R}_N)$ of the sphere centers. The symbol of integration dj can be replaced by $d\boldsymbol{R}_j$.

In the thermodynamic limit the susceptibility operator $\chi(1)$ will have the form

$$\lim_{\substack{N\to\infty \\ \Omega\to\infty}} \chi_\infty = \chi(\boldsymbol{r} - \boldsymbol{R}_1, \boldsymbol{r}' - \boldsymbol{R}_1). \tag{7.9}$$

The susceptibility χ_∞ is given by

$$\chi_\infty(\boldsymbol{q}) = \lim_{\substack{N\to\infty \\ \Omega\to\infty}} n(1)(\boldsymbol{q}|\chi(1)|\boldsymbol{q})\Big|_{\boldsymbol{R}_1=0} \tag{7.10}$$

The matrix element is independent of the position $\boldsymbol{R}_1$, so that without loss of generality one can choose the position $\boldsymbol{R}_1$ to be at the origin.

In the thermodynamic limit the operator $F(1,2)$ depends on the positions $\boldsymbol{R}_1$, $\boldsymbol{R}_2$, $\boldsymbol{r}$, $\boldsymbol{r}'$ in translation-invariant manner, and takes the form

$$\lim_{\substack{N\to\infty \\ \Omega\to\infty}} F(1,2) = F(\boldsymbol{R}_2 - \boldsymbol{R}_1; \boldsymbol{r} - \boldsymbol{R}_1, \boldsymbol{r}' - \boldsymbol{R}_2). \tag{7.11}$$

Taking matrix-elements of the equation

$$\chi(1) = B(1) + \int d2\, n(2) B(1) F(1,2) B(2) \tag{7.12}$$

we find

$$\chi_\infty(\boldsymbol{q}) = n(\boldsymbol{q}|B|\boldsymbol{q}) + n^2(\boldsymbol{q}|BF(\boldsymbol{q})B|\boldsymbol{q}). \tag{7.13}$$

Here the operators B are centered at the origin and $F(\boldsymbol{q})$ is given by the integral kernel

$$F(\boldsymbol{q}; \boldsymbol{s}, \boldsymbol{s}') = \int d\boldsymbol{R}\, e^{i\boldsymbol{q}\cdot\boldsymbol{R}} F(\boldsymbol{R}; \boldsymbol{s}, \boldsymbol{s}') \tag{7.14}$$

with $\boldsymbol{R} = \boldsymbol{R}_2 - \boldsymbol{R}_1$, $\boldsymbol{s} = \boldsymbol{r} - \boldsymbol{R}_1$, $\boldsymbol{s}' = \boldsymbol{r}' - \boldsymbol{R}_2$.

From the Ornstein-Zernike equation for $F(1,2)$ one finds

$$F(\boldsymbol{q}) = S^{(2)}(\boldsymbol{q}) + nS^{(2)}(\boldsymbol{q})BF(\boldsymbol{q}) \tag{7.15}$$

where $S^{(2)}(\boldsymbol{q})$ is defined from the kernel $S(1,2)$ in the thermodynamic limit as above

$$S^{(2)}(\boldsymbol{q}; \boldsymbol{s}, \boldsymbol{s}') = \int d\boldsymbol{R}\, e^{i\boldsymbol{q}\cdot\boldsymbol{R}} S(\boldsymbol{R}; \boldsymbol{s}, \boldsymbol{s}'). \tag{7.16}$$

Equation (7.15) is solved formally by

$$F(\boldsymbol{q}) = [I - nS^{(2)}(\boldsymbol{q})B]^{-1} S^{(2)}(\boldsymbol{q}). \tag{7.17}$$

Substitution in the equation for $\chi_\infty(\boldsymbol{q})$ yields

$$\chi_\infty(\boldsymbol{q}) = n(\boldsymbol{q}|B(I - nS^{(2)}(\boldsymbol{q})B)^{-1}|\boldsymbol{q}). \tag{7.18}$$

Here we employ the expression

$$B(1) = M(1)[I - S(1)M(1)]^{-1} \tag{7.19}$$

for the bridge-operator. The expression for $\chi_\infty(\boldsymbol{q})$ can then be rewritten as

$$\chi_\infty(\boldsymbol{q}) = n(\boldsymbol{q}|M(I - nR(\boldsymbol{q})M)^{-1}|\boldsymbol{q}) \tag{7.20}$$

with the operator $R(\boldsymbol{q})$ given by

$$nR(\boldsymbol{q}) = S^{(1)} + nS^{(2)}(\boldsymbol{q}), \tag{7.21}$$

where the operator $S^{(1)}$ is defined by

$$S^{(1)} = \lim_{\substack{N\to\infty \\ \Omega\to\infty}} S(1)\Big|_{\boldsymbol{R}_1=0} \tag{7.22}$$

As mentioned at the end of the last Chapter, an important contribution to the short-range connector $S(1,2)$ is given by the overlap-contribution to $S_2(1,2)$. Therefore we write

$$S(1,2) = S_{\text{ov}}(1,2) + S_{\text{no}}(1,2) \tag{7.23}$$

with

$$S_{\text{ov}}(1,2) = -\theta(2a - |\boldsymbol{R}_1 - \boldsymbol{R}_2|)G_0. \tag{7.24}$$

Correspondingly we have

$$R(\boldsymbol{q}) = R_{\text{ov}}(\boldsymbol{q}) + R_{\text{no}}(\boldsymbol{q}) \tag{7.25}$$

with

$$R_{\text{ov}}(\boldsymbol{q};\boldsymbol{s},\boldsymbol{s}') = -\int\limits_{R\le 2a} d\boldsymbol{R}\, e^{i\boldsymbol{q}\cdot\boldsymbol{R}}\, G_0(\boldsymbol{s}-\boldsymbol{s}'-\boldsymbol{R}). \tag{7.26}$$

We define

$$K(\boldsymbol{r};\boldsymbol{q}) = \int\limits_{R\le 2a} G_0(\boldsymbol{r}-\boldsymbol{R})e^{i\boldsymbol{q}\cdot\boldsymbol{R}}\, d\boldsymbol{R}. \tag{7.27}$$

Then one has

$$R_{\text{ov}}(\boldsymbol{q};\boldsymbol{s},\boldsymbol{s}') = -K(\boldsymbol{s}-\boldsymbol{s}';\boldsymbol{q}). \tag{7.28}$$

The calculation of the overlap-contribution therefore amounts to that of the function $K(\boldsymbol{r};\boldsymbol{q})$.

In the next Chapter we consider as application of this formalism the calculation of the effective dielectric constant of a suspension of spherical polarizable particles.

Chapter 8

Effective dielectric constant

We return to the theory of the effective dielectric constant. We consider spherical particles of radius a and with spherically symmetric dielectric profile. We apply the formalism of Chapters 6 and 7 to the present problem [42].

The microscopic dielectric constant is given by

$$\varepsilon(1,\dots,N;\boldsymbol{r}) = \begin{cases} \varepsilon(|\boldsymbol{r}-\boldsymbol{R}_j|) & \text{for } |\boldsymbol{r}-\boldsymbol{R}_j| < a \\ \varepsilon_1 & \text{for } |\boldsymbol{r}-\boldsymbol{R}_j| > a, \end{cases} \qquad j = 1,\dots,N. \tag{8.1}$$

The basic equations for the electric field $\boldsymbol{E}$ and the dielectric displacement $\boldsymbol{D}$ are Maxwell's equations of electrostatics

$$\nabla\cdot\boldsymbol{D} = 4\pi\rho_0, \qquad \nabla\times\boldsymbol{E} = 0, \qquad \boldsymbol{D} = \epsilon\boldsymbol{E} \tag{8.2}$$

with given charge density ρ_0, that is independent of the particle positions.

The field $\boldsymbol{E}_0(\boldsymbol{r})$ is the solution of the equations for $\varepsilon(\boldsymbol{r}) = \varepsilon_1$. In the presence of the spheres the field is [2]

$$\boldsymbol{E}(1,\dots,N) = \boldsymbol{K}(1,\dots,N)\cdot\boldsymbol{E}_0 \tag{8.3}$$

with a linear operator $\boldsymbol{K}(1,\dots,N)$, that depends parametrically on the particle positions. The induced polarization, relative to the medium in the absence of particles, is defined by

$$\boldsymbol{D} = \epsilon_1\boldsymbol{E} + 4\pi\boldsymbol{P}. \tag{8.4}$$

The polarization is linear in the applied field

$$\boldsymbol{P}(1,\dots,N) = \chi(1,\dots,N)\boldsymbol{K}(1,\dots,N)\cdot\boldsymbol{E}_0 \tag{8.5}$$

with relative dielectric susceptibility

$$\chi(1,\dots,N) = \frac{\varepsilon(1,\dots,N)-\varepsilon_1}{4\pi}. \tag{8.6}$$

This microscopic susceptibility is a sum of one-particle terms

$$\chi(1,\dots,N) = \sum_{j=1}^{N}\chi(j), \qquad \chi(j) = \frac{\varepsilon(j)-\varepsilon_1}{4\pi}\theta(j). \tag{8.7}$$

On account of the step-function $\theta(j) = \theta(a - |\boldsymbol{r} - \boldsymbol{R}_j|)$ the field point $\boldsymbol{r}$ is localized inside sphere j.

The particles are distributed in disordered fashion, as described by the probability distribution $W(1,\dots,N)$. The distribution is normalized to unity and is symmetric in the labels $(1,\dots,N)$. The partial distribution functions are defined by

$$n(1,\dots,s) = \frac{N!}{(N-s)!}\int\cdots\int d\boldsymbol{R}_{s+1}\cdots\boldsymbol{R}_N\, W(1,\dots,N) \tag{8.8}$$

The correlation function $g(1,\dots,s)$ is defined by

$$n(1,\dots,s) = n(1)\cdots n(s)g(1,\dots,s). \tag{8.9}$$

From the equation $\nabla\times\boldsymbol{E} = 0$ it follows that $\boldsymbol{E}$ can be derived from a potential ψ via $\boldsymbol{E} = -\nabla\psi$. The field equation for ψ reads

$$\varepsilon_1\nabla^2\psi + 4\pi\nabla\cdot\chi\cdot\nabla\psi = -4\pi\rho_0. \tag{8.10}$$

We shall consider here only the limit $\boldsymbol{q}\to 0$. In that case it is easier to consider the electrical field $\boldsymbol{E}$ instead of the potential ψ.

The average electrical field in the presence of particles is

$$<\boldsymbol{E}>=\int\cdots\int d\boldsymbol{R}_1\cdots d\boldsymbol{R}_N\, W(1,\dots,N)\boldsymbol{E}(1,\dots,N) \tag{8.11}$$

and similarly for $<\boldsymbol{P}>$. Averaging the microscopic equations one finds

$$<\boldsymbol{E}>=<\boldsymbol{K}>\cdot\boldsymbol{E}_0, \qquad <\boldsymbol{P}>=<\chi\boldsymbol{K}>\cdot\boldsymbol{E}_0. \tag{8.12}$$

By elimination of the arbitrary longitudinal field $\boldsymbol{E}_0(\boldsymbol{r})$ one obtains

$$< \boldsymbol{P} > = \boldsymbol{X} \cdot < \boldsymbol{E} > \tag{8.13}$$

with susceptibility kernel $\boldsymbol{X}(\boldsymbol{r}, \boldsymbol{r}')$ given by

$$\boldsymbol{X} = < \chi \boldsymbol{K} >< \boldsymbol{K} >^{-1} . \tag{8.14}$$

One recognizes the form of Chapter 6 by writing

$$\boldsymbol{T}(1, \ldots, N) = \chi(1, \ldots, N) \boldsymbol{K}(1, \ldots, N) \tag{8.15}$$

and

$$\boldsymbol{K}(1, \ldots, N) = \boldsymbol{I} + \boldsymbol{G}_0 \boldsymbol{T}(1, \ldots, N). \tag{8.16}$$

The Green function $\boldsymbol{G}_0(\boldsymbol{r} - \boldsymbol{r}')$ is given by

$$\begin{aligned} \boldsymbol{G}_0(\boldsymbol{r} - \boldsymbol{r}') = & -\frac{4\pi}{3\varepsilon_1} \mathbf{1} \delta(\boldsymbol{r} - \boldsymbol{r}') \\ & + \frac{3(\boldsymbol{r} - \boldsymbol{r}')(\boldsymbol{r} - \boldsymbol{r}') - (\boldsymbol{r} - \boldsymbol{r}')^2 \mathbf{1}}{\varepsilon_1 |\boldsymbol{r} - \boldsymbol{r}'|^5} \theta(|\boldsymbol{r} - \boldsymbol{r}'| - \epsilon) \end{aligned} \tag{8.17}$$

with infinitesimal $\epsilon > 0$. The validity of this expression follows from the identity

$$< \boldsymbol{E}(\boldsymbol{r}) > = \boldsymbol{E}_0(\boldsymbol{r}) + \int \boldsymbol{G}_0(\boldsymbol{r} - \boldsymbol{r}') \cdot < \boldsymbol{P}(\boldsymbol{r}') > \, d\boldsymbol{r}' \tag{8.18}$$

and the expression for the Lorentz-field

$$< \boldsymbol{E} > = \boldsymbol{E}_L - \frac{4\pi}{3\epsilon_1} < \boldsymbol{P} >, \tag{8.19}$$

in combination with the realization that the Lorentz-field is given by

$$\boldsymbol{E}_L(\boldsymbol{r}) = \boldsymbol{E}_0(\boldsymbol{r}) + \int_\epsilon \frac{3(\boldsymbol{r} - \boldsymbol{r}')(\boldsymbol{r} - \boldsymbol{r}') - (\boldsymbol{r} - \boldsymbol{r}')^2 \mathbf{1}}{\varepsilon_1 |\boldsymbol{r} - \boldsymbol{r}'|^5} \cdot < \boldsymbol{P}(\boldsymbol{r}') > \, d\boldsymbol{r}'. \tag{8.20}$$

In the thermodynamic limit for a spatially uniform system the constitutive equation becomes after Fourier transformation

$$< \boldsymbol{P}_{\boldsymbol{q}} > = \boldsymbol{\chi}_\infty(\boldsymbol{q}) \cdot < \boldsymbol{E}_{\boldsymbol{q}} > \tag{8.21}$$

with Fourier components

$$\begin{aligned} < \boldsymbol{P}_{\boldsymbol{q}} > &= \frac{1}{8\pi^3} \int e^{-i\boldsymbol{q}\cdot\boldsymbol{r}} < \boldsymbol{P}(\boldsymbol{r}) > \, d\boldsymbol{r}, \\ < \boldsymbol{E}_{\boldsymbol{q}} > &= \frac{1}{8\pi^3} \int e^{-i\boldsymbol{q}\cdot\boldsymbol{r}} < \boldsymbol{E}(\boldsymbol{r}) > \, d\boldsymbol{r}. \end{aligned} \tag{8.22}$$

The tensor $\boldsymbol{\chi}_{\infty}(\boldsymbol{q})$ is given by the expression (7.20).

The average electrical field $< \boldsymbol{E} >$ is longitudinal, on account of $\nabla \times < \boldsymbol{E} > = 0$. Therefore $< \boldsymbol{E}_{\boldsymbol{q}} >$ is parallel to $\boldsymbol{q}$. In case the distribution of spheres is isotropic, as well as uniform, the relation between $< \boldsymbol{P}_{\boldsymbol{q}} >$ and $< \boldsymbol{E}_{\boldsymbol{q}} >$ must be invariant under rotations. This implies that the susceptibility tensor must have the form

$$\boldsymbol{\chi}_{\infty}(\boldsymbol{q}) = \chi_L(q)\hat{\boldsymbol{q}}\hat{\boldsymbol{q}} + \chi_T(q)(\boldsymbol{1} - \hat{\boldsymbol{q}}\hat{\boldsymbol{q}}) \tag{8.23}$$

with scalar functions $\chi_L(q)$ and $\chi_T(q)$. For such a system the average polarization field is also longitudinal, i.e. one has $< \boldsymbol{P}_{\boldsymbol{q}} >$ parallel to $\boldsymbol{q}$.

In the limit $q \to 0$ the difference between $\chi_L(q)$ and $\chi_T(q)$ vanishes. We write

$$\chi_L(0) = \chi_T(0) = \chi_{\text{eff}}. \tag{8.24}$$

We are interested in the effective dielectric constant

$$\varepsilon_{\text{eff}} = \varepsilon_1 + 4\pi\chi_{\text{eff}}. \tag{8.25}$$

We consider first the bridge-operator

$$\boldsymbol{B}(1) = \boldsymbol{M}(1)\left[\boldsymbol{I} - \boldsymbol{S}(1)\boldsymbol{M}(1)\right]^{-1}. \tag{8.26}$$

In the limit $\boldsymbol{q} \to 0$ we consider a uniform external field $\boldsymbol{E}_0$. For a sphere $\boldsymbol{M}(1)\boldsymbol{E}_0$ is the corresponding induced polarization. The total induced dipole moment is given by

$$\boldsymbol{p}(1) = (0|\boldsymbol{M}(1)|0) \cdot \boldsymbol{E}_0 \tag{8.27}$$

with matrix element

$$(0|\boldsymbol{M}(1)|0) = \int \boldsymbol{M}(1; \boldsymbol{r}, \boldsymbol{r}') \, d\boldsymbol{r} d\boldsymbol{r}'. \tag{8.28}$$

The dipole polarizability of the particle is defined by

$$\boldsymbol{p}(1) = \alpha_1 \boldsymbol{E}_0, \tag{8.29}$$

so that we find

$$\alpha_1 \mathbf{1} = (0|\boldsymbol{M}(1)|0). \tag{8.30}$$

We consider the field $\boldsymbol{S}(1)\boldsymbol{M}(1)|0)$ as a function the variable $\boldsymbol{r}$. The operator $\boldsymbol{S}(1)$ implies propagation via $\boldsymbol{G}_0$ to particles in the neighborhood, averaging over certain correlation functions, as given by the cluster expansion for $\boldsymbol{S}(1)$, and finally again propagation with $\boldsymbol{G}_0$. Therefore we can write

$$[\boldsymbol{S}(1)\boldsymbol{M}(1)|0) \cdot \boldsymbol{E}_0](\boldsymbol{r}) = \int \boldsymbol{G}_0(\boldsymbol{r} - \boldsymbol{r}') \cdot \mathsf{F}(\boldsymbol{r}') \cdot \boldsymbol{E}_0, \tag{8.31}$$

where $\mathsf{F}(\boldsymbol{r}') \cdot \boldsymbol{E}_0$ is the polarization induced in the surroundings. This polarization vanishes for $|\boldsymbol{r} - \boldsymbol{R}_1| < a$. The field induced inside the sphere $|\boldsymbol{r} - \boldsymbol{R}_1| < a$ satisfies the Laplace-equation. Since the environment is isotropic it follows by symmetry that the field in the sphere is uniform and proportional to $\boldsymbol{E}_0$. Therefore we can write

$$[\boldsymbol{S}(1)\boldsymbol{M}(1)|0) \cdot \boldsymbol{E}_0](\boldsymbol{r}) = \frac{4\pi}{3\varepsilon_1} \lambda n \alpha_1 \boldsymbol{E}_0, \quad \text{for } |\boldsymbol{r} - \boldsymbol{R}_1| < a \tag{8.32}$$

with a constant factor λ.

By repeated application of this argument we find

$$(0|\boldsymbol{B}(1)|0) = \frac{\alpha_1}{1 - \frac{4\pi}{3\varepsilon_1} \lambda n \alpha_1} \mathbf{1}. \tag{8.33}$$

It is natural to introduce a corresponding renormalized polarizability

$$\alpha_1' = \frac{\alpha_1}{1 - \frac{4\pi}{3\epsilon_1} \lambda n \alpha_1}. \tag{8.34}$$

Furthermore we must consider the contribution

$$\int d\boldsymbol{R}(0|\boldsymbol{B}(1)\boldsymbol{F}(1,2)\boldsymbol{B}(2)|0) \tag{8.35}$$

where $\boldsymbol{F}(1,2)$ is given by the integral equation

$$\boldsymbol{F}(1,2) = \boldsymbol{S}(1,2) + \int d3 n(3) \boldsymbol{S}(1,3) \boldsymbol{B}(3) \boldsymbol{F}(3,2). \tag{8.36}$$

As in the last Chapter we write

$$\boldsymbol{S}(1,2) = \boldsymbol{S}_{\text{ov}}(1,2) + \boldsymbol{S}_{\text{no}}(1,2)$$

with

$$\boldsymbol{S}_{\text{ov}}(1,2) = -\theta(2a - |\boldsymbol{R}_1 - \boldsymbol{R}_2|)\boldsymbol{G}_0. \tag{8.37}$$

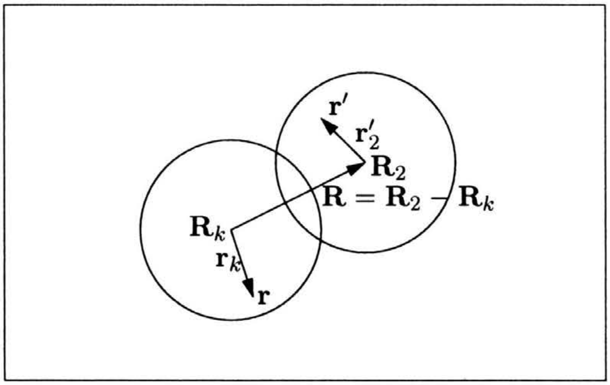

FIGURE 8.1. Geometry of the overlap integral.

First we consider the field

$$\boldsymbol{S}_{\text{ov}}(k,2)\boldsymbol{B}(2)|0)\cdot\boldsymbol{E}_0=-\boldsymbol{G}_0\boldsymbol{B}(2)|0)\cdot\boldsymbol{E}_0 \tag{8.38}$$

with the condition that spheres k and 2 overlap (see Fig. 8.1). The field generated by sphere 2 is given by

$$\boldsymbol{E}'_{\text{ind}}(2)=\boldsymbol{G}_0\boldsymbol{B}(2)|0)\cdot\boldsymbol{E}_0. \tag{8.39}$$

According to the argument above one has

$$\boldsymbol{E}'_{\text{ind}}(2)=\frac{1}{1-\frac{4\pi}{3\epsilon_1}\lambda n\alpha_1}\boldsymbol{E}_{\text{ind}}(2), \tag{8.40}$$

where $\boldsymbol{E}_{\text{ind}}(2)$ is the field induced by sphere 2 in a medium ε_1,

$$\boldsymbol{E}_{\text{ind}}(2)=\boldsymbol{G}_0\boldsymbol{M}(2)|0)\cdot\boldsymbol{E}_0. \tag{8.41}$$

More explicitly

$$\boldsymbol{E}_{\text{ind}}(2;\boldsymbol{r})=\frac{\partial}{\partial\boldsymbol{r}}\int d\boldsymbol{r}'\,\frac{\partial}{\partial\boldsymbol{r}}\cdot\frac{\boldsymbol{P}(2;\boldsymbol{r}')}{\varepsilon_1|\boldsymbol{r}-\boldsymbol{r}'|}, \tag{8.42}$$

where $\boldsymbol{P}(2)$ is the polarization induced in the sphere by the applied field $\boldsymbol{E}_0$. This polarization depends only on the relative position $\boldsymbol{r}_2=\boldsymbol{r}-\boldsymbol{R}_2$. With $\boldsymbol{r}_k=\boldsymbol{r}-\boldsymbol{R}_k$ and $\boldsymbol{R}=\boldsymbol{R}_2-\boldsymbol{R}_k$ we can therefore write

$$\boldsymbol{E}_{\text{ind}}(2;\boldsymbol{r})=-\frac{\partial}{\partial\boldsymbol{r}_k}\int d\boldsymbol{r}'_2\,\frac{\partial}{\partial R}\cdot\frac{\boldsymbol{P}(2;\boldsymbol{r}'_2)}{\varepsilon_1|\boldsymbol{r}_k-\boldsymbol{r}'_2-\boldsymbol{R}|}. \tag{8.43}$$

We now integrate both sides of this equation over the overlap region $|\boldsymbol{R}_2 - \boldsymbol{R}_k| > 2a$. This yields by use of Gauss' theorem

$$\int\limits_{R<2a} d\boldsymbol{R}_2 \boldsymbol{E}_{\mathrm{ind}}(2;\boldsymbol{r}) = -\frac{\partial}{\partial \boldsymbol{r}_k} \int d\boldsymbol{r}'_2 \int d\Omega (2a)^2 \, \frac{\hat{\boldsymbol{R}} \cdot \boldsymbol{P}(2;\boldsymbol{r}'_2)}{\varepsilon_1 |\boldsymbol{r}_k - \boldsymbol{r}'_2 - 2a\hat{\boldsymbol{R}}|}. \quad (8.44)$$

Here $d\Omega$ is the angular element for direction $\hat{\boldsymbol{R}}$. In the integral on the right $r'_2 < a$, since the polarization $\boldsymbol{P}(2;\boldsymbol{r}'_2)$ vanishes for $r'_2 > a$. We need the integral only for points inside the sphere k, so that $r_k < a$. Hence $|\boldsymbol{r}_k - \boldsymbol{r}'_2| < 2a$ and we can use the expansion

$$\frac{1}{|\boldsymbol{r}_k - \boldsymbol{r}'_2 - 2a\hat{\boldsymbol{R}}|} = \sum_{l=0}^{\infty} \frac{|\boldsymbol{r}_k - \boldsymbol{r}'_2|^l}{(2a)^{l+1}} P_l\left(\hat{\boldsymbol{R}} \cdot \frac{\boldsymbol{r}_k - \boldsymbol{r}'_2}{|\boldsymbol{r}_k - \boldsymbol{r}'_2|}\right). \quad (8.45)$$

It follows from the orthonormality properties of the Legendre-polynomials that

$$\int d\Omega \, \hat{\boldsymbol{R}} \cdot \boldsymbol{A} \, P_l(\hat{\boldsymbol{R}} \cdot \hat{\boldsymbol{n}}) = \frac{4\pi}{3} \, \hat{\boldsymbol{n}} \cdot \boldsymbol{A} \, \delta_{l1} \quad (8.46)$$

for arbitrary vectors $\boldsymbol{A}$ and $\hat{\boldsymbol{n}}$. We find therefore after substitution of the expansion

$$\int\limits_{R<2a} d\boldsymbol{R}_2 \, \boldsymbol{E}_{\mathrm{ind}}(2;\boldsymbol{r}) = -\frac{4\pi}{3\varepsilon_1} \int d\boldsymbol{r}'_2 \, \boldsymbol{P}(2;\boldsymbol{r}'_2) \quad \text{for } r_k < a. \quad (8.47)$$

The integral on the right-hand side is the total dipole moment induced in sphere 2 by the field $\boldsymbol{E}_0$. Hence

$$\int\limits_{R<2a} d\boldsymbol{R}_2 \, \boldsymbol{E}_{\mathrm{ind}}(2;\boldsymbol{r}) = -\frac{4\pi}{3\epsilon_1} \alpha_1 \boldsymbol{E}_0 \quad \text{for } r_k < a. \quad (8.48)$$

Thus the field is uniform in sphere k. Analogously we find

$$\int\limits_{|\boldsymbol{R}_k - \boldsymbol{R}_2|<2a} d\boldsymbol{R}_2 \, \left[\boldsymbol{G}_0 \boldsymbol{B}(2)|0) \cdot \boldsymbol{E}_0\right](\boldsymbol{r}) = -\frac{4\pi}{3\varepsilon_1} \alpha'_1 \boldsymbol{E}_0 \quad \text{for } |\boldsymbol{r} - \boldsymbol{R}_k| < a. \quad (8.49)$$

Next we consider the field $\boldsymbol{S}_{\mathrm{no}}(k,2)\boldsymbol{B}(2)|0) \cdot \boldsymbol{E}_0$ as a function of the position $\boldsymbol{r}$. The integral of this field over the position of sphere 2, under condition that spheres k and 2 do not overlap, is given by

$$\int d\boldsymbol{R}_2 \, \left[\boldsymbol{S}_{\mathrm{no}}(k,2)\boldsymbol{B}(2)|0) \cdot \boldsymbol{E}_0\right](\boldsymbol{r}) = \int \boldsymbol{G}_0(\boldsymbol{r} - \boldsymbol{r}') \cdot \mathsf{F}'(\boldsymbol{r}') \cdot \boldsymbol{E}_0 \, d\boldsymbol{r}' \quad (8.50)$$

where $\mathsf{F}'(\boldsymbol{r}') \cdot \boldsymbol{E}_0$ is a polarization field surrounding sphere k that vanishes for $|\boldsymbol{r}' - \boldsymbol{R}_k| \leq a$. The right-hand side of the equation therefore satisfies Laplace's equation for $r_k < a$. By symmetry this is a field that is uniform for $|\boldsymbol{r} - \boldsymbol{R}_k| \leq a$ and can be put equal to

$$\int d\boldsymbol{R}_2 \ \left[\boldsymbol{S}_{\text{no}}(k,2)\boldsymbol{B}(2)|0) \cdot \boldsymbol{E}_0\right](\boldsymbol{r}) = \frac{4\pi}{3\varepsilon_1}\mu\alpha_1'\boldsymbol{E}_0 \quad \text{for } |\boldsymbol{r} - \boldsymbol{R}_k| < a \tag{8.51}$$

with a dimensionless coefficient μ.

Addition of the overlap contribution yields

$$\int d\boldsymbol{R}_2 \ \left[\boldsymbol{S}(k,2)\boldsymbol{B}(2)|0) \cdot \boldsymbol{E}_0\right](\boldsymbol{r}) = \frac{4\pi}{3\varepsilon_1}(1+\mu)\alpha_1'\boldsymbol{E}_0 \quad \text{for } |\boldsymbol{r} - \boldsymbol{R}_k| < a. \tag{8.52}$$

We use the above argument repeatedly in the iterated form of the integral equation for $\boldsymbol{F}(1,2)$. For every pair of factors $\boldsymbol{S}(j-1,j)\boldsymbol{B}(j)$ we find after integration over $\boldsymbol{R}_j$ a uniform field acting on the next sphere. We find therefore

$$\int d\boldsymbol{R}_2 \ \left[\boldsymbol{F}(1,2)\boldsymbol{B}(2)|0)\right](\boldsymbol{r}) = \frac{\frac{4\pi}{3\varepsilon_1}(1+\mu)\alpha_1'}{1 - \frac{4\pi}{3\varepsilon_1}(1+\mu)n\alpha'}\mathbf{1} \quad \text{for } |\boldsymbol{r} - \boldsymbol{R}_1| < a. \tag{8.53}$$

Finally we find the matrix element

$$n^2 \int d\boldsymbol{R} \ (0|\boldsymbol{B}(1)\boldsymbol{F}(1,2)\boldsymbol{B}(2)|0) = \frac{\frac{4\pi}{3\varepsilon_1}(1+\mu)(n\alpha_1')^2}{1 - \frac{4\pi}{3\varepsilon_1}(1+\mu)n\alpha_1'}\mathbf{1}. \tag{8.54}$$

In combination with

$$(0|\boldsymbol{B}(1)|0) = \alpha_1'\mathbf{1} \tag{8.55}$$

we find for the effective dielectric constant the exact expression

$$\varepsilon_{\text{eff}} = \varepsilon_1 + \frac{4\pi n\alpha_1'}{1 - \frac{4\pi}{3\varepsilon_1}(1+\mu)n\alpha_1'}. \tag{8.56}$$

One can write this also as

$$\varepsilon_{\text{eff}} = \varepsilon_1 + \frac{4\pi n\alpha_1}{1 - \frac{4\pi}{3\varepsilon_1}(1+\lambda+\mu)n\alpha_1} \tag{8.57}$$

corresponding to

$$\chi_{\text{eff}} = n\left(0|M[1 - nR(0)M]^{-1}|0\right). \tag{8.58}$$

We can write

$$\varepsilon_{\text{eff}} = \varepsilon_1 + 4\pi n \alpha_1'' \tag{8.59}$$

with renormalized polarizability

$$\alpha_1'' = \frac{\alpha_1}{1 - \frac{4\pi}{3\epsilon_1}(1+\lambda+\mu)n\alpha_1}. \tag{8.60}$$

An alternative expression is

$$\frac{\varepsilon_{\text{eff}} - \varepsilon_1}{\varepsilon_{\text{eff}} + 2\varepsilon_1} = \frac{4\pi}{3\varepsilon_1} \frac{n\alpha_1}{1 - \frac{4\pi}{3\varepsilon_1}(\lambda+\mu)n\alpha_1}. \tag{8.61}$$

This expression has the Clausius–Mossotti form, but is exact.

The cluster expansions for the operators $\boldsymbol{S}(1)$ and $\boldsymbol{S}(1,2)$

$$\boldsymbol{S}(1) = \sum_{s=2}^{\infty} \boldsymbol{S}_s(1), \qquad \boldsymbol{S}(1,2) = \sum_{s=2}^{\infty} \boldsymbol{S}_s(1,2) \tag{8.62}$$

lead to analogous cluster expansions for the coefficients λ and μ

$$\lambda = \sum_{s=2}^{\infty} \lambda_s, \qquad \mu = \sum_{s=2}^{\infty} \mu_s. \tag{8.63}$$

We consider only the contributions λ_2, λ_3, μ_2, μ_3.

The coefficient λ_2 is given by

$$\lambda_2 \mathbf{1} = \int d\boldsymbol{R}_2\, g(1,2) \boldsymbol{F}_{11}(1,2) \tag{8.64}$$

with

$$\boldsymbol{F}_{11}(1,2) = \frac{3\varepsilon_1}{4\pi\alpha_1} \left[\boldsymbol{N}_{11}(1,2)\boldsymbol{M}(1)|0)\right](\mathbf{0}) \tag{8.65}$$

(sphere 1 is centered at the origin).

The coefficient λ_3 is composed of

$$\lambda_3 = \lambda_3(1,2,3) + \lambda_3(1,2|1,3) \tag{8.66}$$

with the two contributions

$$\begin{aligned} \lambda_3(1,2,3)\mathbf{1} &= n \int d\boldsymbol{R}_2 d\boldsymbol{R}_3\, k(1,2,3) \boldsymbol{F}_{11}(1,2,3), \\ \lambda_3(1,2|1,3)\mathbf{1} &= n \int d\boldsymbol{R}_2 d\boldsymbol{R}_3\, k(1,2|1,3) \boldsymbol{F}_{11}(1,2|1,3), \end{aligned} \tag{8.67}$$

with

$$\boldsymbol{F}_{11}(C) = \frac{3\epsilon_1}{4\pi\alpha_1}\left[\boldsymbol{N}_{11}(C)\boldsymbol{M}(1|0)\right](\mathbf{0}). \tag{8.68}$$

Analogously one finds for the coefficient μ_2

$$\mu_2\,\mathbf{1} = \int d\boldsymbol{R}_2\,g(1,2)\left[\boldsymbol{F}_{12}(1,2) - \frac{3\epsilon_1}{4\pi}\boldsymbol{G}_0(\boldsymbol{R}_2)\right] \tag{8.69}$$

with

$$\boldsymbol{F}_{12}(1,2) = \frac{3\varepsilon_1}{4\pi\alpha_1}\left[\boldsymbol{N}_{12}(1,2)\boldsymbol{M}(2)|0)\right](\mathbf{0}). \tag{8.70}$$

The coefficient μ_3 is composed of

$$\mu_3 = \mu_3(1,2,3) + \mu_3(1,2|2,3) + \mu_3(1,3,2) + \mu_3(1,3|1,2) + \mu_3(1,3|3,2) \tag{8.71}$$

with five contributions

$$\begin{aligned}
\mu_3(1,2,3)\mathbf{1} &= n\int d\boldsymbol{R}_2\,d\boldsymbol{R}_3\;k(1,2,3)\boldsymbol{F}_{12}(1,2,3),\\
\mu_3(1,2|2,3)\mathbf{1} &= n\int d\boldsymbol{R}_2\,d\boldsymbol{R}_3\;k(1,2|2,3)\boldsymbol{F}_{12}(1,2|2,3),\\
\mu_3(1,3,2)\mathbf{1} &= n\int d\boldsymbol{R}_2\,d\boldsymbol{R}_3\;k(1,2,3)\boldsymbol{F}_{12}(1,3,2),\\
\mu_3(1,3|1,2)\mathbf{1} &= n\int d\boldsymbol{R}_2\,d\boldsymbol{R}_3\;k(1,3|1,2)\boldsymbol{F}_{12}(1,3|1,2),\\
\mu_3(1,3|3,2)\mathbf{1} &= n\int d\boldsymbol{R}_2\,d\boldsymbol{R}_3\;k(1,3|3,2)\boldsymbol{F}_{12}(1,3|3,2),
\end{aligned} \tag{8.72}$$

with

$$\boldsymbol{F}_{12}(C') = \frac{3\varepsilon_1}{4\pi\alpha_1}\left[\boldsymbol{N}_{12}(C')\boldsymbol{M}(2)|0)\right](\mathbf{0}). \tag{8.73}$$

For the explicit calculation of these coefficients one needs the nodal connectors for two and three particles. For polarizable point particles these are known explicitly. The two-particle term is calculated below. For the three-particle term see Cichocki and Felderhof [43]. In principle the 2- and 3-particle coefficients can therefore be calculated. As we shall show, the calculation of the 2-particle coefficient can be performed largely analytically. The calculation of the 3-particle coefficient is more complicated.

One obtains the Kirkwood–Yvon integrals from the contributions λ_2, μ_2 and $\mu_3(1,2|2,3)$ by expansion in powers of α_1 keeping only the contributions of lowest order.

For polarizable point dipoles the 1-particle T-Operator is given by

$$\boldsymbol{M}(1) \equiv \boldsymbol{M}(1; \boldsymbol{r}, \boldsymbol{r}') = \alpha_1 \mathbf{1} \delta(\boldsymbol{r} - \boldsymbol{R}_1) \delta(\boldsymbol{r}' - \boldsymbol{R}_1). \tag{8.74}$$

For two polarizable point dipoles under the influence of an applied field $\boldsymbol{E}_0(\boldsymbol{r})$ one has the coupled equations

$$\begin{aligned} \boldsymbol{p}_1 &= \alpha_1 \left[\boldsymbol{E}_0(1) + \boldsymbol{T}_{12} \cdot \boldsymbol{p}_2 \right], \\ \boldsymbol{p}_2 &= \alpha_1 \left[\boldsymbol{E}_0(2) + \boldsymbol{T}_{12} \cdot \boldsymbol{p}_1 \right], \end{aligned} \tag{8.75}$$

with (for $\varepsilon_1 = 1$)

$$\boldsymbol{T}_{12} = \frac{-\mathbf{1} + 3\hat{\boldsymbol{R}}\hat{\boldsymbol{R}}}{R^3}, \qquad \boldsymbol{R} = \boldsymbol{R}_2 - \boldsymbol{R}_1. \tag{8.76}$$

One can easily solve these equations by writing

$$\boldsymbol{T}_{12} = \frac{-\mathbf{1} + \hat{\boldsymbol{R}}\hat{\boldsymbol{R}} + 2\hat{\boldsymbol{R}}\hat{\boldsymbol{R}}}{R^3}, \tag{8.77}$$

and taking account of the projection properties of the tensors $-\mathbf{1} + \hat{\boldsymbol{R}}\hat{\boldsymbol{R}}$ and $\hat{\boldsymbol{R}}\hat{\boldsymbol{R}}$. In particular

$$\boldsymbol{T}_{12} \cdot \boldsymbol{T}_{12} = \frac{-\mathbf{1} + \hat{\boldsymbol{R}}\hat{\boldsymbol{R}} + 4\hat{\boldsymbol{R}}\hat{\boldsymbol{R}}}{R^6}. \tag{8.78}$$

Substitution and projection perpendicular and parallel to $\hat{\boldsymbol{R}}$ yields

$$\begin{aligned} \boldsymbol{p}_1 = {} & \frac{\alpha_1}{1 - \alpha_1^2/R^6} (\mathbf{1} - \hat{\boldsymbol{R}}\hat{\boldsymbol{R}}) \cdot \boldsymbol{E}_0(1) + \frac{\alpha_1}{1 - 4\alpha_1^2/R^6} \hat{\boldsymbol{R}}\hat{\boldsymbol{R}} \cdot \boldsymbol{E}_0(1) \\ & + \frac{\alpha_1^2/R^3}{1 - \alpha_1^2/R^6} (\mathbf{1} - \hat{\boldsymbol{R}}\hat{\boldsymbol{R}}) \cdot \boldsymbol{E}_0(2) + \frac{2\alpha_1^2/R^3}{1 - 4\alpha_1^2/R^6} \hat{\boldsymbol{R}}\hat{\boldsymbol{R}} \cdot \boldsymbol{E}_0(2). \end{aligned} \tag{8.79}$$

After interchange of labels

$$\begin{aligned} \boldsymbol{p}_2 = {} & \frac{\alpha_1^2/R^3}{1 - \alpha_1^2/R^6} (\mathbf{1} - \hat{\boldsymbol{R}}\hat{\boldsymbol{R}}) \cdot \boldsymbol{E}_0(1) + \frac{2\alpha_1^2/R^6}{1 - 4\alpha_1^2/R^6} \hat{\boldsymbol{R}}\hat{\boldsymbol{R}} \cdot \boldsymbol{E}_0(1) \\ & + \frac{\alpha_1}{1 - \alpha_1^2/R^6} (\mathbf{1} - \hat{\boldsymbol{R}}\hat{\boldsymbol{R}}) \cdot \boldsymbol{E}_0(2) + \frac{\alpha_1}{1 - 4\alpha_1^2/R^6} \hat{\boldsymbol{R}}\hat{\boldsymbol{R}} \cdot \boldsymbol{E}_0(2). \end{aligned} \tag{8.80}$$

Hence one can read off the nodal connectors $\boldsymbol{N}_{11}(1,2)$ and $\boldsymbol{N}_{12}(1,2)$.

The formal expressions are

$$\begin{aligned}\boldsymbol{N}_{11}(1,2) &= \theta(1)\boldsymbol{G}_0\boldsymbol{M}(2)\boldsymbol{G}_0\theta(1)\\ &\quad + \theta(1)\boldsymbol{G}_0\boldsymbol{M}(2)\boldsymbol{G}_0\boldsymbol{M}(1)\boldsymbol{G}_0\boldsymbol{M}(2)\boldsymbol{G}_0\theta(1) + \cdots\\ &= \theta(1)\boldsymbol{G}_0\boldsymbol{M}(2)\left[\boldsymbol{I} - \boldsymbol{G}_0\boldsymbol{M}(1)\boldsymbol{G}_0\boldsymbol{M}(2)\right]^{-1}\boldsymbol{G}_0\theta(1),\end{aligned} \tag{8.81}$$

$$\begin{aligned}\boldsymbol{N}_{12}(1,2) &= \theta(1)\boldsymbol{G}_0\theta(2) + \theta(1)\boldsymbol{G}_0\boldsymbol{M}(2)\boldsymbol{G}_0\boldsymbol{M}(1)\boldsymbol{G}_0\theta(2) + \cdots\\ &= \theta(1)\boldsymbol{G}_0\left[\boldsymbol{I} - \boldsymbol{M}(2)\boldsymbol{G}_0\boldsymbol{M}(1)\boldsymbol{G}_0\right]^{-1}\theta(2).\end{aligned} \tag{8.82}$$

For polarizable point dipoles

$$\begin{aligned}\boldsymbol{N}_{11}(1,2;\boldsymbol{r},\boldsymbol{r}') &= \theta(a-|\boldsymbol{r}-\boldsymbol{R}_1|)\boldsymbol{G}_0(\boldsymbol{r}-\boldsymbol{R}_2)\left[\frac{\alpha_1}{1-\alpha_1^2/R^6}(\boldsymbol{1}-\hat{\boldsymbol{R}}\hat{\boldsymbol{R}})\right.\\ &\quad \left. + \frac{\alpha_1}{1-4\alpha_1^2/R^6}\hat{\boldsymbol{R}}\hat{\boldsymbol{R}}\right]\boldsymbol{G}_0(\boldsymbol{r}'-\boldsymbol{R}_2)\theta(a-|\boldsymbol{r}'-\boldsymbol{R}_1|),\end{aligned} \tag{8.83}$$

$$\begin{aligned}\boldsymbol{N}_{12}(1,2;\boldsymbol{r},\boldsymbol{r}') &= \theta(a-|\boldsymbol{r}-\boldsymbol{R}_1|)\Big\{\boldsymbol{G}_0(\boldsymbol{r}-\boldsymbol{r}')\\ &+ \boldsymbol{G}_0(\boldsymbol{r}-\boldsymbol{R}_2)\left[\frac{-\alpha_1^2/R^3}{1-\alpha_1^2/R^6}(\boldsymbol{1}-\hat{\boldsymbol{R}}\hat{\boldsymbol{R}}) + \frac{2\alpha_1^2/R^3}{1-4\alpha_1^2/R^6}\hat{\boldsymbol{R}}\hat{\boldsymbol{R}}\right]\boldsymbol{G}_0(\boldsymbol{r}'-\boldsymbol{R}_1)\Big\}\\ &\cdot\theta(a-|\boldsymbol{r}'-\boldsymbol{R}_2|).\end{aligned} \tag{8.84}$$

In particular

$$\boldsymbol{F}_{11}(1,2) = \frac{3\alpha_1}{4\pi}\left[\frac{1}{R^6-\alpha_1^2}(\boldsymbol{1}-\hat{\boldsymbol{R}}\hat{\boldsymbol{R}}) + \frac{4}{R^6-4\alpha_1^2}\hat{\boldsymbol{R}}\hat{\boldsymbol{R}}\right] \tag{8.85}$$

and

$$\begin{aligned}\boldsymbol{F}_{12}(1,2) &= \frac{3}{4\pi}\boldsymbol{G}_0(\boldsymbol{R})\\ &\quad + \frac{3\alpha_1^2}{4\pi R^3}\left[\frac{-1}{R^6-\alpha_1^2}(\boldsymbol{1}-\hat{\boldsymbol{R}}\hat{\boldsymbol{R}}) + \frac{8}{R^6-4\alpha_1^2}\hat{\boldsymbol{R}}\hat{\boldsymbol{R}}\right].\end{aligned} \tag{8.86}$$

This yields

$$\begin{aligned}\lambda_2 &= \frac{3\alpha_1}{4\pi}\int d\boldsymbol{R}g(R)\left[\frac{2/3}{R^6-\alpha_1^2} + \frac{4/3}{R^6-4\alpha_1^2}\right],\\ \mu_2 &= \frac{3\alpha_1^2}{4\pi}\int d\boldsymbol{R}\frac{g(R)}{R^3}\left[\frac{-2/3}{R^6-\alpha_1^2} + \frac{8/3}{R^6-4\alpha_1^2}\right],\end{aligned} \tag{8.87}$$

or

$$\lambda_2 = 2\alpha_1 \int_{2a}^{\infty} dR\, R^2 g(R) \left[\frac{1}{R^6-\alpha_1^2} + \frac{2}{R^6-4\alpha_1^2}\right],$$
$$\mu_2 = 2\alpha_1^2 \int_{2a}^{\infty} dR \frac{g(R)}{R} \left[\frac{-1}{R^6-\alpha_1^2} + \frac{4}{R^6-4\alpha_1^2}\right]. \tag{8.88}$$

By addition

$$\lambda_2 + \mu_2 = 2\alpha_1 \int_{2a}^{\infty} dR \frac{g(R)}{R} \left[\frac{1}{R^3+\alpha_1} + \frac{2}{R^3-2\alpha_1}\right]$$
$$= 6\alpha_1 \int_{2a}^{\infty} \frac{1}{(R^3+\alpha_1)(R^3-2\alpha_1)} g(R) R^2 dR. \tag{8.89}$$

If one expands in powers of α_1, the term of lowest order is

$$\lambda_2^{(1)} = 6\alpha_1 \int_{2a}^{\infty} \frac{g(R)}{R^4}\, dR, \qquad \mu_2^{(1)} = 0. \tag{8.90}$$

This is precisely the first Kirkwood–Yvon integral.

It is easy to see that the only term of order α_1 in λ_3 and μ_3 originates from the term $\mu_3(1,3|3,2)$. This yields

$$\mu_3^{(1)}\mathbf{1} = \frac{3}{4\pi} n\alpha_1 \int d\boldsymbol{R}_2\, d\boldsymbol{R}_3\, k(1,3|2,3) \boldsymbol{G}_0(\boldsymbol{R}_{13}) \cdot \boldsymbol{G}_0(\boldsymbol{R}_{32}) \tag{8.91}$$

or equivalently

$$\mu_3^{(1)} = \frac{3}{2\pi} n\alpha_1 \int d\boldsymbol{R}_2\, d\boldsymbol{R}_3 \left[g(1,2,3) - g(1,2)g(2,3)\right] \frac{P_2(\cos\theta)}{R_{12}^3 R_{23}^3} \tag{8.92}$$

with $\cos\theta = \hat{\boldsymbol{R}}_{12} \cdot \hat{\boldsymbol{R}}_{23}$. This is precisely the second Kirkwood–Yvon integral. Note that the combination of correlation functions here has been derived in quite different fashion than in the Kirkwood–Yvon theory.

Conventionally the correction to the Clausius–Mossotti formula is expressed as

$$\frac{\varepsilon_{\text{eff}} - \varepsilon_1}{\varepsilon_{\text{eff}} + 2\varepsilon_1} = \frac{4\pi}{3\varepsilon_1}(1+S). \tag{8.93}$$

The quantity $S(n,\alpha_1)$ yields the correction to Clausius–Mossotti. In an expansion in powers of α_1 this is the first non-vanishing term of order $\sim \alpha_1^2$. One writes

$$S(n,\alpha_1) = S_2 + O(\alpha_1^3). \tag{8.94}$$

We have found above

$$S_2 = \frac{4\pi}{3\varepsilon_1}\left[\lambda_2^{(1)} + \mu_3^{(1)}(1,3|3,2)\right] n\alpha_1. \tag{8.95}$$

This expression yields the result of Kirkwood and Yvon.
If we take account of only 2-particle contributions we obtain

$$\begin{aligned} S^{(2)}(n,\alpha_1) &= \frac{4\pi}{3\epsilon_1}(\lambda_2 + \mu_2) n\alpha_1 \\ &= 8\pi\, n\alpha_1^2 \int_{2a}^{\infty} dR\, g(R) \frac{R^2}{(\epsilon_1 R^3 - 2\alpha_1)(\epsilon_1 R^3 + \alpha_1)}. \end{aligned} \tag{8.96}$$

This result was first derived by Nijboer [44].

If one expands $S(n,\alpha_1)$ in powers of density n, one obtains the so-called dielectric virial expansion

$$S(n,\alpha_1) = Bn + Cn^2 + \cdots . \tag{8.97}$$

The second virial coefficient B is determined by 2-particle contributions.

From $\lambda_2 + \mu_2$ we find

$$B = 8\pi\alpha_1^2 \int_{2a}^{\infty} dR\, e^{-\beta v(R)} \frac{R^2}{(\varepsilon_1 R^3 - 2\alpha_1)(\varepsilon_1 R^3 + \alpha_1)}, \tag{8.98}$$

where $v(R)$ is the pair interaction potential. The expression is due to Buckingham and Pople [45].

Chapter 9

Spectral representation and computer simulation

The comparison of the theory of the effective dielectric constant with experiments on real systems is not simple. For suspensions it is difficult to make it mono-disperse with well characterized geometrical disorder. For fluids of nonpolar molecules the system is mono-disperse, and the ensemble is rather well known, but in this case there are quantum-mechanical effects causing an additional pair polarizability. It is best to compare with computer simulations. Then one can choose a simple model. For a fluid of hard spheres such simulations were first performed by Cichocki and Felderhof [36].

We return to the deliberations of Chapter 4. There we studied a system of N coupled polarizable dipoles. The dipoles induced in a uniform applied field are given by

$$\boldsymbol{p}_j = \alpha_1 \left[\boldsymbol{E}_0 + \sum_{k \neq j} \boldsymbol{T}_{jk} \cdot \boldsymbol{p}_k \right], \quad j = 1, \ldots, N. \tag{9.1}$$

Equivalently we write

$$\begin{aligned} \mathsf{p} &= (\boldsymbol{p}_1, \ldots, \boldsymbol{p}_N), & \mathsf{E}_0 &= (\boldsymbol{E}_0, \ldots, \boldsymbol{E}_0), \\ \mathsf{p} &= \alpha_1 \left[\mathsf{E}_0 + a^{-3} \mathsf{T} \cdot \mathsf{p} \right], & \mathsf{T}_{j\alpha,k\beta} &= a^3\, T_{jk,\alpha\beta}. \end{aligned} \tag{9.2}$$

The formal solution is

$$\mathsf{p} = a^3 (z\mathsf{I} - \mathsf{T})^{-1} \cdot \mathsf{E}_0, \quad z = a^3/\alpha_1. \tag{9.3}$$

With $\boldsymbol{\lambda} = (\boldsymbol{e}_\lambda, \ldots, \boldsymbol{e}_\lambda)$, $\lambda = x, y, z$ the total induced dipole moment is

$$\boldsymbol{M} = \sum_{j=1}^{N} \boldsymbol{p}_j = \sum_{\lambda} (\boldsymbol{\lambda} \cdot \mathbf{p}) e_\lambda. \tag{9.4}$$

It is given by

$$\boldsymbol{M} = a^3 \boldsymbol{A}(\mathbf{X}) \cdot \boldsymbol{E}_0, \qquad A^{\lambda\mu}(\mathbf{X}) = \boldsymbol{\lambda} \cdot (z\mathbf{I} - \mathbf{T})^{-1} \cdot \boldsymbol{\mu}. \tag{9.5}$$

One defines

$$A(\mathbf{X}) = \frac{1}{3} Tr \boldsymbol{A}(\mathbf{X}). \tag{9.6}$$

This scalar has the value

$$A(\mathbf{X}) = \frac{1}{3} \sum_{\lambda} \boldsymbol{\lambda} \cdot (z\mathbf{I} - \mathbf{T})^{-1} \cdot \boldsymbol{\lambda}. \tag{9.7}$$

Since the real $3N \times 3N$ Matrix $\mathbf{T}$ is symmetrical, it has a complete set of eigenvectors

$$\mathbf{T} \cdot \mathbf{c}_{l\gamma} = \lambda_{l\gamma} \mathbf{c}_{l\gamma}, \tag{9.8}$$

labeled by $l = 1, \ldots, N$, $\gamma = x, y, z$. The eigenvectors $\mathbf{c}_{l\gamma}$ and eigenvalues $\lambda_{l\gamma}$ are real. We can choose the eigenvectors to be orthonormal

$$\mathbf{c}_{k\beta} \cdot \mathbf{c}_{l\gamma} = \delta_{kl} \delta_{\beta\gamma}. \tag{9.9}$$

The completeness relation reads

$$\sum_{l\gamma} c_{j\alpha, l\gamma} \, c_{k\beta, l\gamma} = \delta_{jk} \delta_{\alpha\beta}. \tag{9.10}$$

If one expands the three vectors $\boldsymbol{\lambda}$ in terms of the $\mathbf{c}_{l\gamma}$, one obtains

$$A(\mathbf{X}) = \sum_{l\gamma} \frac{g_{l\gamma}}{z - \lambda_{l\gamma}} \tag{9.11}$$

with positive weights

$$g_{l\gamma} = \frac{1}{3} \sum_{\lambda} (\boldsymbol{\lambda} \cdot c_{l\gamma})^2. \tag{9.12}$$

The response scalar $A(\mathbf{X})$, considered as function of the complex variable $z = a^3/\alpha_1$, therefore has a particular analytical structure: It is a sum of simple poles on the real axis with positive residues. Thus we have proven a *spectral theorem* for $A(\mathbf{X}, z)$. This theorem is very important.

It leads immediately to a similar theorem for the dielectric constant.

In Chapter 4 we considered a large sphere with N dipoles, radius R_0, and volume Ω. By comparison with Maxwell theory one finds in the thermodynamic limit

$$\overline{\boldsymbol{M}_S} = \frac{\varepsilon - 1}{\varepsilon + 2} R_0^3 \boldsymbol{E}_0, \qquad \frac{\varepsilon - 1}{\varepsilon + 2} = \lim_{\substack{N \to \infty \\ \Omega \to \infty}} \frac{4\pi a^3}{3\Omega} < A_S(\mathbf{X}) >_N . \tag{9.13}$$

The index S indicates the sphere geometry. We introduce

$$G_S = 3\frac{\varepsilon - 1}{\varepsilon + 2}. \tag{9.14}$$

Then one has

$$\varepsilon = 1 - G, \tag{9.15}$$

with

$$G = \frac{-G_S}{1 - \frac{1}{3}G_S}, \qquad G_S = \frac{-G}{1 - \frac{1}{3}G}. \tag{9.16}$$

The analytic function $G_S(z)$ is given by

$$G_S(z) = \lim_{\substack{N \to \infty \\ \Omega \to \infty}} \frac{4\pi a^3}{\Omega} < A_S(\mathbf{X}) >_N . \tag{9.17}$$

The above proof yields a spectral theorem for $G_S(z)$. One might expect that in the thermodynamic limit the poles merge into a branch cut.

It follows from the relation

$$G = \frac{-G_S}{1 - \frac{1}{3}G_S} \tag{9.18}$$

that a similar spectral theorem holds for the function G, and therefore also for $\varepsilon = 1 - G$.

We can relate the spectral representation of the function G to a theorem derived by Bergman [14]. He showed that for an arbitrary two-phase medium with dielectric constants ε_1, ε_2 the effective dielectric constant ε_{eff} can be represented by

$$\varepsilon_{\text{eff}} = \varepsilon_1 \left[1 - \int_0^1 \frac{g(u)}{t - u}\, du \right] \tag{9.19}$$

with

$$t = \frac{\varepsilon_1}{\varepsilon_1 - \varepsilon_2} \tag{9.20}$$

and the real positive function $g(u)$, that satisfies the sum rules

$$\int_0^1 g(u)\,du = \phi, \qquad \int_0^1 ug(u)\,du = \frac{1}{3}\phi(1-\phi). \tag{9.21}$$

Here ϕ is the volume fraction of phase 2.

We can establish the relation to our dipolar system by considering a system of spheres of radius a and uniform dielectric constant ε_2 embedded in vacuum ($\varepsilon_1 = 1$). The dipole polarizability of a single sphere is

$$\alpha_1 = \frac{\varepsilon_2 - 1}{\varepsilon_2 + 2} a^3 = \frac{a^3}{1-3t}, \tag{9.22}$$

i.e. for such spheres $z = 1 - 3t$.

Bergman's statement that the weight function $g(u)$ differs from zero only on the interval $0 \le u \le 1$ implies that we must expect that the poles of $G(z)$ are located on the interval $-2 \le \mathrm{Re\ z} \le 1$. Actually we can show that for dipolar systems the interval is even smaller. The corresponding weight function for the dipolar system is denoted by $g_D(u)$. For a system of uniform spheres the Bergman-function can be written as

$$g(u) = g_D(u) + g_M(u) \tag{9.23}$$

where $g_D(u)$ is the contribution of the dipoles, and $g_M(u)$ that of the higher order multipoles. It follows from our spectral theorem that $g_D(u) \ge 0$, like for $g(u)$. Of course for $g_M(u)$ this inequality does not hold necessarily.

It follows from the Kirkwood–Yvon theory that

$$\frac{\varepsilon - 1}{\varepsilon + 2} = \frac{4\pi}{3} n\alpha_1 \left[1 + S_2 + O(\alpha_1^3)\right]. \tag{9.24}$$

Comparing this with the representation

$$\varepsilon = 1 - \int_0^1 \frac{g_D(u)}{t-u}\,du, \tag{9.25}$$

we see that an expansion of ε in powers of α_1 corresponds to an expansion in inverse powers of t. Comparing the first three terms

$$\varepsilon = 1 + 4\pi n\alpha_1 + \frac{1}{3}(4\pi n\alpha_1)^2 + O(\alpha_1^3) \tag{9.26}$$

with

$$\varepsilon = 1 - \frac{1}{t} \int_0^1 g_D(u)\, du - \frac{1}{t^2} \int_0^1 u g_D(u)\, du + O(t^{-3}) \tag{9.27}$$

we find

$$\int_0^1 g_D(u)\, du = \phi, \qquad \int_0^1 u\, g_D(u) du = \frac{1}{3}\phi(1-\phi) \tag{9.28}$$

with $\phi = \frac{4\pi}{3} n a^3$, i.e. both sum rules are exhausted by the dipolar contribution. The higher order multipoles cause only a redistribution consistent with these sum rules.

The simplest way of satisfying the sum rules is to put

$$g(u) = g_D(u) = \phi\delta[u - \frac{1}{3}(1-\phi)]. \tag{9.29}$$

This corresponds to

$$\epsilon = 1 - \frac{\phi}{t - \frac{1}{3}(1-\phi)}, \tag{9.30}$$

or

$$\frac{\epsilon - 1}{\epsilon + 2} = \frac{4\pi}{3} n\alpha_1, \tag{9.31}$$

i.e. to the Clausius–Mossotti formula. The contribution S in the corrected formula

$$\frac{\epsilon - 1}{\epsilon + 2} = \frac{4\pi}{3} n\alpha_1[1 + S] \tag{9.32}$$

leads to a broadening of the spectrum. The precise form of the spectral distribution $g_D(u)$ is determined by the geometric distribution of spheres.

The physical significance of the spectrum becomes evident if one considers the Lorentz-model of an atom. Lorentz regarded an atom as a set of electrons bound harmonically to a nucleus. If one considers only a single electron with oscillation frequency ω_0, then the dynamic polarizability at frequency ω is

$$\alpha_1(\omega) = \frac{e^2}{m(\omega_0^2 - \omega^2)}. \tag{9.33}$$

For N atoms coupled by dipole interaction the equations

$$\boldsymbol{p}_j = \alpha_1(\omega)\Big[\boldsymbol{E}_0 + \sum_{k\neq j} \boldsymbol{T}_{jk} \cdot \boldsymbol{p}_k\Big], \quad j = 1, \ldots, N, \tag{9.34}$$

can be written as

$$-(\omega^2-\omega_0^2)\boldsymbol{p}_{j\omega}=\frac{e^2}{m}\Big[\boldsymbol{E}_{o\omega}+\sum_{k\neq j}\boldsymbol{T}_{jk}\cdot\boldsymbol{p}_{k\omega}\Big],\quad j=1,\ldots,N. \tag{9.35}$$

Therefore the eigenvalues $\lambda_{l\gamma}$ of the matrix $\mathbf{T}$ correspond to the resonance frequencies of the dynamical system as

$$\omega_{l\gamma}^2=\omega_0^2-\frac{e^2}{ma^3}\lambda_{l\gamma}. \tag{9.36}$$

Conversely, the variable u in the spectral density $g_D(u)$ is related to frequency ω by

$$u=\frac{1}{3}+\frac{ma^3}{3e^2}(\omega^2-\omega_0^2). \tag{9.37}$$

In this way the spectral density $g_D(u)$ corresponds directly with the resonance spectrum of the system of coupled harmonic oscillators.

In general the frequency dependent dielectric constant of a system with the property $\varepsilon(\omega)\to 1$ for $\omega\to\infty$ can be written as

$$\epsilon(\omega)=1+4\pi\chi(\omega). \tag{9.38}$$

with the susceptibility $\chi(\omega)$. The susceptibility is a "positive-frequency function", i.e. it can be expressed as the Fourier transform of a memory function

$$\chi(\omega)=\int_0^\infty e^{i\omega t}X(t)dt\quad\text{with } X(t)=0 \text{ for } t<0. \tag{9.39}$$

Hence $\chi(\omega)$ is automatically analytic in the upper half of the complex frequency plane $I_+(\omega)$, and $\chi(\omega)\to 0$ for $\omega\to\infty$ in this half-plane.

Inversion of the Fourier transform yields

$$X(t)=\frac{1}{2\pi}\int_{-\infty}^{\infty}\chi(\omega')e^{-i\omega' t}\,d\omega'. \tag{9.40}$$

Hence

$$\begin{aligned}\chi(\omega)&=\frac{1}{2\pi}\int_0^\infty dt\,e^{i\omega t}\int_{-\infty}^{\infty}\chi(\omega')e^{-i\omega' t}d\omega'\\&=\frac{1}{2\pi i}\int_{-\infty}^{\infty}\frac{\chi(\omega')}{\omega'-\omega}d\omega'\qquad\text{for } \omega\in I_+(\omega).\end{aligned} \tag{9.41}$$

Considering $\omega + i\delta$ with ω real, $\delta > 0$ infinitesimal, we obtain

$$\chi(\omega) = \frac{1}{2\pi i} \int\limits_{-\infty}^{\infty} \frac{\chi(\omega' - \omega)}{\omega' - \omega - i\delta}\, d\omega' \qquad \text{for } \omega \text{ real}, \ \delta > 0. \tag{9.42}$$

One has the symbolic formulae

$$\begin{aligned} \frac{1}{\omega' - \omega - i\delta} &= P\frac{1}{\omega' - \omega} + \pi i \delta(\omega' - \omega), \\ \frac{1}{\omega' - \omega + i\delta} &= P\frac{1}{\omega' - \omega} - \pi i \delta(\omega' - \omega), \end{aligned} \tag{9.43}$$

where P indicates the principal value of an integral, as one sees by integration along the real axis and a small semi-circle near ω.

Taking real and imaginary parts one finds the Kramers–Kronig relations

$$\left.\begin{aligned} \chi'(\omega) &= \frac{1}{\pi} P \int\limits_{-\infty}^{\infty} \frac{\chi''(\omega')}{\omega' - \omega}\, d\omega' \\ \chi''(\omega) &= -\frac{1}{\pi} P \int\limits_{-\infty}^{\infty} \frac{\chi'(\omega')}{\omega' - \omega}\, d\omega' \end{aligned}\right\} \text{for } \omega \text{ real}. \tag{9.44}$$

These important expressions relate real and imaginary part of $\chi(\omega)$. They are an expression of causality, i.e. of the fact that $X(t) = 0$ for $t < 0$, so that $\chi(\omega)$ can be written as $\int\limits_{0}^{\infty} X(t) e^{i\omega t}\, dt$.

We can now find a spectral representation for $\chi(\omega)$. One has

$$\chi(\omega) = \frac{1}{\pi} \int\limits_{-\infty}^{\infty} \frac{\chi''(\omega')}{\omega' - \omega}\, d\omega' \qquad \text{for } \omega \in I_+(\omega). \tag{9.45}$$

The integral is clearly analytic in $I_+(\omega)$, and tends to zero for $\omega \to \infty$ in $I_+(\omega)$. Considering $\omega + i\delta$, with ω real, $\delta > 0$ infinitesimal, one finds the correct values on the real axis. This shows that the integral is a correct representation of the complex function $\chi(\omega)$.

The imaginary part $\chi''(\omega)$ for ω real is related to the absorption, as follows by consideration of the energy. The absorption at frequency ω is given by

$$A(\omega) = \frac{1}{2} \omega \chi''(\omega) \qquad \text{for } \omega \text{ real}. \tag{9.46}$$

The absorption is positive: $A(\omega) \geq 0$ for ω real.

It follows from the reality of the memory function $X(t)$ that

$$\chi'(\omega) = \chi'(-\omega), \qquad \chi''(\omega) = -\chi''(-\omega), \qquad \text{for } \omega \text{ real.} \tag{9.47}$$

Hence the total absorption is given by

$$A_{\text{tot}} = \int_{-\infty}^{\infty} A(\omega)d\omega = \int_{0}^{\infty} \omega\chi''(\omega)d\omega. \tag{9.48}$$

If one knows $A(\omega) = \frac{1}{2}\omega\chi''(\omega)$, one can find $\chi(\omega)$ from the spectral representation. If one knows $\chi(\omega)$ in the upper half-plane, one can find the spectrum from the spectral representation:

$$lim_{\delta\to 0}\,\mathrm{Im}\chi(\omega + i\delta) = \frac{2A(\omega)}{\omega} \qquad \text{for } \omega \text{ real.} \tag{9.49}$$

With the interpretation as Lorentz-oscillators the spectral representation

$$\epsilon(t) = 1 - \int_{0}^{1} \frac{g(u)}{t-u}\,du \tag{9.50}$$

can be regarded as a special case. By the transformation

$$t = \frac{1}{3} + \frac{ma^3}{3e^2}(\omega^2 - \omega_0^2), \tag{9.51}$$

a path along $\omega + i\delta$ (ω real, $\delta > 0$) is transformed into a path in the complex t-plane (see Fig. 9.1)

In our case one finds absorption around ω_0 between

$$\omega_- = \sqrt{\omega_0^2 - \frac{e^2}{ma^3}} \qquad \text{and} \qquad \omega_+ = \sqrt{\omega_0^2 + \frac{2e^2}{ma^3}}. \tag{9.52}$$

The upper half-plane $I_+(\omega)$ is mapped onto the complete complex t-plane with a cut along the real axis from $-\frac{ma^3}{3e^2}\,\omega_0^2 + \frac{1}{3}$ to $+\infty$ (see Fig. (9.1)).

Considering the integral

$$\chi(\omega) = \frac{1}{\pi}\int_{-\infty}^{\infty} \frac{\chi''(\omega')}{\omega' - \omega}\,d\omega', \qquad \text{for } \omega \in I_+(\omega), \tag{9.53}$$

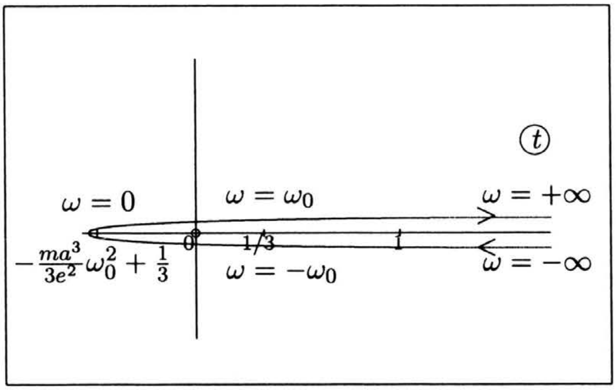

FIGURE 9.1. Real ω-axis mapped into the complex t-plane.

one has

$$\begin{aligned}\chi(\omega) &= \frac{1}{\pi}\int_{-\infty}^{0}\frac{\chi''(\omega')}{\omega'-\omega}\,d\omega' + \frac{1}{\pi}\int_{0}^{\infty}\frac{\chi''(\omega')}{\omega'-\omega}\,d\omega' \\ &= -\frac{1}{\pi}\int_{0}^{\infty}\frac{\chi''(-\omega')}{\omega'+\omega}\,d\omega' + \frac{1}{\pi}\int_{0}^{\infty}\frac{\chi''(\omega')}{\omega'-\omega}\,d\omega' \\ &= \frac{1}{\pi}\int_{0}^{\infty}\chi''(\omega')\left[\frac{1}{\omega'+\omega}+\frac{1}{\omega'-\omega}\right]d\omega' \\ &= \frac{2}{\pi}\int_{0}^{\infty}\frac{\omega'\chi''(\omega')}{\omega'^2-\omega^2}\,d\omega', \qquad \text{for } \omega \in I_+(\omega).\end{aligned} \tag{9.54}$$

In our case

$$\chi(\omega) = \frac{2}{\pi}\int_{\omega_-}^{\omega_+}\frac{\omega'\chi''(\omega')}{\omega'^2-\omega^2}\,d\omega' \qquad \text{for } \omega \in I_+(\omega). \tag{9.55}$$

From

$$\omega^2 = \omega_0^2 + \frac{3e^2}{ma^3}\Big(t-\frac{1}{3}\Big), \qquad \omega'^2 = \omega_0^2 + \frac{3e^2}{ma^3}\Big(u-\frac{1}{3}\Big), \tag{9.56}$$

it follows that

$$2\omega'd\omega' = \frac{3e^2}{ma^3}\,du \tag{9.57}$$

and

$$\omega'^2 - \omega^2 = \frac{3e^2}{ma^3}(u-t), \tag{9.58}$$

so that

$$\chi(\omega) = \frac{1}{\pi}\int_0^1 \frac{\chi''(\omega')}{u-t}\,du. \tag{9.59}$$

Comparison of

$$\varepsilon(t) = 1 - \int_0^1 \frac{g_D(u)}{t-u}\,du \qquad \text{with } \varepsilon = 1 + 4\pi\chi \tag{9.60}$$

yields

$$g_D(u) = 4\chi''\left(\omega' = \sqrt{\omega_0^2 + \frac{3e^2}{ma^3}(u-\frac{1}{3})}\right). \tag{9.61}$$

For the system of Lorentz-oscillators this relation provides the connection between the spectral density $g_D(u)$ and absorption.

In the thermodynamic limit $g_D(u)$ is a function that is fully determined by the geometry. It is interesting to see that in the thermodynamic limit the system of non-dissipative oscillators becomes a dissipative system.

The representation

$$\varepsilon(t) = 1 - \int_0^1 \frac{g_D(u)}{t-u}\,du \tag{9.62}$$

is particularly instructive: If one considers the same geometry with dipole polarizability $\alpha_1(\omega)$, where $\alpha_1(\omega)$ is a positive-frequency function, then the relations

$$z = \frac{a^3}{\alpha_1} = 1 - 3t, \qquad \chi(\omega) = \frac{1}{4\pi}\int_0^1 \frac{g_D(u)}{u-t}\,du \tag{9.63}$$

automatically yield a positive-frequency function $\chi(\omega)$. Clearly the spectral density $g_D(u)$, characterizing the geometry, is the quantity of interest.

From the representation with Lorentz-oscillators we can determine the exact bounds of the spectrum. In the dilute limit all atoms oscillate with frequency ω_0. If one reduces the distances the oscillators get coupled via dipole interaction and the spectrum broadens. The broadening is maximal for dense packing, which is achieved when the dipoles are arranged on the lattice points of the *fcc* lattice. Densely packed spheres on a *fcc* lattice occupy volume fraction $\phi_c = \pi\sqrt{2}/6 \approx 0.74$.

The eigenmodes of coupled oscillators located on the *fcc* lattice are known exactly [46]. The maximal eigenfrequency corresponds to a longitudinal mode with the wavevector $\boldsymbol{q} = \boldsymbol{0}$. The minimal eigenfrequency corresponds to a transverse mode with the wavevector $\boldsymbol{q} = \boldsymbol{0}$.

The Clausius–Mossotti formula is exact for the *fcc* lattice of polarizable point dipoles. It reads:

$$\frac{\varepsilon - 1}{\varepsilon + 2} = \frac{4\pi}{3} n\alpha_1 = \frac{\phi}{z}. \tag{9.64}$$

The longitudinal $\boldsymbol{q} = \boldsymbol{0}$ mode corresponds to $\varepsilon = 0$, the transverse $\boldsymbol{q} = \boldsymbol{0}$ mode corresponds to $\varepsilon = \infty$, as one sees by considering the macroscopic Maxwell equations.

Therefore the extremal values are:

$$z_L = -2\phi_c, \qquad z_T = \phi_c. \tag{9.65}$$

Transformation to the variable u yields

$$u_T = \frac{1}{3}(1 - \phi_c) \approx 0.0865, \qquad u_L = \frac{1}{3}(1 + 2\phi_c) \approx 0.8270. \tag{9.66}$$

We return to the determination of the spectral density $g_D(u)$ by computer simulation. One has

$$\varepsilon = 1 - G, \qquad G = \frac{-G_S}{1 - \frac{1}{3}G_S}, \qquad G_S = \lim_{\substack{N\to\infty \\ \Omega\to\infty}} \frac{4\pi a^3}{\Omega} < A_s >_N . \tag{9.67}$$

In such a simulation one prefers to use periodic boundary conditions in order to avoid boundary effects.

For a system with dipole-dipole interactions an infinite periodical system has no meaning. It is known from Maxwell theory that the macroscopic Maxwell field is determined by the global geometry. For the infinite periodic system the Maxwell field cannot be found.

Nonetheless one can work with periodic boundary conditions by formulating the problem first for finite geometry. We perform the following thought experiment:

One considers a configuration of N_c particles with positions $\boldsymbol{R}_1, \ldots, \boldsymbol{R}_{N_c}$ in a cube $C(L)$ with the edge length L centered at the origin. We consider $\mathcal{N}$ such cubic cells in periodically repeated configuration arranged in such a manner that the total crystal fits precisely inside a large sphere (see Fig. 9.2).

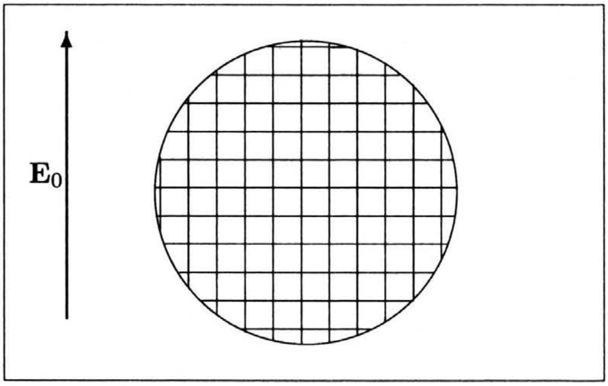

FIGURE 9.2. Geometry envisaged in simulation with periodic boundary conditions.

We apply a uniform external field $\boldsymbol{E}_0$ to this system. It follows from the macroscopic Maxwell theory that the system is polarized uniformly with the polarization $\boldsymbol{P}$ and uniform depolarization field $-\frac{4\pi}{3}\boldsymbol{P}$. This statement is correct disregarding small boundary effects. In the thermodynamic limit the boundary effects disappear.

For a description of the interactions it suffices, on account of periodicity, to consider only the N_c dipoles in the central cube $C(L)$. The dipoles are coupled as

$$\boldsymbol{p}_j = \alpha_1 \left[\boldsymbol{E}_0 + \sum_{k \neq j}^{N_c} \boldsymbol{T}_w\left(\boldsymbol{R}_j - \boldsymbol{R}_k\right) \cdot \boldsymbol{p}_k \right], \qquad j = 1, \dots, N_c, \tag{9.68}$$

where $\boldsymbol{T}_w(\boldsymbol{r})$ is given by the tensor function

$$\boldsymbol{T}_w(\boldsymbol{r}) = \frac{1}{L} \nabla\nabla\, w(\boldsymbol{r}/L) - \frac{4\pi}{3L^3}\mathbf{1}. \tag{9.69}$$

Here $w(\boldsymbol{r})$ is the so-called Wigner potential, i.e. the periodic electrostatic potential of a simple cubic lattice of unit point charges with a uniform neutralizing background. The lattice distance is unity. The additional term $-\frac{4\pi}{3L^3}\,\mathbf{1}$ and the inequality $k \neq j$ originate in the macroscopic sphere geometry. The Wigner potential takes account of the periodic images of the dipoles in the other unit cells [47].

For every configuration $\mathbf{X}_c$ in $C(L)$ one can now define a response scalar $A_c(\mathbf{X}_c)$ as before. In the thermodynamic limit $N_c \to \infty$, $L \to \infty$, at constant

$n = N_c/L_c^3$ one obtains

$$G_S = \lim_{\substack{N_c \to \infty \\ L \to \infty}} \frac{4\pi a^3}{L^3} < A_c >_{N_c} . \tag{9.70}$$

In practice one uses a finite number N_c, about 100 to 500 particles. One averages over an ensemble of configurations. In practice one uses about 200 configurations. So far calculations have been performed for an ensemble of hard spheres, but one could equally well consider a thermal equilibrium ensemble of particles with e.g. Lennard–Jones interactions.

From the exact formula

$$\frac{\varepsilon - 1}{\varepsilon + 2} = \frac{4\pi}{3} n\alpha_1 \, [1 + S], \tag{9.71}$$

it follows that

$$G_S = 3\frac{\varepsilon - 1}{\varepsilon + 2} = 4\pi \, n\alpha_1 \, [1 + S] = \frac{3\phi}{z} \, [1 + S], \qquad z = a^3/\alpha_1. \tag{9.72}$$

We consider the series expansion

$$S(z) = \sum_{j=1}^{\infty} s_j \, z^{-j}. \tag{9.73}$$

As shown before, $s_1 = 0$ on account of isotropy. The coefficient s_2 is related to the coefficient S_2 calculated by Kirkwood and Yvon via $s_2 = \frac{a^6}{\alpha_1^2} \, S_2$.

From the expression

$$A(\mathbf{X}) = \frac{1}{3} \sum_{\lambda} \boldsymbol{\lambda} \cdot (z\mathbf{I} - \mathbf{T})^{-1} \cdot \boldsymbol{\lambda}, \tag{9.74}$$

one finds by series expansion

$$A(\mathbf{X}) = \frac{1}{3z} \sum_{j=0}^{\infty} \sum_{\lambda} \boldsymbol{\lambda} \cdot \mathbf{T}^j \cdot \boldsymbol{\lambda} \, z^{-j}. \tag{9.75}$$

Hence with use of periodic boundary conditions one has exactly

$$s_j = \lim_{\substack{N_c \to \infty \\ L \to \infty}} \frac{1}{3N_c} < \sum_{\lambda} \boldsymbol{\lambda} \cdot \mathbf{T}_w^j \cdot \boldsymbol{\lambda} >_{N_c} . \tag{9.76}$$

In the computer simulation for finite N_c one must apply the interaction matrix $\mathbf{T}_w$ repeatedly, starting with the three vectors $\boldsymbol{\lambda}$. In practice it suffices to calculate s_j up to about $j = 40$, since then asymptotic behavior is achieved.

The asymptotic behavior of the coefficients s_j can be understood from the theory of continued fractions. From the representation

$$\epsilon = 1 - G(t) = 1 - \int_0^1 \frac{g_D(u)}{t-u}\,du, \qquad g_D(u) \geq 0 \tag{9.77}$$

it follows that

$$G(t) = \int_0^1 \frac{g_D(u)}{t-u}\,du \tag{9.78}$$

is a Stieltjes integral.

Stieltjes showed that such a function can be represented by a continued fraction

$$G(t) = \frac{\overline{a}_0}{t+\overline{b}_1-}\,\frac{\overline{a}_1}{t+\overline{b}_2-}\,\frac{\overline{a}_2}{t+\overline{b}_3-}\cdots \tag{9.79}$$

with real coefficients $\{\overline{a}_j, \overline{b}_j\}$.

On account of the sum rules

$$\int_0^1 g_D(u)du = \phi, \qquad \int_0^1 u g_D(u)du = \frac{1}{3}\phi(1-\phi) \tag{9.80}$$

one finds immediately

$$\overline{a}_0 = \phi, \qquad \overline{b}_1 = \frac{1}{3}(1-\phi). \tag{9.81}$$

The higher coefficients can be calculated from the higher moments of the spectral density $g_D(u)$.

Expanding $G(t)$ for large t

$$G(t) = \sum_{j=1}^{\infty} g_j\, t^{-j} \tag{9.82}$$

one has

$$g_j = \int_0^1 u^{j-1}\, g(u)du. \tag{9.83}$$

The coefficients $\{\overline{a}_j, \overline{b}_j\}$ can be calculated from the moments g_j by use of an algorithm due to Stieltjes [48]. From the relation $z = 1 - 3t$ it follows that the continued fraction can be written as function of the variable z as

$$G(z) = \frac{-3\phi}{z-\phi-}\,\frac{a_1}{z+b_2-}\,\frac{a_2}{z+b_3-}\cdots \tag{9.84}$$

with coefficients

$$a_j = 9\overline{a}_j, \qquad b_j = -1 - 3\overline{b}_j. \tag{9.85}$$

From the relation

$$G_S = \frac{-G}{1 - \frac{1}{3}G} \tag{9.86}$$

one finds for the function G_S the corresponding continued fractions

$$G_S = \frac{-\phi}{t - \frac{1}{3} -}\,\frac{\overline{a}_1}{t + \overline{b}_2 -}\,\frac{\overline{a}_2}{t + \overline{b}_3 -}\cdots = \frac{3\phi}{z-}\,\frac{a_1}{z + b_2 -}\,\frac{a_2}{z + b_2 -}\cdots. \tag{9.87}$$

From the coefficients $\{s_j\}$ one finds the coefficients $\{a_j, b_j\}$ by use of the Stieltjes algorithm.

It turns out that the coefficients $\{a_j, b_j\}$ saturate to constant values a_∞, b_∞ at about $j = 10$. If we assume that this corresponds to the exact behavior, then the continued fraction can be calculated precisely. Assuming that one can replace the coefficients of the continued fraction by a_∞, b_∞ starting at level n, we find for the continued fraction starting at level n

$$f_n(z) = \frac{a_\infty}{z + b_\infty - f_n(z)}. \tag{9.88}$$

This equation has the solution:

$$f_n(z) = \frac{1}{2}(z + b_\infty) - \frac{1}{2}\sqrt{(z + b_\infty)^2 - 4a_\infty}. \tag{9.89}$$

The function

$$G_S(z) = \frac{3\phi}{z-}\,\frac{a_1}{z + b_2 -}\cdots\frac{a_{n-1}}{z + b_n - f_n(z)} \tag{9.90}$$

clearly has a branch cut along the real axis between

$$-2\sqrt{a_\infty} - b_\infty < z < 2\sqrt{a_\infty} - b_\infty. \tag{9.91}$$

In the variable t this corresponds to a cut between

$$\frac{1}{3} + \frac{1}{3}b_\infty - \frac{2}{3}\sqrt{a_\infty} < t < \frac{1}{3} + \frac{1}{3}b_\infty + \frac{2}{3}\sqrt{a_\infty}. \tag{9.92}$$

The continued fraction converges everywhere in the complex plane outside the cut. The procedure yields a good approximation to the exact function $G(t)$. Finally one finds the spectral density $g_D(u)$ from the limit

$$g_D(u) = \lim_{\delta\to 0}\frac{1}{\pi}\operatorname{Im} G(u - i\delta). \tag{9.93}$$

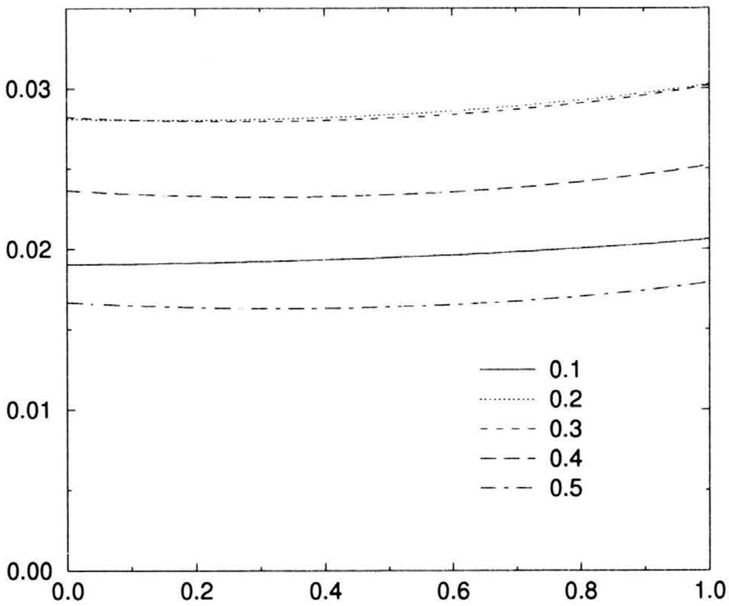

FIGURE 9.3. $a^3 S/\alpha_1^2$ as function of α_1/a^3 for a system of hard spheres with volume fraction $\phi = 0.1, \ldots, 0.5$.

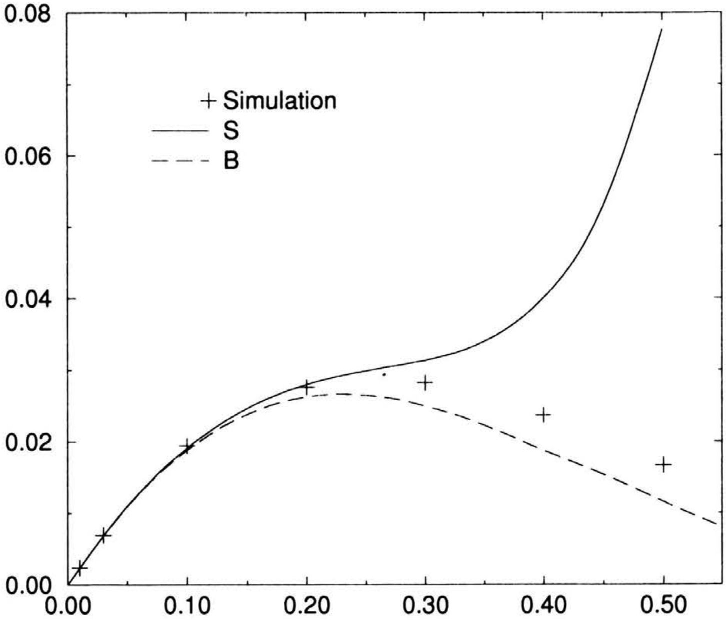

FIGURE 9.4. s_2 for a system of hard spheres as a function of volume fraction ϕ.

From the expression for $G_S(z)$ and the relation $G_S = \frac{3\pi}{z}(1+S)$ one finds values for $S(n, \alpha_1)$ for real values of α_1. The results of simulations are depicted in Fig. 9.3.

It turns out that $a^3 S/\alpha_1^2$ varies only little with α_1/a^3. A good approximation is

$$S \approx \frac{\alpha_1^2}{a^3}\, s_2 = S_2. \tag{9.94}$$

S_2 can be calculated theoretically from the Kirkwood–Yvon integrals. The values for s_2 form the computer simulations are presented in Table 9.1.

TABLE 9.1.

ϕ	0.1	0.2	0.3	0.4	0.4628	0.5
s_2	0.0192	0.0276	0.0282	0.0235	0.0190	0.0160

The value for $\phi = 0.4628$ agrees well with the value ($s_2 = 0.0188$) calculated in 1973 by Alder et al.

Figure 9.4 presents a comparison of the values for s_2 with those calculated theoretically. S means: superposition approximation $g(1,2,3) \approx g(1,2)g(1,3)g(2,3)$ and Percus–Yevick approximation with Verlet–Weis correction for $g(1,2)$. B means: $g(1,2,3)$ as calculated by Blawzdziewicz, Cichocki, and Szamel [37]. In addition one finds spectral functions $g_D(u)$ for several volume fractions. It seems that a self-consistent theory is necessary to explain the spectra [50], at least at low density. At higher density spectra similar to those of crystalline structures have been found [51][52]. The computer simulations have been extended to include quadrupoles [53]. Finally simulations including a sufficient number of multipoles to achieve convergence for a system of uniform spheres have been performed [54, 55, 56].

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