ON ELECTRIC AND MAGNETIC PROPERTIES OF DISPERSIONS OF SPHERES

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PREFACE

Composite materials are of considerable practical importance. This becomes immediately clear when one thinks of such familiar examples as concrete (gravel embedded in cement), paint (pigment particles suspended in a solvent) or ruby glass (gold particles dispersed in glass).

The study of composite materials is a well established branch of statistical physics, reaching back to the work of Faraday, Mossotti and Maxwell (cf. ref. 1 for historical notes). In spite of this long history, however, even apparently rather simple problems from this field are not yet completely understood.

The easiest of these problems is probably the calculation of the effective static dielectric constant of a dispersion. This effective dielectric constant, which describes the dielectric properties of a composite on a coarse length scale on which the material looks homogeneous, has up to now been determined exactly only in the case that the two components of the composite are arranged in plane parallel layers (see e.g. ref. 2). When studying more complicated composites, in which particles of one component are distributed randomly in the other component, one immediately faces the problem that the probability distribution governing the arrangement of the particles is in general not known for real dispersions. The term 'random' alone does not at all suffice to describe the statistical properties of a composite. This was demonstrated very clearly by Hashin and Shtrikman[3], who showed that the bounds which they derived for the effective dielectric constant of a macroscopically homogeneous and isotropic composite can be attained by suitably constructed dispersions: therefore every value of the effective dielectric constant which lies between the bounds can occur in principle. From the fact that the Hashin-Shtrikman bounds depend only on the volume fractions of the components and their dielectric constants, it follows that one cannot do without further information about the statistics of a composite's microgeometry if one wants to calculate its effective dielectric constant.

As long as the difference between the dielectric constants of the components is small, the Hashin-Shtrikman bounds lie very close to each other; in this case, however, the difference between the composite and a pure material is also small. In the more interesting case of components with very different dielectric properties the bounds open up, and the upper bound even becomes infinite for conducting particles embedded in an insulating matrix. Thus in general more information about the structure of a composite than only the volume fractions is needed. Unfortunately, however, this was not always realized: in fact we do not know of any experiment in which at the same time the effective dielectric constant and also correlation functions, describing the statistics of the composite's spatial structure, were measured.

In order to derive explicit results one therefore is forced to consider model dispersions. A particularly popular one is a dispersion of spherical particles which are distributed in the 'most random' fashion, i.e. with equal probabilities for all configurations in which the spheres do not overlap (this is the equilibrium distribution of a hard-sphere fluid). We stress that the specification of the particles' distribution is not less important than that of their form: if the particles are spherical but associated e.g. in dimers, this will as strongly influence the effective dielectric constant as a change of the particle form from spherical to elliptical. The different theories put forward for the effective dielectric constant of a dispersion of spheres are sufficiently flexible to treat also distributions of the spheres different from that in a hard-sphere fluid; they need, however, the corresponding correlation functions as input.

Once the statistical properties of the dispersion are specified, its response to an applied electric field - e.g. the polarization or the potential the polarization gives rise to - must be calculated for a given configuration of the dispersed particles. From the relation between the ensemble average of the response and the applied field one can then deduce an expression for the effective dielectric constant.

Calculation of the electrostatic potential in a dispersion of dielectric particles requires the solution of a many-body interaction problem. For arbitrary shape of the particles this problem is hopelessly difficult, but in the case of spheres one can by consequent multipole expansion obtain a sufficiently explicit yet workable expression for the potential.

Using such an expression together with the knowledge about the distribution of the spheres, one could in principle proceed to evaluate the ensemble average by brute force in a computer experiment. Alternatively one may, guided by physical intuition, try to devise a rapidly converging approximation scheme, which allows to calculate the dominant contributions to the effective dielectric constant with small numerical effort.

One such scheme is the density expansion of the effective dielectric constant in powers of the volume fraction of dispersed spheres. The coefficient of the first order was determined already by Maxwell[4]. The next coefficient, however, which requires the solution of the two-sphere problem, has been calculated only rather recently[5,6]. The first terms of this density expansion should yield a satisfactory description of the effective dielectric constant at low volume fractions, but they are surely insufficient in concentrated dispersions.

In another scheme[7,8,9], developed originally by Kirkwood and Yvon in a somewhat different context, the so-called Clausius-Mossotti function is expanded in powers of the spheres' polarizability. Since just the first non-vanishing order is taken into account, one would only expect the theory to apply when the difference between the dielectric constants of the two components is small.

In addition bounds on the effective dielectric constant of a dispersion of spheres were derived[10,11], using information about the two- and three-particle correlation functions of a hard-sphere fluid. These bounds are appreciably narrower than the Hashin-Shtrikman bounds, yet as the dielectric constant of the inclusions becomes larger and larger, the upper bound still diverges.

In chapter one of this thesis we explore still another approach to the calculation of the effective dielectric constant of a dispersion of spheres. This systematic scheme is neither restricted to dilute dispersions nor to small differences between the dielectric constants of the spheres and the background medium. It rather makes use of the fact that fluctuations of the number density of spheres are small, an idea already used by Bedeaux and Mazur[12] in a molecular theory of a non-polar fluid's dielectric constant. The lowest order of the scheme is equivalent to a mean-field theory. The next non-vanishing order gives a contribution of the second moment of density fluctuations. Its evaluation requires knowledge of only the pair correlation function, which for the hard-sphere fluid has been studied extensively (cf. e.g. ref. 13). This is a major advantage with respect to theories of Kirkwood-Yvon type and the theories yielding bounds, since in these the three-body correlation function, not nearly as well-known as the pair correlation, is indispensable.

Our theory shows that - somewhat surprisingly - the effective dielectric constant of a hard-sphere fluid like dispersion is even for high volume fractions and highly polarizable inclusions well described by the classical Clausius-Mossotti formula. For low volume fractions this fact was already known from the result obtained with the first few terms of the density expansion, which in that domain agrees with our theory. In the correction to the Clausius-Mossotti formula higher-order multipoles turn out to be essential.

We are also able to confirm a conjecture of Stell and Rushbrooke[14)], who supposed that in the Kirkwood-Yvon scheme higher-order terms in the polarizability are never important, although one would naively not expect so when the polarizability of the inclusions is large.

Our theory agrees rather well with recent measurements by van Dijk, Broekman, Joosten and Bedeaux[15)] of the effective dielectric constant of water-in-oil microemulsions at temperatures at which the water droplets do not form clusters. Experiments by Guillien[16)] and by Mettout and Broniatowski[17)] on systems of metal spheres dispersed in an insulator, however, yield much higher values for the effective dielectric constant than predicted by the theory based on the hard-sphere fluid model-distribution. This fact reveals that in practice this model-distribution is often insufficient, and it again underscores the need for quantitative experimental investigations of the spatial correlations in dispersions of spheres.

The second chapter of this thesis treats another aspect of the physics of dispersions, that in contrast to the effective dielectric constant became important only recently[18,19)]. It concerns dispersions of superconducting spheres, which are brought into a metastable superheated state by an external magnetic field. The spheres, made of type I superconductors, are perfectly diamagnetic when superconducting

(Meissner effect) and therefore show strong magnetostatic interactions.

Dispersions of this type are not only interesting from a fundamental point of view, viz. for the study of the phenomenon of superheating itself, but are potentially also of practical importance: it has been suggested that they might be used as detection medium for elementary particles[20] or even for the development of a gamma ray camera for medical applications[21].

The metastable state of a superconducting sphere in such a dispersion is destroyed when the field at its surface becomes greater than a certain threshold value. Clearly, therefore, the maximum field strengths at the surfaces of the spheres are relevant, rather than the polarization of the spheres as in the dielectric problem. This alone already makes the study of superconducting dispersions more difficult than the calculation of the effective dielectric constant, since the maximum field strength at the surface of a sphere depends strongly on higher-order multipoles and its maximum cannot be determined analytically. Furthermore the distribution of the superconducting spheres is not independent of the diamagnetic interactions between them. Due to these interactions some of the spheres already become normal conducting at lower external field strength than others. In general the distribution of the still superconducting spheres therefore differs from that at zero external field strength.

In view of the various specific difficulties occurring in dispersions of superheated superconducting spheres we can only treat the case of dilute dispersions, in the framework of a density expansion. In particular we calculate the fraction of spheres which are superconducting at a given external field strength, as well as the probability distribution for the maximum field strength at the surface of a sphere. As in chapter I, the spheres are assumed to be distributed as in a hard-sphere fluid; the remarks concerning this point made above also apply here.

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CHAPTER I

THE EFFECTIVE DIELECTRIC CONSTANT OF A DISPERSION OF SPHERES

1. Introduction

The effective dielectric constant ε_e of a dispersion of dielectric spheres depends, as is well-known, essentially on the non-additive electrostatic interactions between them. Therefore it is attractive to use as basis of a systematic theory for ε_e a mean-field result, e.g. the familiar Clausius-Mossotti formula, which implicitly takes into account many-body interactions.

In the context of a molecular theory of dielectrics this approach was first pursued by Kirkwood[1] and Yvon[2], and later by de Boer, van der Maesen and ten Seldam[3], who calculated the deviation S of the Clausius-Mossotti formula

$$\frac{\varepsilon_e - 1}{\varepsilon_e + 2} = \frac{4\pi}{3}\,\alpha\, n_o\,(\,1 + S\,)\,. \tag{1.1}$$

Here α is the dipole-polarizability of the molecules and n_o their number density. If one disregards a (for molecules actually important) density dependence of the polarizability and also higher-order multipole-interactions between the molecules, S is just due to correlations between their positions. The above authors expanded S in powers of α and calculated only the lowest non-vanishing order S_2, i.e. the part of S proportional to α^2. In this approximation only two- and three-particle interactions contribute. For the correlation functions needed to perform the averaging the first few terms of their density expansions were employed, which restricted the validity of the results to low concentrations. In 1974, Stell and Rushbrooke[4] overcame this restriction by using for the evaluation of S_2 the Percus-Yevick pair-correlation function together with the Kirkwood superposition approximation as well as a Monte-Carlo result of Alder, Weis and Strauss[5].

A generalization of the Kirkwood-Yvon theory to higher order multipole interactions was given in 1965 by Günther and Heinrich[6], who in a little known paper studied the effective dielectric constant of a dispersion of dielectric spheres (actually these authors did not cite Kirkwood or Yvon and seem to have reinvented implicitly the whole theory). Although they had in mind the description of a system in which the spheres are distributed as in a hard-sphere fluid, they used lattice correlation functions.

Recently also Felderhof[7] independently gave a generalization of the Kirkwood-Yvon theory to higher-order multipole interactions. He evaluated[8] the formula obtained for S_2 by density expansion of the two- and three-particle correlation functions, taking additionally a 'weak-coupling' limit.

All the above theories approximate the deviation S from the Clausius-Mossotti formula by its part S_2, which is of second order in the polarizabilities. Whether this is a good approximation remained an open question. Kirkwood originally took the point of view that it was only valid in a regime where also in the Clausius-Mossotti value for ε_e the order α^2 suffices, which is the case for low concentrations. Later, however, the theory was also applied at higher densities, and Stell and Rushbrooke[4] "believe that the effect [of the terms of order α^3] will always be small".

In this chapter we shall study the effective dielectric constant of a dispersion of dielectric spheres from a somewhat different point of view, using a modification of the fluctuation expansion introduced by Mazur and Bedeaux[9]. In the lowest order of this expansion the microscopic number density of the spheres is replaced by its average. The next order gives a correction which is related to the quantity S of the Kirkwood-Yvon theory, and is due to correlations of density fluctuations which we describe using the Percus-Yevick pair correlation function. Our treatment is not restricted to dipole interactions nor to second order in the polarizabilities. We can explicitly show that the higher orders of the polarizabilities do not contribute significantly to S within the second order of the fluctuation expansion.

The outline of this chapter is as follows. In section 2 we give a solution of the electrostatic potential problem with the aid of electrostatic interaction tensors, called connectors, which are generalizations of the dipole-dipole interaction tensor to higher order multipoles. In section 3 we derive on the basis of this solution a formal expansion of ε_e in terms of density-fluctuation correlation functions of higher and higher order. This expansion requires a continuation of the connector fields for the case of overlapping spheres, which is not uniquely specified by the potential problem. The resulting ambiguity vanishes if all orders of the fluctuation expansion are taken into account; its rate of convergence, however, is influenced by the particular choice for the continuation. In section 4 we perform the fluctuation expansion with a first choice for the connector fields (which we call cut-out connector fields), and calculate the first two nonvanishing orders of the fluctuation expansion. We also give a generalization of the Clausius-Mossotti expression for ε_e to finite wavelengths. The following section deals with another choice of connector fields, which was employed by Beenakker[10)] in his treatment of an analogous hydrodynamic problem. In section 6 a method devised by Beenakker and Mazur[11)] for the resummation of ring self-correlations is applied for both types of connector fields. In the last section the results found in this chapter, in particular the influence of higher-order multipoles and of the choice of connector fields, are summarized and compared to other theories and to experimental results.

2. Formal solution of the potential problem

2.1 Multipole expansion of the electrostatic potential

We consider a collection of uncharged homogeneous dielectric spheres of radius a, sufficiently large to be described by macroscopic electrostatic continuum theory. The spheres have dielectric constant ε_2 and are embedded at positions $\vec{R}_1, \vec{R}_2, \ldots$ in a homogeneous medium with dielectric constant ε_1. An external charge density ρ_{ex} gives rise to an electrostatic potential U. The associated dielectric displacement

$$\vec{D}(\vec{r}) = -\left(\varepsilon_1 + \sum_j (\varepsilon_2-\varepsilon_1)\, \Theta(a-|\vec{r}-\vec{R}_j|)\right) \frac{\partial}{\partial \vec{r}} U(\vec{r}) \; , \tag{2.1}$$

where Θ is the Heaviside function, satisfies

$$\frac{\partial}{\partial \vec{r}} \cdot \vec{D}(\vec{r}) = 4\pi\, \rho_{ex}(\vec{r}) \quad . \tag{2.2}$$

The aim of this second section is to find an expression of the form

$$U(\vec{r}) = \int M(\vec{r},\vec{r}\,')\rho_{ex}(\vec{r}\,')d\vec{r}\,' \quad , \tag{2.3}$$

where the Green function $M(\vec{r},\vec{r}\,')$ is given in terms of the positions of the spheres and the ratio $\varepsilon_2/\varepsilon_1$. To this end we define on each sphere j an induced charge density ρ_j with the Poisson equation

$$-\Delta\, U(\vec{r}) = \frac{4\pi}{\varepsilon_1}\left(\rho_{ex}(\vec{r}) + \sum_j \rho_j(\vec{r})\right) \quad . \tag{2.4}$$

On the other hand one finds from eqs. (2.1) and (2.2)

$$-\Delta\, U(\vec{r}) = \frac{4\pi}{\varepsilon_1}\Big(\rho_{ex}(\vec{r}) + \sum_j \Big\{\Theta(a-|\vec{r}-\vec{R}_j|)\big[\frac{\varepsilon_1}{\varepsilon_2} - 1\big]\,\rho_{ex}(\vec{r})$$

$$+ \frac{\varepsilon_1}{4\pi}\,\delta(a-|\vec{r}-\vec{R}_j|)\big[\lim_{r'\uparrow a} - \lim_{r'\downarrow a}\big]\frac{\partial}{\partial r'}\,U(\vec{R}_j + r'\frac{\vec{r}-\vec{R}_j}{|\vec{r}-\vec{R}_j|})\Big\}\Big) \quad . \tag{2.5}$$

Comparison of eqs. (2.4) and (2.5) shows that ρ_j vanishes outside of sphere j, and that it consists of two parts: a charge density concentrated at the sphere's surface, and a regular part inside the sphere given by

$$\rho_j(\vec{r}) = (\frac{\varepsilon_1}{\varepsilon_2} - 1)\,\rho_{ex}(\vec{r}) \qquad (|\vec{r}-\vec{R}_j| < a) \quad . \tag{2.6}$$

Thus there is no regular part to ρ_j if sphere j contains no external charge.

Next we expand the potential $U(\vec{r})$ in multipole contributions. Consider first a position $\vec{r}$ exterior to all spheres. We use the Taylor expansion

$$\frac{1}{|\vec{r}-\vec{r}\,'|} = \sum_{\ell=0}^{\infty} \frac{1}{\ell!} (-\vec{r}\,')^{\ell} \odot^{\ell} \left(\frac{\partial}{\partial \vec{r}}\right)^{\ell} \frac{1}{r}$$

$$= \sum_{\ell=0}^{\infty} \frac{(2\ell-1)!!}{\ell!} \frac{r'^{\ell}}{r^{\ell+1}} \hat{r}'^{\ell} \odot^{\ell} \overline{\hat{r}^{\ell}} \qquad (r' < r) \quad . \tag{2.7}$$

Here $\hat{r} = \vec{r}/r$ is the unit vector pointing into the direction of $\vec{r}$, and

$$\overline{\hat{r}^{\ell}} \equiv \frac{(-1)^{\ell}}{(2\ell-1)!!} r^{\ell+1} \left(\frac{\partial}{\partial \vec{r}}\right)^{\ell} \frac{1}{r} \qquad (r > 0) \tag{2.8}$$

defines the irreducible part of the ℓ^{th} tensorial power of $\hat{r}$. We call a tensor irreducible if it is symmetric and traceless in all pairs of its indices. The cartesian elements of $\overline{\hat{r}^{\ell}}$, of which $2\ell+1$ are independent, are linear combinations of the spherical harmonics $Y_{\ell}^{-\ell}(\hat{r})$, $Y_{\ell}^{-\ell+1}(\hat{r}), \ldots, Y_{\ell}^{+\ell}(\hat{r})$. A detailed discussion of irreducible tensors is given in appendix A. The symbol $\odot^{\ell}$ between two tensors indicates an ℓ-fold contraction, with the convention that the first index of the second tensor is contracted with the last index of the first tensor, etc. We furthermore use the definitions $(2\ell-1)!! = 1\cdot 3\cdot 5\cdot \ldots \cdot(2\ell-1)$ for $\ell > 1$ and $(-1)!! = 1$.

With eq. (2.7) and the formula (cf. eqs. (A.15),(A.18) of appendix A)

$$\hat{r}'^{\ell} \odot^{\ell} \overline{\hat{r}^{\ell}} = \overline{\hat{r}'^{\ell}} \odot^{\ell} \overline{\hat{r}^{\ell}} \tag{2.9}$$

we find for the solution of eq. (2.4)

$$U(\vec{r}) = \frac{1}{\varepsilon_1} \int \frac{1}{|\vec{r}-\vec{r}\,'|} \rho_{ex}(\vec{r}\,')\, d\vec{r}\,' + \frac{1}{\varepsilon_1} \sum_j \int \frac{1}{|(\vec{r}-\vec{R}_j) - (\vec{r}\,'-\vec{R}_j)|} \rho_j(\vec{r}\,')\, d\vec{r}\,'$$

$$= \frac{1}{a\varepsilon_1} \left\{ \int \frac{a}{|\vec{r}-\vec{r}\,'|} \rho_{ex}(\vec{r}\,') d\vec{r}\,' + \sum_j \sum_{\ell=1}^{\infty} \underline{A}^{(0,\ell)}(\vec{r}-\vec{R}_j) \odot^{\ell} \underline{\rho}_j^{(\ell)} \right\} \quad , \tag{2.10}$$

with connector fields given by

$$\underline{A}^{(0,\ell)}(\vec{R}) \equiv (2\ell-1)!! \left(\frac{a}{R}\right)^{\ell+1} \overline{\hat{R}^{\ell}} \qquad (R > a,\ \ell > 1) \tag{2.11}$$

and charge multipoles

$$\underline{\rho}_j^{(\ell)} \equiv \frac{1}{\ell!\, a^{\ell}} \int \overline{(\vec{r}-\vec{R}_j)^{\ell}}\ \rho_j(\vec{r})\, d\vec{r} \quad . \tag{2.12}$$

Note that the sum in eq. (2.10) begins at $\ell = 1$, since according to eqs. (2.1), (2.2) and (2.4) the monopole moments $\underline{\rho}_j^{(0)}$ vanish, as they should:

$$4\pi \int_{|\vec{r}-\vec{R}_j|<a+0} \rho_{ex}(\vec{r})\, d\vec{r} = \int_{|\vec{r}-\vec{R}_j|=a+0} \hat{n}\cdot\vec{D}(\vec{r})\, ds = -\varepsilon_1 \int_{|\vec{r}-\vec{R}_j|=a+0} \hat{n}\cdot\frac{\partial}{\partial\vec{r}} U(\vec{r})\, ds$$

$$= -\varepsilon_1 \int_{|\vec{r}-\vec{R}_j|<a+0} \Delta U(\vec{r})\, d\vec{r} = 4\pi \int_{|\vec{r}-\vec{R}_j|<a+0} \left(\rho_{ex}(\vec{r})+\rho_j(\vec{r})\right) d\vec{r} \quad . \tag{2.13}$$

In other words, as a consequence of the definition (2.4) of the induced charges, the spheres carry no total charge besides the enclosed external one.

Let us now consider the potential in the case $|\vec{r}-\vec{R}_i| < a$ for a given sphere i. The contribution of ρ_i to $a\varepsilon_1 U(\vec{r})$ is then found to be, using eqs. (2.7) and (2.9),

$$\int \frac{a}{|\vec{r}-\vec{r}\,'|} \rho_i(\vec{r}\,')\, d\vec{r}\,' = \int_{a+0>|\vec{r}\,'-\vec{R}_i|>a-0} \frac{a}{|(\vec{r}-\vec{R}_i)-(\vec{r}\,'-\vec{R}_i)|} \rho_i(\vec{r}\,')\, d\vec{r}\,'$$

$$+ \int_{|\vec{r}\,'-\vec{R}_i|<a-0} \frac{a}{|\vec{r}-\vec{r}\,'|} \rho_i(\vec{r}\,')\, d\vec{r}\,'$$

$$= \sum_{\ell=0}^{\infty} a \frac{(2\ell-1)!!}{\ell!} \overline{(\vec{r}-\vec{R}_i)^{\ell}} \odot^{\ell} \int_{a+0>|\vec{r}\,'-\vec{R}_i|>a-0} a^{-2\ell-1} \overline{(\vec{r}\,'-\vec{R}_i)^{\ell}} \rho_i(\vec{r}\,')\, d\vec{r}\,'$$

$$+ \int_{|\vec{r}\,'-\vec{R}_i|<a-0} \frac{a}{|\vec{r}-\vec{r}\,'|} \rho_i(\vec{r}\,')\, d\vec{r}\,'$$

$$= \sum_{\ell=0}^{\infty} \frac{(2\ell-1)!!}{a^{\ell}} \overline{(\vec{r}-\vec{R}_i)^{\ell}} \odot^{\ell} \frac{1}{\ell!\, a^{\ell}} \int_{a+0>|\vec{R}_i-\vec{r}\,'|} \overline{(\vec{r}\,'-\vec{R}_i)^{\ell}} \rho_i(\vec{r}\,')\, d\vec{r}\,'$$

$$+ \int_{|\vec{r}\,'-\vec{R}_i|<a-0} \Big\{\frac{a}{|\vec{r}-\vec{r}\,'|} - \sum_{\ell=0}^{\infty} \frac{1}{\ell!\, a^{\ell}} \overline{(\vec{r}-\vec{R}_i)^{\ell}}$$

$$\odot^{\ell} (-a)^{-\ell} (2\ell-1)!! \overline{(\vec{R}_i-\vec{r}\,')^{\ell}} \Big\} \rho_i(\vec{r}\,')\, d\vec{r}\,' \quad . \tag{2.14}$$

In the first term of the last member we have extended the integration over the whole sphere and compensated this by subtracting the additional contribution from the second term. We now introduce connector fields for $R < a$ and $\ell \geq 1$ by

$$\underline{A}^{(0,\ell)}(\vec{R}) \equiv \underline{A}^{(\ell,0)}(-\vec{R}) \equiv (2\ell-1)!!\ \left(\frac{R}{a}\right)^{\ell}\ \overline{\hat{R}^{\ell}} \qquad (R < a) \ . \qquad (2.15)$$

Using the definition (2.12) of the charge multipoles, the fact that the induced charge monopole vanishes, and also the relation (2.6) for the regular part of the induced charge densities one obtains

$$\int \frac{a}{|\vec{r}-\vec{r}\,'|}\ \rho_i(\vec{r}\,')\ d\vec{r}\,' = \sum_{\ell=1}^{\infty} \underline{A}^{(0,\ell)}(\vec{r}-\vec{R}_i) \odot^{\ell} \underline{\rho}_i^{(\ell)} +$$

$$+ \left(\frac{\varepsilon_1}{\varepsilon_2}-1\right) \int_{|\vec{r}\,'-\vec{R}_i|<a} \left\{ \frac{a}{|\vec{r}-\vec{r}\,'|} - 1 - \sum_{\ell=1}^{\infty} \frac{1}{\ell!}\, a^{-\ell}\ \overline{(\vec{r}-\vec{R}_i)^{\ell}} \right.$$

$$\left. \odot^{\ell}\ \underline{A}^{(\ell,0)}(\vec{R}_i-\vec{r}\,')\right\}\ \rho_{ex}(\vec{r}\,')\ d\vec{r}\,' \qquad (|\vec{r}-\vec{R}_i| < a) \ . \qquad (2.16)$$

Collecting the results (2.10) and (2.16) one obtains a formula for $U(\vec{r})$ which holds outside as well as inside the spheres:

$$U(\vec{r}) = \frac{1}{\varepsilon_1 a} \left\{ \int \frac{a}{|\vec{r}-\vec{r}\,'|}\ \rho_{ex}(\vec{r}\,')\ d\vec{r}\,' + \sum_j \sum_{\ell=1}^{\infty} \underline{A}^{(0,\ell)}(\vec{r}-\vec{R}_j) \odot^{\ell} \underline{\rho}_j^{(\ell)} \right.$$

$$+ \left(\frac{\varepsilon_1}{\varepsilon_2}-1\right) \sum_j \Theta(a-|\vec{r}-\vec{R}_j|) \int_{|\vec{r}\,'-\vec{R}_j|<a} \left(\frac{a}{|\vec{r}-\vec{r}\,'|} - 1 \right.$$

$$\left. \left. - \sum_{\ell=1}^{\infty} \frac{a^{-\ell}}{\ell!}\ \overline{(\vec{r}-\vec{R}_j)^{\ell}} \odot^{\ell} \underline{A}^{(\ell,0)}(\vec{R}_j-\vec{r}\,')\right) \rho_{ex}(\vec{r}\,')\ d\vec{r}\,' \right\} \ . \qquad (2.17)$$

The presence of the last term in the right member of this equation reflects the well-known fact that the multipoles of a charge distribution alone do not contain sufficient information to describe the potential it produces in those regions of space where the charge distribution is non-zero.

2.2 Determination of the induced charge multipoles

It now rests to find an expression for the multipole moments $\underline{\rho}_i^{(\ell)}$ in terms of the external charge density. This requires the exploitation of the boundary conditions at the spheres' surfaces:

$$\hat{r}\cdot\vec{D}(\vec{R}_i+\vec{r})\Big|_{r=a+0} = -\varepsilon_1 \frac{\partial}{\partial r} U(\vec{R}_i+\vec{r})\Big|_{r=a+0}$$
$$= \hat{r}\cdot\vec{D}(\vec{R}_i+\vec{r})\Big|_{r=a-0} = -\varepsilon_2 \frac{\partial}{\partial r} U(\vec{R}_i+\vec{r})\Big|_{r=a-0} \quad . \tag{2.18}$$

Substitution of formula (2.17) for U into this condition leads after multiplication by $\varepsilon_1 a^2$ and a rearrangement of terms to

$$\sum_{\ell=1}^{\infty} (2\ell-1)!!\ \left(\varepsilon_1(\ell+1)+\varepsilon_2\ell\right)\ \overline{\hat{r}^{\ell}} \odot^{\ell} \underline{\rho}_i^{(\ell)} =$$
$$= (\varepsilon_1-\varepsilon_2)\ a\frac{\partial}{\partial r} \Big\{ \sum_{j\neq i} \sum_{p=1}^{\infty} \underline{A}^{(0,p)}(\vec{r}+\vec{R}_i-\vec{R}_j) \odot^{p} \underline{\rho}_j^{(p)}$$
$$+ \int_{|\vec{r}\,'-\vec{R}_i|>a} \frac{a}{|\vec{r}+\vec{R}_i-\vec{r}\,'|}\ \rho_{ex}(\vec{r}\,')\ d\vec{r}\,'$$
$$+ \sum_{\ell=1}^{\infty} \frac{a^{-\ell}}{\ell!}\ \overline{\vec{r}^{\,\ell}} \odot^{\ell} \int_{|\vec{r}\,'-\vec{R}_i|<a} \underline{A}^{(\ell,0)}(\vec{R}_i-\vec{r}\,')\ \rho_{ex}(\vec{r}\,')\ d\vec{r}\,' \Big\}_{r=a} \ . \tag{2.19}$$

The following step is a Taylor expansion in $\vec{r}$ of the first two terms on the r.h.s. of eq. (2.19). Defining

$$\underline{A}^{(\ell,p)}(\vec{R}) \equiv \left(a\frac{\partial}{\partial\vec{R}}\right)^{\ell} \underline{A}^{(0,p)}(\vec{R}) = \left(a\frac{\partial}{\partial\vec{R}}\right)^{\ell} (-1)^p\ a^{p+1} \left(\frac{\partial}{\partial\vec{R}}\right)^p \frac{1}{R}$$
$$= (-1)^{\ell}\ (2\ell+2p-1)!!\ \left(\frac{a}{R}\right)^{\ell+p+1}\ \overline{\hat{R}^{\ell+p}} \qquad (R > 2a) \tag{2.20}$$

(cf. eqs. (2.11), (2.8)) and

$$\underline{A}^{(\ell,0)}(\vec{R}) \equiv \underline{A}^{(0,\ell)}(-\vec{R}) \qquad \text{for } R > a \text{ and } \ell \geq 1 \tag{2.21}$$

one obtains, using also eq. (2.9),

$$\sum_{\ell=1}^{\infty} (2\ell-1)!! \left(\ell(\varepsilon_1+\varepsilon_2)+\varepsilon_1\right) \overline{\hat{r}^{\ell}} \odot^{\ell} \underline{\rho}_i^{(\ell)} =$$

$$= (\varepsilon_1-\varepsilon_2) \sum_{\ell=1}^{\infty} \frac{a^{-\ell}}{\ell!} \left(a\frac{\partial}{\partial r} \overline{\vec{r}^{\ell}}\right)_{r=a} \odot^{\ell} \Big\{ \sum_{j\neq i} \sum_{p=1}^{\infty} \underline{A}^{(\ell,p)}(\vec{R}_i-\vec{R}_j) \odot^p \underline{\rho}_j^{(p)} +$$

$$\int_{|\vec{r}\,'-\vec{R}_i|>a} \underline{A}^{(\ell,0)}(\vec{R}_i-\vec{r}\,') \, \rho_{ex}(\vec{r}\,') \, d\vec{r}\,' + \int_{|\vec{r}\,'-\vec{R}_i|<a} \underline{A}^{(\ell,0)}(\vec{R}_i-\vec{r}\,') \, \rho_{ex}(\vec{r}\,') \, d\vec{r}\,' \Big\}$$

$$= (\varepsilon_1-\varepsilon_2) \sum_{\ell=1}^{\infty} \frac{\ell}{\ell!} \overline{\hat{r}^{\ell}} \odot^{\ell} \Big\{ \sum_{j\neq i} \sum_{p=1}^{\infty} \underline{A}^{(\ell,p)}(\vec{R}_i-\vec{R}_j) \odot^p \underline{\rho}_j^{(p)}$$

$$+ \int \underline{A}^{(\ell,0)}(\vec{R}_i-\vec{r}\,') \, \rho_{ex}(\vec{r}\,') \, d\vec{r}\,' \Big\} . \tag{2.22}$$

To derive from this equation an expression for a particular multipole moment $\underline{\rho}_i^{(\ell)}$ we employ the orthogonality property (cf. eqs. (A.11)-(A.13))

$$\frac{(2m+1)!!}{4\pi \; m!} \int \overline{\hat{r}^{m}} \; \overline{\hat{r}^{\ell}} \; d\hat{r} = \delta_{\ell,m} \, \underline{\Delta}^{(\ell,\ell)} . \tag{2.23}$$

For $\ell = m$ this equation defines the isotropic tensor $\underline{\Delta}^{(\ell,\ell)}$ of rank 2ℓ, which has the property (see eq. (A.18))

$$\underline{\Delta}^{(\ell,\ell)} \odot^{\ell} \overline{\hat{r}^{\ell}} = \overline{\hat{r}^{\ell}} . \tag{2.24}$$

If we then multiply both sides of eq. (2.22) with $\overline{\hat{r}^{m}} \, 4\pi m!/(2m+1)!!$ and integrate we find, according to eqs. (2.23) and (2.24),

$$\underline{\rho}_i^{(m)} = \beta_m \frac{-1}{m!(2m-1)!!} \Big\{ \int \underline{A}^{(m,0)}(\vec{R}_i-\vec{r}) \, \rho_{ex}(\vec{r}) \, d\vec{r} +$$

$$+ \sum_{j\neq i} \sum_{p=1}^{\infty} \underline{A}^{(m,p)}(\vec{R}_i-\vec{R}_j) \odot^p \underline{\rho}_j^{(p)} \Big\} \quad (i,m=1,2,\ldots) . \tag{2.25}$$

The coefficients β_ℓ are given by

$$\beta_\ell = \frac{\ell\,(\varepsilon_2-\varepsilon_1)}{\ell\,(\varepsilon_2+\varepsilon_1)+\varepsilon_1} \qquad (\ell \geq 1) . \tag{2.26}$$

They are related to the multipole polarizabilities[12] α_ℓ, which connect an induced charge multipole $\underline{\rho}_1^{(\ell)}$ with the ℓ^{th} derivative of the polarizing potential at position $\vec{R}_1$, by

$$\alpha_\ell = \varepsilon_1 \, a^{2\ell+1} \, \beta_\ell \qquad (\ell \geq 1) \, . \tag{2.27}$$

We shall refer to the β_ℓ as reduced polarizabilities. For conducting spheres (i.e. $\varepsilon_2 \to \infty$) all β_ℓ are equal to unity.

Let us furthermore introduce the quantities

$$b_\ell = \beta_\ell \, \frac{-1}{\ell!(2\ell-1)!!} \tag{2.28}$$

and

$$\underline{A}^{(0,0)}(\vec{r}) = \frac{a}{r} \quad . \tag{2.29}$$

With this notation we finally arrive at the desired expression for the Green function $M(\vec{r},\vec{r}\,')$ by inserting the iterative solution of the system of eqs. (2.25) into eq. (2.17) (cf. also eq. (2.3))

$$\begin{aligned} \varepsilon_1 a \, M(\vec{r},\vec{r}\,') = \underline{A}^{(0,0)}(\vec{r}-\vec{r}\,') &+ \sum_{s=1}^{\infty} \sum_{\substack{j_1,\ldots,j_s \\ j_m \neq j_{m-1}}} \sum_{\ell_1,\ldots,\ell_s=1}^{\infty} \{\underline{A}^{(0,\ell_1)}(\vec{r}-\vec{R}_{j_1}) \\ &\odot^{\ell_1} b_{\ell_1} \underline{A}^{(\ell_1,\ell_2)}(\vec{R}_{j_1}-\vec{R}_{j_2}) \odot^{\ell_2} \ldots \odot^{\ell_s} b_{\ell_s} \underline{A}^{(\ell_s,0)}(\vec{R}_{j_s}-\vec{r}\,')\} \\ &+ \left(\frac{\varepsilon_1}{\varepsilon_2}-1\right) \sum_j \Theta(a-|\vec{r}-\vec{R}_j|)\Theta(a-|\vec{R}_j-\vec{r}\,'|) \, \{\underline{A}^{(0,0)}(\vec{r}-\vec{r}\,') - 1 \\ &- \sum_{\ell=1}^{\infty} \frac{a^{-\ell}}{\ell!} \, \overline{(\vec{r}-\vec{R}_j)^\ell} \odot^\ell \underline{A}^{(\ell,0)}(\vec{R}_j-\vec{r}\,')\} \, . \end{aligned} \tag{2.30}$$

Note that our formalism also allows for the case that there is an external charge density inside the volume occupied by the spheres.

Instead of the irreducible tensors $\overline{\hat{r}^\ell}$ we could also have used spherical harmonics, as has been done by Günther and Heinrich[6] and by Felderhof[7]. The difference between both formulations may be compared to the difference between abstract vector notation and a notation using components relative to a given basis.

3. The fluctuation expansion scheme

In order to calculate the effective dielectric constant we perform an ensemble average $\langle \ldots \rangle$ of equation (2.3),

$$\langle U(\vec{r})\rangle = \int \langle M(\vec{r},\vec{r}\,')\rangle \, \rho_{ex}(\vec{r}\,') \, d\vec{r}\,' \quad . \tag{3.1}$$

Since the system is statistically homogeneous and isotropic, the average of the Green function $M(\vec{r},\vec{r}\,')$ depends on $|\vec{r}-\vec{r}\,'|$ only. In Fourier language this means that there is a function $M(k)$ with

$$\langle M(\vec{k},\vec{k}')\rangle = M(k) \, \delta(\vec{k}-\vec{k}') \tag{3.2}$$

and

$$\langle U(\vec{k})\rangle = \int \langle M(\vec{k},\vec{k}')\rangle \, \rho_{ex}(\vec{k}') \, d\vec{k}' = M(k) \, \rho_{ex}(\vec{k}) \quad . \tag{3.3}$$

If, on the other hand, the average dielectric properties of the system can be described by an effective dielectric constant $\varepsilon_e(k)$ one has

$$\langle U(\vec{k})\rangle = \frac{4\pi}{\varepsilon_e(k)\, k^2} \, \rho_{ex}(\vec{k}) \quad . \tag{3.4}$$

Comparison of eqs. (3.3) and (3.4) shows that

$$\frac{1}{\varepsilon_e(k)} = \frac{k^2}{4\pi} M(k) \quad . \tag{3.5}$$

For a fluctuation expansion of $\langle M(\vec{r},\vec{r}\,')\rangle$ we now have to reformulate the Green function in terms of the microscopic density of the spheres

$$n(\vec{r}) = \sum_j \delta(\vec{r}-\vec{R}_j) \quad . \tag{3.6}$$

This density vanishes for all configurations in which two or more spheres overlap. Furthermore we adopt for the connector fields the convention

$$\underline{A}^{(\ell,p)}(\vec{r}) = 0 \qquad \text{for } r < \delta \quad \text{and} \quad \ell,p \geq 1 \tag{3.7}$$

with $\delta \ll a$ an arbitrarily small positive number. We can then write

$$\sum_{\substack{j \\ i\neq j\neq k}} \underline{A}^{(\ell,m)}(\vec{R}_i-\vec{R}_j) \odot^m b_m \underline{A}^{(m,p)}(\vec{R}_j-\vec{R}_k) =$$

$$= \int \underline{A}^{(\ell,m)}(\vec{R}_i-\vec{r}) \odot^m n(\vec{r})\, b_m \underline{A}^{(m,p)}(\vec{r}-\vec{R}_k)\, d\vec{r}$$

$$= \left(\underline{A}^{(\ell,m)} \odot^m n\, b_m \underline{A}^{(m,p)}\right)(\vec{R}_i,\vec{R}_k) \ . \qquad (3.8)$$

In the last member of this equation n and $\underline{A}^{(\ell,m)}$ are understood to be operators with matrixelements

$$n(\vec{r},\vec{r}\,') = n(\vec{r})\, \delta(\vec{r}-\vec{r}\,') \qquad (3.9)$$

$$\underline{A}^{(\ell,m)}(\vec{r},\vec{r}\,') = \underline{A}^{(\ell,m)}(\vec{r}-\vec{r}\,') \ . \qquad (3.10)$$

We thus find from eq. (2.30)

$$\begin{aligned}
\varepsilon_1 a\, M(\vec{r},\vec{r}\,') = &\Big(\underline{A}^{(0,0)} + \sum_{\ell=1}^{\infty} \underline{A}^{(0,\ell)} \odot^{\ell} b_{\ell}\, n\, \underline{A}^{(\ell,0)} + \\
&+ \sum_{\ell_1,\ell_2=1}^{\infty} \underline{A}^{(0,\ell_1)} \odot^{\ell_1} b_{\ell_1} n\, \underline{A}^{(\ell_1,\ell_2)} \odot^{\ell_2} b_{\ell_2} n\, \underline{A}^{(\ell_2,0)} + \dots\Big)(\vec{r},\vec{r}\,') \\
&+ \left(\frac{\varepsilon_1}{\varepsilon_2}-1\right) \int d\vec{r}\,'' \,\Theta(a-|\vec{r}-\vec{r}\,''|)\Theta(a-|\vec{r}\,''-\vec{r}\,'|)\, n(\vec{r}\,'')\Big\{\underline{A}^{(0,0)}(\vec{r}-\vec{r}\,') - 1 \\
&- \sum_{\ell=1}^{\infty} \frac{a^{-\ell}}{\ell!}\, \overline{(\vec{r}-\vec{r}\,'')^{\ell}} \odot^{\ell} \underline{A}^{(\ell,0)}(\vec{r}\,''-\vec{r}\,')\Big\} \ .
\end{aligned} \qquad (3.11)$$

If we furthermore consider the upper indices of $\underline{A}^{(\ell,p)}$ as matrix indices, put

$$\mathcal{A}_{\ell p} \equiv \underline{A}^{(\ell,p)} \ , \qquad (3.12)$$

$$\mathcal{B}_{\ell p} \equiv \underline{A}^{(\ell,\ell)}\, b_{\ell}\, \delta_{\ell,p}\, (1-\delta_{\ell,0}) \ , \qquad (3.13)$$

and define matrix multiplication by

$$(\mathcal{A}\mathcal{A})_{\ell p} = \sum_{m=0}^{\infty} \mathcal{A}_{\ell m} \odot^m \mathcal{A}_{mp} \ , \qquad (3.14)$$

we arrive at the compact notation

$$a\varepsilon_1 \; M(\vec{r},\vec{r}\,') = \left(\mathcal{A} + \mathcal{A}\mathcal{B}\,n\mathcal{A} + \mathcal{A}\mathcal{B}\,n\mathcal{A}\mathcal{B}\,n\mathcal{A} + \ldots\right)_{00}(\vec{r},\vec{r}\,')$$

$$+ \left(\frac{\varepsilon_1}{\varepsilon_2} - 1\right) \int d\vec{r}\,'' \; \Theta(a-|\vec{r}-\vec{r}\,''|)\Theta(a-|\vec{r}\,''-\vec{r}\,'|)\; n(\vec{r}\,'')\; \{\underline{A}^{(0,0)}(\vec{r}-\vec{r}\,') - 1$$

$$- \sum_{\ell=1}^{\infty} \frac{a^{-\ell}}{\ell!} \, \overline{(\vec{r}-\vec{r}\,'')^{\ell}} \odot^{\ell} \underline{A}^{(\ell,0)}(\vec{r}\,''-\vec{r}\,')\} \; . \quad (3.15)$$

The geometric series on the r.h.s. can be summed, and the average Green function then takes the form

$$a\varepsilon_1\langle M(\vec{r},\vec{r}\,')\rangle = \langle(\{1 - \mathcal{A}\mathcal{B}n\}^{-1}\mathcal{A})_{00}(\vec{r},\vec{r}\,')\rangle + \phi\left(\frac{\varepsilon_1}{\varepsilon_2} - 1\right)K(\vec{r}-\vec{r}\,') \; . \quad (3.16)$$

Here $\phi = n_o 4\pi a^3/3 = \langle n(\vec{r})\rangle\, 4\pi a^3/3$ is the volume fraction occupied by the spheres, and the dimensionless function K is given by

$$K(\vec{r}-\vec{r}\,') = \frac{3}{4\pi a^3} \int d\vec{r}\,'' \; \Theta(a-|\vec{r}-\vec{r}\,''|)\Theta(a-|\vec{r}\,''-\vec{r}\,'|) \; \{\underline{A}^{(0,0)}(\vec{r}-\vec{r}\,') - 1$$

$$- \sum_{\ell=1}^{\infty} \frac{a^{-\ell}}{\ell!} \, \overline{(\vec{r}-\vec{r}\,'')^{\ell}} \odot^{\ell} \underline{A}^{(\ell,0)}(\vec{r}\,''-\vec{r}\,')\} \; . \quad (3.17)$$

Formula (3.16) is the starting point of our expansion of the effective dielectric constant in density fluctuations $\delta n(\vec{r}) \equiv n(\vec{r}) - n_o$. The second term on the r.h.s. depends only on the average density n_o, while the first term also depends on δn and may be expanded in powers thereof. Introducing the renormalized connector field

$$\mathcal{R} = \{1 - \mathcal{A}\mathcal{B}n_o\}^{-1}\mathcal{A} \quad (3.18)$$

one has

$$\langle\{1 - \mathcal{A}\mathcal{B}n\}^{-1}\mathcal{A}\rangle = \langle\{[1 - \mathcal{A}\mathcal{B}n_o] - \mathcal{A}\mathcal{B}\delta n\}^{-1}\mathcal{A}\rangle$$

$$= \langle\{[1 - \mathcal{A}\mathcal{B}n_o](1 - [1 - \mathcal{A}\mathcal{B}n_o]^{-1}\mathcal{A}\mathcal{B}\delta n)\}^{-1}\mathcal{A}\rangle = \langle\{1 - \mathcal{R}\mathcal{B}\delta n\}^{-1}\mathcal{R}\rangle$$

$$= \mathcal{R} + \mathcal{R}\mathcal{B}\langle\delta n\,\mathcal{R}\mathcal{B}\,\delta n\rangle\mathcal{R} + \text{terms containing higher order moments of density fluctuations} \; . \quad (3.19)$$

The equations (3.5), (3.15) and (3.19) together lead to the fluctuation expansion of the inverse of the effective dielectric constant

$$\varepsilon_1/\varepsilon_e(k) \equiv \lambda(k) = \lambda^{(0)}(k) + \lambda^{(2)}(k) + \ldots \tag{3.20}$$

$$\lambda^{(0)}(k)\ \delta(\vec{k}-\vec{k}') = \frac{k^2}{4\pi a}\left\{\mathcal{R}_{00}(\vec{k},\vec{k}') + \delta(\vec{k}-\vec{k}')\phi\left(\frac{\varepsilon_1}{\varepsilon_2} - 1\right)K(\vec{k})\right\} \tag{3.21}$$

$$\lambda^{(2)}(k)\ \delta(\vec{k}-\vec{k}') = \frac{k^2}{4\pi a}\left(\mathcal{R}\,\mathcal{B}\langle\delta n\,\mathcal{R}\,\mathcal{B}\,\delta n\rangle\mathcal{R}\right)_{00}(\vec{k},\vec{k}')\ . \tag{3.22}$$

The upper index of $\lambda^{(j)}$ indicates the order in the fluctuation expansion. The equivalent expansion of the effective dielectric constant itself reads

$$\varepsilon_e(k) = \varepsilon_e^{(0)}(k) + \varepsilon_e^{(2)}(k) + \ldots = \frac{\varepsilon_1}{\lambda^{(0)}(k)}\left\{1 - \frac{\lambda^{(2)}(k)}{\lambda^{(0)}(k)} + \ldots\right\}\ . \tag{3.23}$$

We now have to discuss an important technical point concerning the definition of the renormalized connector fields. Since in (3.18) the actual microscopic density $n(\vec{r})$ is replaced by the average density n_o, the situation of overlapping spheres is no longer excluded. The integrations occurring in the calculation of $\underline{R}^{(\ell,p)}(\vec{r},\vec{r}')$,

$$\underline{R}^{(\ell,p)}(\vec{r},\vec{r}') = \underline{A}^{(\ell,p)}(\vec{r}-\vec{r}') +$$

$$+ \sum_{m=1}^{\infty} \int d\vec{r}_1\ \underline{A}^{(\ell,m)}(\vec{r}-\vec{r}_1) \odot^m b_m n_o\ \underline{A}^{(m,p)}(\vec{r}_1-\vec{r}') + \ldots \tag{3.24}$$

extend over the entire space, so that we also have to define $\underline{A}^{(\ell,p)}(\vec{r})$ for $r < 2a$ in the case $\ell,p \geq 1$. We recall that this quantity was only determined uniquely by the potential problem for $r > 2a$, cf. eq. (2.20). For $r < 2a$ one is free to choose any continuation of $\underline{A}^{(\ell,p)}(\vec{r})$ which satisfies condition (3.7). If one calculates λ exactly, or equivalently, if one takes into account all orders of the fluctuation expansion, all continuations must yield the same result. Each term of the expansion (3.20) separately, however, does depend on the choice made, and so does the rate of convergence of the expansion.

The perhaps most obvious choice is

$$\underline{C}^{(\ell,p)}(\vec{R}) \equiv \begin{cases} \underline{A}^{(\ell,p)}(\vec{R}) & \text{for } \ell=0 \text{ and/or } p=0 \text{ and all } R \\ \underline{A}^{(\ell,p)}(\vec{R}) & \text{for } \ell,p \geq 1 \text{ and } R > 2a \\ 0 & \text{for } \ell,p \geq 1 \text{ and } R < 2a \end{cases} \tag{3.25}$$

This choice incorporates in the connector fields as much information as possible about the distribution of the spheres. The connector fields given by eq. (3.25), to which we shall refer as the cut-out (C) connector fields*), lead in zeroth order of the fluctuation expansion to the Clausius-Mossotti result for ε_e.

A different continuation was used by C.Beenakker[10] in his theory of the effective viscosity of a suspension, a problem closely related to ours from a mathematical point of view. These connector fields, called factorizing (F) connector fields here, give in zeroth order of the fluctuation expansion $\varepsilon_1/\varepsilon_e$ up to linear order in the volume fraction (cf. sec. 5). They have the advantage of considerably simplifying the calculation of the renormalized connector fields.

4. Fluctuation expansion with cut-out connector fields

4.1 Renormalized cut-out connector fields

In sections 4.2 and 4.3 we shall determine the coefficients $\lambda^{(0)}$ and $\lambda^{(2)}$, as given in eqs. (3.21) and (3.22), using the cut-out connector fields defined in eq. (3.25). This first requires the evaluation of the renormalized connector fields in Fourier representation $\underline{R}_C^{(\ell,p)}(\vec{k},\vec{k}') = \underline{R}_C^{(\ell,p)}(\vec{k})\, \delta(\vec{k}-\vec{k}')$ (the index C reminds of the fact that we work with cut-out connector fields). According to eq. (3.18) they satisfy

$$\underline{R}_C^{(\ell,p)}(\vec{k}) = \underline{C}^{(\ell,p)}(\vec{k}) + n_o \sum_{m=1}^{\infty} \underline{C}^{(\ell,m)}(\vec{k})\, b_m \odot^m \underline{R}_C^{(m,p)}(\vec{k}) \; . \tag{4.1}$$

*) Note that the term "cut-out connector field" is used with a different meaning in ref. 10.

In order to solve equation (4.1) we need the Fourier-transforms $\underline{C}^{(\ell,p)}(\vec{k})$ of the cut-out connector fields. In appendix B we show that these are

$$\underline{C}^{(\ell,p)}(\vec{k}) = \int d\vec{r}\; e^{-i\vec{k}\cdot\vec{r}}\; \underline{C}^{(\ell,p)}(\vec{r})$$

$$= i^{\ell-p}\,\frac{4\pi a^3}{3}\,(2\ell+2p-1)!!\,\frac{\ell!\,p!}{(\ell+p)!}\,c_{\ell p}(ka)\,\overline{\hat{k}^{\ell+p}} \tag{4.2}$$

with scalar coefficients $c_{\ell p}$ given by

$$c_{\ell p}(x) = \begin{cases} \dfrac{(\ell+p)!}{\ell!\,p!}\,\dfrac{12}{2^{\ell+p}}\,\dfrac{j_{\ell+p-1}(2x)}{2x} & \text{for } \ell,p \geqq 1\,, \\[2ex] = c_{p0}(x) = 3(2p+1)\,j_p(x)/x^2 & \text{for } \ell = 0 \text{ and } p \geqq 1\,, \\[2ex] 3/x^2 & \text{for } \ell = p = 0\,. \end{cases} \tag{4.3}$$

Here j_ℓ denotes the spherical Bessel function[13] of order ℓ. Note that

$$c_{\ell p}(x) = \mathcal{O}(x^{\ell+p-2}) \quad \text{for } x \ll 1 \text{ and all } \ell,p, \tag{4.4}$$

because

$$j_\ell(x) = x^\ell/(2\ell+1)!! + \mathcal{O}(x^{\ell+2}) \quad \text{for } x \ll 1\,. \tag{4.5}$$

Inserting the result (4.2) into eq. (4.1) one obtains

$$\underline{R}_C^{(\ell,p)}(\vec{k}) = i^{\ell-p}\,\frac{4\pi}{3}\,a^3\,(2\ell+2p-1)!!\,\frac{\ell!\,p!}{(\ell+p)!}\,c_{\ell p}(ka)\,\overline{\hat{k}^{\ell+p}}$$

$$-\,\phi\sum_{m=1}^{\infty} i^{\ell-m}\,\frac{(2\ell+2m-1)!!\,\ell!}{(\ell+m)!\,(2m-1)!!}\,\beta_m\,c_{\ell m}(ka)\,\overline{\hat{k}^{\ell+m}}\odot^m \underline{R}_C^{(m,p)}(\vec{k})\,. \tag{4.6}$$

To proceed we have to make some remarks about the tensorial structure of $\underline{R}^{(\ell,p)}(\vec{k})$. From eq. (2.8) it is clear that $\overline{\hat{k}^j}$ is built-up exclusively from combinations of $\hat{k}$ and the unit tensor $\underline{1}$ of rank 2. Considering the iterative solution of eq. (4.6) one may convince oneself that the same is true for $\underline{R}_C^{(\ell,p)}(\vec{k})$, and that this tensor is furthermore irreducible in its first ℓ and its last p indices. It therefore is a linear combination of terms of the form

$$\overline{\hat{k}^{\ell-j}}\llcorner j \lrcorner\overline{\hat{k}^{p-j}} \equiv \underline{\Delta}^{(\ell,\ell)} \odot^{\ell}\left(\hat{k}^{\ell-j} \llcorner j \lrcorner \hat{k}^{p-j}\right) \odot^{p} \underline{\Delta}^{(p,p)} , \tag{4.7}$$

where the tensor $\llcorner j \lrcorner$ of rank $2j$ has components

$$(\llcorner j \lrcorner)_{\alpha_1\alpha_2\ldots\alpha_j\beta_j\beta_{j-1}\ldots\beta_1} = \delta_{\alpha_1\beta_1}\,\delta_{\alpha_2\beta_2}\ldots\delta_{\alpha_j\beta_j} . \tag{4.8}$$

Under permutations of the indices of the tensor between brackets in expression (4.7) this expression either remains invariant or vanishes, since the $\underline{\Delta}$ tensors with which the term between brackets is contracted form both sides are symmetric and traceless. Consequently tensors of the form (4.7) are the most general ones that satisfy our conditions, and we may write

$$\underline{R}_C^{(\ell,p)}(\vec{k}) = r_0^{\ell p}(k)\,\overline{\hat{k}^{\ell}}\,\overline{\hat{k}^{p}} + r_1^{\ell p}(k)\,\overline{\hat{k}^{\ell-1}}\llcorner 1 \lrcorner\overline{\hat{k}^{p-1}}$$

$$+ r_2^{\ell p}(k)\,\overline{\hat{k}^{\ell-2}}\llcorner 2 \lrcorner\overline{\hat{k}^{p-2}} + \ldots \tag{4.9}$$

where the scalar coefficients $r_j^{\ell p}(k)$ vanish for $j > \ell$ or $j > p$.

4.2 Zeroth order of the fluctuation expansion

We now turn to the evaluation of the zeroth order of the fluctation expansion, for which we need to know the 0,0 element of the renormalized connector field (cf. eq.(3.21)). Inserting eq. (4.9) into eq. (4.6) for $p = 0$ we find

$$r_0^{\ell 0}(k)\,\overline{\hat{k}^{\ell}} = i^{\ell}\,\frac{4\pi}{3}\,a^3\,(2\ell-1)!!\;c_{\ell 0}(ka)\,\overline{\hat{k}^{\ell}}$$

$$-\,\phi\sum_{m=1}^{\infty} i^{\ell-m}\,\frac{(2\ell+2m-1)!!\;\ell!}{(\ell+m)!(2m-1)!!}\,\beta_m\,c_{\ell m}(ka)\,\overline{\hat{k}^{\ell+m}}\odot^{m}\overline{\hat{k}^{m}}\,r_0^{m0}(k) . \tag{4.10}$$

The tensor contraction can easily be performed (cf. eqs. (A.22), (A.4))

$$\overline{\hat{k}^{\ell+m}} \odot^m \overline{\hat{k}^m} = (\overline{\hat{k}^{\ell+m}} \cdot \hat{k}) \odot^{m-1} \hat{k}^{m-1} = \frac{\ell+m}{2\ell+2m-1} \overline{\hat{k}^{\ell+m-1}} \odot^{m-1} \hat{k}^{m-1}$$

$$= \frac{(\ell+m)!}{(2\ell+2m-1)!!} \frac{(2\ell-1)!!}{\ell!} \overline{\hat{k}^{\ell}} , \tag{4.11}$$

so that eq. (4.10) reduces to

$$\left\{\frac{i^{-\ell}}{(2\ell-1)!!} r_0^{\ell 0}(k)\right\} = \frac{4\pi}{3} a^3 c_{\ell 0}(ka)$$

$$- \phi \sum_{m=1}^{\infty} c_{\ell m}(ka) \beta_m \left\{\frac{i^{-m}}{(2m-1)!!} r_0^{m0}(ka)\right\} . \tag{4.12}$$

$r_0^{00}(k)$, the quantity which we need for the evaluation of $\lambda^{(0)}$, can thus in matrix notation be written as

$$r_0^{00}(k) = \frac{4\pi}{3} a^3 \left\{\left(1 + \phi c(ka)\cdot\beta\right)^{-1} \cdot c(ka)\right\}_{00} , \tag{4.13}$$

with the matrix β given by

$$\beta_{\ell m} = \delta_{\ell,m} (1-\delta_{\ell,0}) \beta_\ell . \tag{4.14}$$

Before discussing the general case let us first calculate $\lambda^{(0)}$ in the limit of infinite wavelength. In this limit one obtains from eqs. (3.21) and (4.13)

$$\lambda_C^{(0)}(0) = \lim_{k\to 0} \frac{k^2}{4\pi a} \left\{\underline{R}_C^{(0,0)}(\vec{k}) + \phi \left(\frac{\varepsilon_1}{\varepsilon_2} - 1\right) K(\vec{k})\right\}$$

$$= \lim_{k\to 0} \frac{(ka)^2}{3} \left\{c(ka) - \phi\, c(ka)\cdot\beta\cdot\left(1 + \phi c(ka)\cdot\beta\right)^{-1}\cdot c(ka)\right\}_{00}$$

$$= \frac{1}{3} \lim_{x\to 0} \left\{x^2 c_{00}(x) - \phi x c_{01}(x)\beta_1 \frac{1}{1 + \phi c_{11}(x)\beta_1} x c_{10}(x)\right\}$$

$$= \frac{1 - \phi\beta_1}{1 + 2\phi\beta_1} . \tag{4.15}$$

Note that $k^2 K(\vec{k})$ vanishes for $k \to 0$ since $K(\vec{r})$ is absolutely integrable. Also, because of the behaviour (4.4) of the $c_{\ell p}(ka)$ for small k, only the dipole moment contributes to $\lambda_C^{(0)}(0)$.

The effective dielectric constant given by eq. (4.15) is just the well-known Clausius-Mossotti expression ε_{CM}:

$$\varepsilon_{eC}^{(0)}(0) = \frac{\varepsilon_1}{\lambda_C^{(0)}(0)} = \varepsilon_1 \frac{1 + 2\phi\beta_1}{1 - \phi\beta_1} = \varepsilon_{CM} , \tag{4.16a}$$

perhaps more familiar in the form

$$\frac{\varepsilon_{CM} - \varepsilon_1}{\varepsilon_{CM} + 2\varepsilon_1} = \phi \frac{\varepsilon_2 - \varepsilon_1}{\varepsilon_2 + 2\varepsilon_1} . \tag{4.16b}$$

We may therefore consider $\varepsilon_1/\lambda_C^{(0)}(k)$ as the generalization of the Clausius-Mossotti value for the effective dielectric constant to non-zero wave vectors.

We shall now evaluate this quantity. The necessary calculation of the Fourier transform $K(\vec{k})$ of the function $K(\vec{r})$ is performed in appendix B, where we show that

$$K(\vec{k}) = \frac{4\pi a}{k^2} \left(1 - 3 \frac{j_1(2ka)}{2ka} + 3\, j_0^2(ka) - 3 \frac{\mathrm{Si}(2ka)}{2ka}\right) . \tag{4.17}$$

Here Si(x) denotes the sine integral[13] of x. Insertion into (3.21) yields

$$\varepsilon_1/\varepsilon_{eC}^{(0)}(k) = \lambda_C^{(0)}(k) = \frac{(ka)^2}{3} \left[(1 + \phi c(ka)\cdot\beta)^{-1}\cdot c(ka)\right]_{00}$$
$$+ \phi\, (\varepsilon_1/\varepsilon_2 - 1) \left(1 - 3 \frac{j_1(2ka)}{2ka} + 3\, j_0^2(ka) - 3 \frac{\mathrm{Si}(2ka)}{2ka}\right) . \tag{4.18}$$

Fig. 1 shows values of $\lambda_C^{(0)}(k)$ calculated with this formula for conducting spheres, $\beta_j = 1$, and wave vectors in the range $0 < ka < 10$. In the numerical evaluation the infinite matrices c and β were approximated by finite ones, neglecting charge multipoles of order L + 1 and higher. The number L of multipoles needed to achieve a prescribed accuracy increases with wave number and volume fraction. To give an idea of the rate of convergence with respect to L values of $\lambda_C^{(0)}(10)$, calculated with L = 1,...,16, are listed in table 1.

In the limit of vanishing wavelength formula (4.18) leads to

$$\lim_{k\to\infty} 1/\varepsilon_{eC}^{(0)}(k) = \frac{1-\phi}{\varepsilon_1} + \frac{\phi}{\varepsilon_2} . \tag{4.19}$$

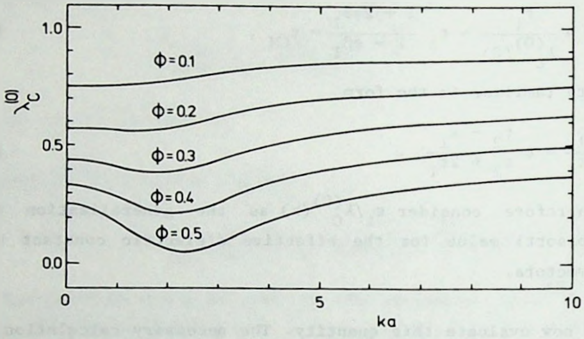


Fig. 1: The zeroth order of the fluctuation expansion with C connector fields and conducting spheres as function of the wavenumber k for different values of the volume fraction ϕ.

L	1	4	7	10	13	16
$\lambda_C^{(0)}(10)$	0.6876	0.6739	0.6304	0.5113	0.5010	0.5009

Table 1: The zeroth order of the fluctuation expansion for conducting spheres at ka = 10 and ϕ = 0.4 as function of the number L of multipoles taken into account.

L	$\lambda_C^{(2)}(0)$	$\lambda_F^{(2)}(0)$
1	-0.0103	-0.114
2	-0.0161	-0.129
3	-0.0187	-0.136
4	-0.0201	-0.139
5	-0.0206	-0.141
6	-0.0208	-0.142
7	-0.0208	-0.143
∞		-0.145

Table 2: The second order of the fluctuation expansion for conducting spheres at ka = 0 and ϕ = 0.4 as function of the number L of multipoles taken into account.

This is what can be expected on the basis of considerations of a physical nature, as argued by Felderhof, Ford and Cohen[14]. These authors also gave an extension of the Clausius-Mossotti formula to finite wavelengths. They start from a cluster-expansion of the effective dielectric constant, identify the terms that lead to the Clausius-Mossotti formula for infinite wavelength, and use the same terms of the cluster-expansion to define the generalization of the Clausius-Mossotti formula to finite wavelengths. They do, however, consider 'polarizable point' inclusions instead of homogeneous spheres, i.e. they consider a dispersion of spheres of radius a which have the background dielectric constant but contain in the centre a point-dipole of polarizability α. To derive their result (for the longitudinal dielectric constant) as a special case of ours we first have to set $\beta_1 = \alpha/(\varepsilon_1 a^3)$ and $\beta_\ell = 0$ for $\ell \geq 2$, since there are no higher order charge multipoles in the polarizable point model. The r.h.s. of eq. (4.18) then becomes

$$1 - \frac{4\pi\alpha}{9\varepsilon_1} n_o \, ka \, c_{01}(ka) \left(1 + \frac{4\pi\alpha}{3\varepsilon_1} n_o c_{11}(ka)\right)^{-1} c_{10}(ka) \, ka$$
$$+ \frac{4\pi}{3} a^3 n_o \left(\frac{\varepsilon_1}{\varepsilon_2} - 1\right)\left(1 - 3\frac{j_1(2ka)}{2ka} + 3j_0^2(ka) - 3\frac{\mathrm{Si}(2ka)}{2ka}\right) . \qquad (4.20)$$

Next we recall that the radius a entered $c_{11}(ka)$ because of our definition of cut-out connectors (cf. eqs. (3.25), (B.1), (4.2) and (4.3)), which partly took into account the impenetrability of the spheres. Everywhere else in eq. (4.20) the radius a is due to the dielectric discontinuity on the surfaces of the spheres. To obtain the polarizable point model, in which the dielectric properties of the dispersion are uniform except in the centres of the spheres, we therefore have to take the limit $a \to 0$ in eq. (4.20) everywhere but in $c_{11}(ka)$. The result that we then find is

$$\left(\varepsilon_e^{(0)}(k)\right)_{\mathrm{pol.point}} = \varepsilon_1 + \frac{4\pi n_o \alpha}{1 - 4\pi n_o(\alpha/\varepsilon_1)\left(1 - 2j_1(2ka)/(2ka)\right)} . \qquad (4.21)$$

This expression corresponds precisely to formula (4.9) of reference 14.

4.3 Second order of the fluctuation expansion

Let us now turn to the determination of $\lambda_C^{(2)}$, the second order term of the fluctuation expansion. It gives corrections to the Clausius-Mossotti formula due to the correlations

$$\langle\delta n(\vec r)\delta n(\vec r\,')\rangle = n_o\delta(\vec r-\vec r\,') + n_o^2\left(g_2(|\vec r-\vec r\,'|) - 1\right) \quad . \tag{4.22}$$

of density fluctuations. The first part on the r.h.s. is a contribution of self correlations and the second one a contribution of pair correlations, described by the pair correlation function g_2.

With eq. (4.22) one obtains from eq. (3.22)

$$\lambda_C^{(2)}(k)\,\delta(\vec k-\vec k\,') = \frac{k^2}{4\pi a}(2\pi)^{-3}\int d\vec r\int d\vec r\,' e^{-i\vec k\cdot\vec r+i\vec k\,'\cdot\vec r\,'}\sum_{\ell,p=1}^{\infty}\{\int d\vec r_1\int d\vec r_2$$

$$\underline{R}_C^{(0,\ell)}(\vec r-\vec r_1)\odot^{\ell} b_\ell \langle\delta n(\vec r_1)\,\underline{R}_C^{(\ell,p)}(\vec r_1-\vec r_2)\,\delta n(\vec r_2)\rangle\odot^{p} b_p\,\underline{R}_C^{(p,0)}(\vec r_2-\vec r\,')\}$$

$$= \delta(\vec k-\vec k\,')\frac{1}{4\pi a}\sum_{\ell,p=1}^{\infty} k\,\underline{R}_C^{(0,\ell)}(\vec k)\odot^{\ell} b_\ell\int d\vec r\, e^{-i\vec k\cdot\vec r}\,\underline{R}_C^{(\ell,p)}(\vec r)\,\{n_o\delta(\vec r)$$

$$+ n_o^2(g_2(r)-1)\}\odot^{p} b_p\,\underline{R}_C^{(p,0)}(\vec k)\,k\ . \tag{4.23}$$

We restrict the evaluation of $\lambda_C^{(2)}(k)$ to the infinite wavelength limit. In this case eq. (4.23) greatly simplifies, since according to eq. (4.4) only renormalized dipole interactions then contribute:

$$\lim_{k\to 0} k\,\underline{R}_C^{(\ell,0)}(\vec k) = -\lim_{k\to 0} k\,\underline{R}_C^{(0,\ell)}(\vec k) = i\,\frac{4\pi a^2}{1+2\phi\beta_1}\,\hat k\,\delta_{\ell,1}\qquad (\ell\geq 1)\,. \tag{4.24}$$

It now rests to calculate the integral over $\underline{R}_C^{(1,1)}(\vec r)$, which in Fourier representation takes the form

$$\int d\vec r\,\underline{R}_C^{(1,1)}(\vec r)\{n_o\delta(\vec r)+n_o^2(g_2(r)-1)\} = (2\pi)^{-3}\int d\vec k\,\underline{R}_C^{(1,1)}(\vec k)\{n_o+n_o^2\nu(k)\}$$

$$= (2\pi)^{-3}\int_0^{\infty} dk\,k^2\left(\int d\hat k\,\underline{R}_C^{(1,1)}(\vec k)\right)\{n_o + n_o^2\,\nu(k)\}\ , \tag{4.25}$$

where

$$v(k) = \int e^{i\vec{k}\cdot\vec{r}}\left(g_2(r)-1\right)\, d\vec{r} \ . \tag{4.26}$$

In appendix C we show, in a calculation along the lines of the evaluation of $r_0^{00}(k)$ (cf. eqs. (4.10) - (4.13)), that

$$\int d\hat{k}\ \underline{R}_C^{(1,1)}(\vec{k}) = -\frac{1}{}\ \frac{2a^3}{9\pi}\ (2\pi)^3\ \phi\ h(ka)\ , \tag{4.27}$$

with a scalar function h(x) defined by

$$h(x) \equiv \left\{c(x)\cdot\beta\cdot\left(1 + \phi\ c(x)\cdot\beta\right)^{-1}\cdot c(x)\right.$$

$$\left. + \ c(x)\cdot\beta\cdot\left(1 - \phi f\cdot c(x)\cdot\beta\right)^{-1}\cdot f\cdot c(x)\right\}_{11} \ . \tag{4.28}$$

The constant matrix f occurring in the last formula has elements

$$f_{\ell m} \equiv \delta_{\ell,m}\ \frac{\ell}{\ell+1} \ . \tag{4.29}$$

We then obtain

$$-\frac{\varepsilon_1\ \varepsilon_{eC}^{(2)}(0)}{\left(\varepsilon_{eC}^{(0)}(0)\right)^2} = \lambda_C^{(2)} = -\left(\frac{\phi\beta_1}{1+2\phi\beta_1}\right)^2\ \frac{2}{3\pi}$$

$$\times \int_0^\infty \left(1 + \frac{3\phi}{4\pi a^3}\ v(x/a)\right)\ x^2\ h(x)\ dx \ . \tag{4.30}$$

The integral has been evaluated numerically*), using for the pair-correlation function the Wertheim-Thiele solution[15] of the Percus-Yevick equation. The infinite matrices appearing in the function h were again approximated by finite ones, setting $\beta_m = 0$ for $m > L$. The result converges rather well with increasing L (see table 2): Even in the case of conducting spheres, when the influence of the higher order multipoles is greatest, L = 6 suffices for an accuracy of 1%. Values for L = 6 and conducting spheres are given in fig. 2 and table 3 for different volume fractions ϕ.

*) Use was made of the adaptive Gaussian quadrature routine D01AMF of the NAG program library.

ϕ	$(\lambda_C^{(2)})_{self}+(\lambda_C^{(2)})_{pair}=\lambda_C^{(2)}$	$(\lambda_F^{(2)})_{self}+(\lambda_F^{(2)})_{pair}=\lambda_F^{(2)}$
0.1	-0.0078 + 0.0019 = -0.0059	-0.0258 - 0.0139 = -0.0397
0.2	-0.0226 + 0.0095 = -0.0131	-0.0584 - 0.0304 = -0.0888
0.3	-0.0386 + 0.0208 = -0.0178	-0.0817 - 0.0415 = -0.1232
0.4	-0.0545 + 0.0337 = -0.0208	-0.0965 - 0.0487 = -0.1452
0.5	-0.0700 + 0.0477 = -0.0223	-0.1053 - 0.0534 = -0.1587

Table 3: The second order of the fluctuation expansion for conducting spheres at infinite wavelength as function of the volume fraction ϕ. The subscripts "self" and "pair" mark the contributions of self and pair correlations respectively.

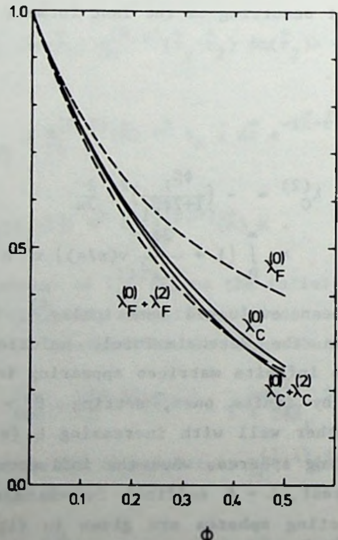


Fig. 2: The first two non-vanishing orders of the fluctuation expansion with C and F connector fields for conducting spheres at infinite wavelength as functions of the volume fraction ϕ.

ϕ	Integral I with all powers of β retained	only terms linear in β retained
0.1	0.851	0.873
0.2	0.640	0.658
0.3	0.505	0.512
0.4	0.420	0.420
0.5	0.357	0.352

Table 4: The integral I occurring in $\lambda_c^{(2)}(0)$ and S as function of the volume fraction ϕ (conducting spheres).

ϕ	w_1	w_2	w_3	w_4	w_5	w_6
0.05	0.6199	0.2572	0.0916	0.0295	0.0089	0.0026
0.10	0.5109	0.2321	0.0887	0.0297	0.0090	0.0026
0.15	0.4224	0.2068	0.0850	0.0298	0.0091	0.0026
0.20	0.3531	0.1823	0.0804	0.0298	0.0093	0.0026
0.25	0.3007	0.1597	0.0748	0.0297	0.0095	0.0027
0.30	0.2621	0.1404	0.0682	0.0293	0.0097	0.0027
0.35	0.2333	0.1256	0.0608	0.0286	0.0100	0.0028
0.40	0.2098	0.1162	0.0530	0.0274	0.0103	0.0029
0.45	0.1875	0.1124	0.0455	0.0257	0.0105	0.0030
0.50	0.1633	0.1133	0.0392	0.0232	0.0106	0.0031

Table 5: The first order Taylor coefficients of the integral I with respect to $\beta_1, \ldots, \beta_6$ as function of the volume fraction ϕ.

It is a remarkable fact that the integral

$$I \equiv \frac{2}{3\pi}\int_0^\infty \left(1 + \frac{3\phi}{4\pi a^3}\,\nu(x/a)\right) x^2\, h(x)\, dx \equiv \sum_{\ell=1}^\infty w_\ell(\phi)\,\beta_\ell + \mathcal{O}(\beta^2) \qquad (4.31)$$

occurring in eq. (4.30) is with accuracy better than 5% given by its part linear in β (see table 4). The expansion coefficients $w_\ell(\phi)$ are listed in table 5.

From eqs. (1.1), (4.16) and (4.30) we find

$$S = \frac{\varepsilon_e - \varepsilon_1}{\varepsilon_e + 2\varepsilon_1}\,\frac{1}{\beta_1\phi} - 1 = \frac{\beta_1\phi}{3}\, I + \text{contributions of higher 'powers' of density fluctuations.} \qquad (4.32)$$

Since the integral I, as discussed above, is nearly linear in the β_ℓ, the quantity S is well approximated by its part of order β^2. This justifies Kirkwood's procedure, who in the dipole case only calculated the correction S to order α_1^2.

4.4 The Gaussian approximation

The fluctuation expansion developed in section 3 is essentially an expansion in moments of the density fluctuations. Alternatively one can also perform an expansion in the cumulants of these quantities *). Neglecting third- and higher-order cumulants in the latter scheme is equivalent to making the Gaussian approximation for the probability distribution governing the density fluctuations. Though this probability distribution can in fact not be Gaussian, since the third moment of δn does not vanish, it is nevertheless interesting to investigate how much the fourth and higher-order moments of δn contribute to $\lambda = \varepsilon_1/\varepsilon_e$ in Gaussian approximation.

The cumulants κ_ℓ of the operator $\mathcal{R}\,\mathcal{B}\,\delta n$, which are linear functions of the cumulants of δn itself, are defined by

$$\langle e^{i\xi \mathcal{R}\mathcal{B}\delta n}\rangle = \exp\left\{ \sum_{\ell=1}^\infty \frac{1}{\ell!}\,(i\xi)^\ell \kappa_\ell \right\} . \qquad (4.33)$$

*) This approach, and in particular the trick (4.35) below, have been suggested to us by Prof. H. van Beijeren.

They are connected to the moments of $\mathcal{R}\mathcal{L}\delta n$ in the usual way, e.g.

$$\kappa_1 = \langle \mathcal{R}\mathcal{L}\delta n\rangle = 0 \;, \tag{4.34a}$$

$$\kappa_2 = \langle(\mathcal{R}\mathcal{L}\,\delta n)^2\rangle - \langle\mathcal{R}\mathcal{L}\,\delta n\rangle^2 = \langle(\mathcal{R}\,\mathcal{L}\,\delta n)^2\rangle \;. \tag{4.34b}$$

To perform the cumulant expansion it is convenient, in view of the definition (4.33), to reformulate the expression (3.19) such that the operator $\mathcal{R}\,\mathcal{L}\,\delta n$ appears as the argument of an exponential function:

$$\begin{aligned}\langle(1 - \mathcal{R}\mathcal{L}\delta n)^{-1}\mathcal{R}\rangle &= \langle\int_0^\infty d\xi\;(e^{-(1-\mathcal{R}\mathcal{L}\delta n)\xi})\mathcal{R}\rangle \\ &= \int_0^\infty d\xi\; e^{-\xi}\;(\exp\sum_{\ell=1}^{\infty}\frac{1}{\ell!}\,\xi^{\ell}\kappa_{\ell})\mathcal{R} \;. \end{aligned}\tag{4.35}$$

Using this formula together with eqs. (3.5), (3.16) and (3.19) we find for λ in the Gaussian approximation

$$\begin{aligned}\delta(\vec{k}-\vec{k}')\;(\lambda_C(k))_{\mathrm{Gauss}} &= \frac{k^2}{4\pi a}\;\{(\int_0^\infty d\xi\;[e^{-\xi+\frac{1}{2}\xi^2\kappa_2}]\;\mathcal{R}\;)_{00}(\vec{k},\vec{k}') \\ &+ \delta(\vec{k}-\vec{k}')\;\phi\;(\frac{\varepsilon_1}{\varepsilon_2}-1)\;K(\vec{k})\}\;. \end{aligned}\tag{4.36}$$

Next we have to evaluate the integral in eq. (4.36). Due to the translational invariance of the density fluctuation correlation function the cumulant κ_2 occurring in this integral is a diagonal operator in Fourier space

$$\begin{aligned}\kappa_2(\vec{k},\vec{k}') &= (2\pi)^{-3}\int d\vec{r}\int d\vec{r}\,'\int d\vec{r}_1\; e^{-i\vec{k}\cdot\vec{r}+i\vec{k}'\cdot\vec{r}\,'}\;\mathcal{R}(\vec{r}-\vec{r}_1)\mathcal{L} \\ &\qquad \langle\delta n(\vec{r}_1)\;\mathcal{R}(\vec{r}_1-\vec{r}\,')\;\mathcal{L}\;\delta n(\vec{r}\,')\rangle \\ &= \delta(\vec{k}-\vec{k}')\;\mathcal{R}(\vec{k})\;\mathcal{L}\int d\vec{r}\;e^{-i\vec{k}\cdot\vec{r}}\;\;\mathcal{R}(\vec{r})\;\mathcal{L}\langle\delta n(\vec{r})\delta n(0)\rangle \\ &\equiv \delta(\vec{k}-\vec{k}')\;\kappa_2(\vec{k})\;. \end{aligned}\tag{4.37}$$

Therefore the operator products of κ_2 contained in the exponential function in the integrand in the right member of eq. (4.36) reduce to ordinary products,

$$(\lambda_C(k))_{Gauss} = \frac{k^2}{4\pi a} \{ (\int_0^\infty d\xi \, e^{-\xi} [1 + \frac{\xi^2}{2} \kappa_2(\vec{k})$$

$$+ \frac{1}{2!} (\frac{\xi^2}{2})^2 \kappa_2(\vec{k})\kappa_2(\vec{k}) + \ldots] \, \mathcal{R}(\vec{k}))_{00} + \phi(\frac{\varepsilon_1}{\varepsilon_2} - 1) K(\vec{k}) \} . \quad (4.38)$$

The further evaluation of this formula will be restricted to the limit of infinite wavelength. In this limit renormalized quadrupoles and higher order multipoles do not contribute, since

$$(\kappa_2(\vec{k}))_{\ell p} = \mathcal{O}((ka)^{\ell+p-2}) \quad (4.39)$$

holds, as can be seen from eq. (4.37) together with eqs. (4.4) and (4.6). After abbreviating the remaining matrix elements of κ_2 by

$$\lim_{k \to 0} k(\kappa_2(\vec{k}))_{01} \equiv u_o \hat{k} , \quad (4.40a)$$

$$\lim_{k \to 0} (\kappa_2(\vec{k}))_{11} \equiv u_\ell \hat{k}\hat{k} + u_t(\underline{1} - \hat{k}\hat{k}) , \quad (4.40b)$$

the exponential function of matrices in the integrand on the r.h.s. of (4.38) (written in expanded form there) can be reduced to a scalar exponential function

$$(\lambda_C(0))_{Gauss} = \frac{\varepsilon_1}{\varepsilon_{CM}} + \frac{1}{4\pi a} \int_0^\infty d\xi \, e^{-\xi} \, (\frac{\xi^2}{2} u_o \hat{k}$$

$$+ \frac{1}{2!} (\frac{\xi^2}{2})^2 u_o \hat{k} \cdot (u_\ell \hat{k}\hat{k} + u_t(\underline{1} - \hat{k}\hat{k})) + \ldots) \cdot \frac{i 4\pi a^2}{1+2\beta_1\phi} \hat{k}$$

$$= \frac{\varepsilon_1}{\varepsilon_{CM}} + \frac{ia}{1+2\beta_1\phi} \frac{u_o}{u_\ell} (\int_0^\infty d\xi \, e^{-\xi + \frac{1}{2} u_\ell \xi^2} - 1) . \quad (4.41)$$

Here we also made use of eqs. (4.15) and (4.24).

The coefficients u_o and u_ℓ can be expressed in terms of $\lambda_C^{(2)}(0)$. With the aid of eqs. (4.22) and (4.24)-(4.27) as well as eq. (4.30) it is not difficult to verify the following relations:

$$\int d\vec{r} \, \underline{R}^{(1,1)}(\vec{r}) \, \langle \delta n(\vec{r}) \delta n(0) \rangle = \underline{1} \, \frac{(1+2\beta_1\phi)^2}{4\pi\beta_1^2 a^3} \, \lambda_C^{(2)}(0) , \quad (4.42)$$

$$u_o = \lim_{k\downarrow 0} \vec{k}\cdot\left(\underline{R}^{(0,1)}(\vec{k})\cdot b_1 \int d\vec{r}\ \underline{R}^{(1,1)}(\vec{r})\ \langle\delta n(\vec{r})\delta n(0)\rangle b_1\right)$$

$$= -i\ \frac{1+2\beta_1\phi}{a}\ \lambda_C^{(2)}(0)\ , \tag{4.43a}$$

$$u_\ell = \lim_{k\downarrow 0} \hat{k}\hat{k}\ :\ \left(\underline{R}^{(1,1)}(k)\cdot b_1 \int d\vec{r}\ \underline{R}^{(1,1)}(\vec{r})\langle\delta n(\vec{r})\delta n(0)\rangle b_1\right)$$

$$= \frac{2}{3}\ (1+2\beta_1\phi)\ \lambda_C^{(2)}(0)\ . \tag{4.43b}$$

In terms of the parameter

$$\gamma \equiv \frac{1}{2}\left(-\ \frac{1}{3}\ (1+2\beta_1\phi)\ \lambda_C^{(2)}(0)\right)^{-\ \frac{1}{2}} = \frac{1}{\sqrt{-2u_\ell}} \tag{4.44}$$

one finally obtains from eqs. (4.41) and (4.43) for the Gaussian approximation of λ the simple expression

$$\left(\lambda_C(0)\right)_{Gauss} = \frac{\varepsilon_1}{\varepsilon_{CM}} + \frac{3}{2(1+2\beta_1\phi)}\ \left\{\int_0^\infty d\xi\ \exp\left(-\xi^2/(4\gamma^2)-\xi\right)\ -1\right\}$$

$$= \frac{\varepsilon_1}{\varepsilon_{CM}} + \frac{3}{2(1+2\phi\beta_1)}\ \left\{e^{\gamma^2}\ \sqrt{\pi}\ \gamma\ \mathrm{erfc}(\gamma)\ -1\right\}\ . \tag{4.45}$$

erfc(x) denotes the complementary error function[13] of x. If one inserts into formula (4.45) the values for $\lambda_C^{(2)}(0)$ from table 3, one finds that $\left(\lambda_C(0)\right)_{Gauss}$ and $\lambda_C^{(0)}(0) + \lambda_C^{(2)}(0)$ differ by less than 0.02% for $\phi = 0.1$ and less than 1% for $\phi = 0.5$. In the Gaussian approximation the fourth and higher moments of δn thus do not significantly contribute to λ_C, and up to second order the moment- and the cumulant-expansion are virtually equivalent. It is, however, not clear to which extent this indicates a rapid convergence of the expansion scheme, since we know that the actual probability distribution for the density fluctuations must deviate from the Gaussian form.

5. Fluctuation expansion with factorizing connector fields

5.1 Renormalized factorizing connector fields

We now turn to the calculation of $\lambda^{(0)}$ and $\lambda^{(2)}$ with factorizing connector fields. In appendix D it is shown that the inverse Fourier-transform of

$$\underline{F}^{(\ell,p)}(\vec{k}) \equiv \begin{cases} 4\pi a^3 \left(i^{\ell}(2\ell+1)!! \dfrac{j_\ell(ka)}{ka} \overline{\hat{k}^{\ell}}\right) \\ \quad \times \left(i^{-p}(2p+1)!! \dfrac{j_p(ka)}{ka} \overline{\hat{k}^{p}}\right) & \text{for } \ell,p \geq 1 \\ \underline{C}^{(\ell,p)}(\vec{k}) & \text{for } \ell = 0 \text{ and/or } p = 0 \end{cases} \tag{5.1}$$

yields for $r > 2a$ the connector field $\underline{A}^{(\ell,p)}(\vec{r})$:

$$\underline{F}^{(\ell,p)}(\vec{r}) = (2\pi)^{-3} \int e^{i\vec{k}\cdot\vec{r}}\, \underline{F}^{(\ell,p)}(\vec{k})\, d\vec{k} = \underline{A}^{(\ell,p)}(\vec{r}) \quad (r > 2a) \; . \tag{5.2}$$

Because of this and the freedom of choice for the continuation of connector fields for overlapping spheres, cf. section 3, we can also use

$$\underline{F}_{\delta}^{(\ell,p)}(\vec{r}) \equiv \Theta(r-\delta)\, \underline{F}^{(\ell,p)}(\vec{r}) \tag{5.3}$$

instead of $\underline{C}^{(\ell,p)}(\vec{r})$. The modification (5.3) is needed to satisfy the requirement $\underline{A}^{(\ell,p)}(\vec{r}) = 0$ for $r < \delta$ (see eq. (3.7)). We call $\underline{F}_{\delta}$, which in the limit $\delta \to 0$ factorizes in wave vector representation, the factorizing (F) connector field. Its use facilitates the calculation of the renormalized connector fields.

We observe that the tensorial contraction of two $\underline{F}^{(\ell,p)}(\vec{k})$ can very easily be performed with the aid of formula (4.11):

$$\underline{F}^{(\ell,m)}(\vec{k}) \odot^{m} \underline{F}^{(m,p)}(\vec{k}) =$$

$$= \frac{4\pi a^3}{(ka)^2} (2m+1)!!\,(2m+1)\, m!\, j_m^2(ka)\, \underline{F}^{(\ell,p)}(\vec{k}) \qquad (m \geq 1). \tag{5.4}$$

Expanding the expression (3.18) in a geometric series and using the above relation we find for the renormalized F connector field in wave vector representation

$$\underline{R}_F^{(\ell,p)}(\vec{r}) = [(1 - \mathcal{F}_\delta \ell n_o)^{-1} \mathcal{F}_\delta]_{\ell p}(\vec{r}) =$$

$$= \underline{F}_\delta^{(\ell,p)}(\vec{r}) + \frac{1}{(2\pi)^3} \int d\vec{k}\, e^{i\vec{k}\cdot\vec{r}} \sum_{s=1}^{\infty} \sum_{m_1,\ldots,m_s=1}^{\infty} \underline{F}^{(\ell,m_1)}(\vec{k})$$

$$\odot^{m_1} b_{m_1} n_o \underline{F}^{(m_1,m_2)}(\vec{k}) \odot^{m_2} \ldots \odot^{m_s} b_{m_s} n_o \underline{F}^{(m_s,p)}(\vec{k})$$

$$= \underline{F}_\delta^{(\ell,p)}(\vec{r}) + \frac{1}{(2\pi)^3} \int d\vec{k}\, e^{i\vec{k}\cdot\vec{r}} \sum_{s=1}^{\infty} \Big(-\phi \frac{3}{(ka)^2}$$

$$\times \sum_{m=1}^{\infty} \beta_m (2m+1)^2 j_m^2(ka)\Big)^s \underline{F}^{(\ell,p)}(\vec{k}) , \qquad (5.5)$$

where $\mathcal{F}_\delta$ denotes the matrix of F connector fields (cf. for the notation also eq. (3.12)). Note that in the sums on the r.h.s. $\underline{F}_\delta$ has been replaced by $\underline{F}$. This is admissible for the following reason: The inverse Fourier transform of a product of two or more $\underline{F}_\delta^{(\ell,p)}(\vec{k})$ yields a convolution integral of the form

$$\int \underline{F}_\delta^{(\ell,m_1)}(\vec{r}-\vec{r}_1)\odot^{m_1} \underline{F}_\delta^{(m_1,m_2)}(\vec{r}_1-\vec{r}_2)\ldots\odot^{m_s} \underline{F}_\delta^{(m_s,p)}(\vec{r}_s-\vec{r}\,')d\vec{r}_1\ldots d\vec{r}_s . \quad (5.6)$$

If we replace all $\underline{F}_\delta^{(\ell,m)}$ by $\underline{F}^{(\ell,m)}$ in the above integral, this integral changes for all r only by an amount of order δ^3. This is not true for the first term of the last member of eq. (5.5), since $\underline{F}^{(\ell,m)}(\vec{r}=0) - \underline{F}_\delta^{(\ell,m)}(\vec{r}=0)$ is of order unity, however small δ may be. These considerations justify equation (5.5) for sufficiently small δ.

With the abbreviation

$$\sigma(x) \equiv \frac{3}{x^2} \sum_{m=1}^{\infty} \beta_m \left((2m+1)\, j_m(x)\right)^2 \qquad (5.7)$$

equation (5.5) gets the simple form

$$\underline{R}_F^{(\ell,p)}(\vec{k}) = \underline{F}_\delta^{(\ell,p)}(\vec{k}) - \frac{\phi\sigma(ka)}{1 + \phi\sigma(ka)} \underline{F}^{(\ell,p)}(\vec{k}) . \qquad (5.8)$$

5.2 Zeroth and second order of the fluctuation expansion

The lowest order of the fluctuation expansion with F connector fields is in the limit of infinite wavelength given by (see eq. (3.21))

$$\varepsilon_1/\varepsilon_{eF}^{(0)}(0) = \lambda_F^{(0)}(0) = \lim_{k\to 0} \frac{k^2}{4\pi a} \{\underline{R}_F^{(0,0)}(\vec{k}) + \phi(\frac{\varepsilon_1}{\varepsilon_2} - 1)K(\vec{k})\}$$

$$= \lim_{k\to 0} \frac{k^2}{4\pi a} \left(1 - \frac{3\phi\beta_1}{1+3\phi\beta_1} + \mathcal{O}(k)\right) \frac{4\pi a}{k^2} = \frac{1}{1+3\phi\beta_1} . \qquad (5.9)$$

That the term $k^2K(\vec{k})$ in eq. (3.21) vanishes in the limit $k \to 0$ has been discussed in section 4.2 . $\varepsilon_{eF}^{(0)}(0) = \varepsilon_1/\lambda_F^{(0)}(0)$ is just the first order density expansion[16),12)] of ε_e. Note that $\varepsilon_{eF}^{(0)}(0)$ lies below ε_{CM}, which was shown to be a lower bound for ε_e by Hashin and Shtrikman[17)]. This already indicates that the higher orders in the fluctuation expansion will be more important for F than for C connector fields.

The calculation of the second order term of the fluctuation expansion with F connector fields proceeds along the same lines as the corresponding one with C connector fields (cf. eqs. (4.22) - (4.30)). Using eq. (5.8) one finds

$$\lambda_F^{(2)}(0) = \frac{1}{4\pi a} \lim_{k\to 0} \{k\underline{R}_F^{(0,1)}(\vec{k}) \cdot b_1(2\pi)^{-3} \int d\vec{k}' \left(-n_o \frac{\phi\sigma(k'a)}{1+\phi\sigma(k'a)} + \right.$$

$$\left. n_o^2 \, \nu(k') \frac{1}{1+\phi\sigma(k'a)}\right) \underline{F}^{(1,1)}(\vec{k}') \cdot b_1 k\, \underline{R}_F^{(1,0)}(\vec{k})\}$$

$$= \left(\frac{\phi\beta_1}{1+3\phi\beta_1}\right)^2 \frac{18}{\pi} \int_0^\infty \left(-\sigma(x) + \frac{3}{4\pi a^3}\nu(x/a)\right) \frac{j_1^2(x)}{1+\phi\sigma(x)} dx . \qquad (5.10)$$

The scalar integral was again evaluated numerically. The sum occurring in the expression for σ was for conducting spheres calculated analytically by Beenakker[18)] (see also appendix B for a similar calculation):

$$\sigma(x) = \frac{3}{x^2}\left(x\,\mathrm{Si}(2x) + \frac{\sin 2x}{4x} + \frac{\cos 2x}{2} - \left(\frac{\sin x}{x}\right)^2\right) \quad (\beta_i = 1) . \qquad (5.11)$$

In the general case one has to approximate σ by a finite sum, setting $\beta_\ell = 0$ for ℓ greater than some number $L \gtrsim 1$, as we did in section 4. Again, the result converges rapidly with increasing L (see table 2). For conducting spheres $\lambda_F^{(0)}$ and $\lambda_F^{(0)} + \lambda_F^{(2)}$ are plotted in fig. 2.

The two results for $\lambda^{(0)} + \lambda^{(2)}$ found with C and with F connector fields still show significant differences, although the discrepancy is much less than that between the two $\lambda^{(0)}$. If one uses the ratio $\lambda^{(2)}/\lambda^{(0)}$ as an indication for the convergence of the fluctuation expansion, the C connector fields have to be preferred.

6. Partial resummation of self correlations

6.1 Definition of renormalized polarizabilities

To improve the rate of convergence of the fluctuation expansion, Beenakker and Mazur[11] developed a scheme that allows to include already in the renormalized connector fields the contributions of a special class of self correlations. In order to explain this procedure we return for a moment to the formula (2.30), written now in matrix notation:

$$\begin{aligned} \varepsilon_1 a\, M(\vec{r},\vec{r}\,') = \Big(&\mathcal{A}(\vec{r}-\vec{r}\,') + \sum_{s=1}^{\infty} \sum_{\substack{j_1,\dots,j_s \\ j_i \neq j_{i-1}}} \mathcal{A}(\vec{r}-\vec{R}_{j_1})\,\mathcal{b}\,\mathcal{A}(\vec{R}_{j_1}-\vec{R}_{j_2})\,\mathcal{b} \\ &\mathcal{A}(\vec{R}_{j_2}-\vec{R}_{j_3})\,\mathcal{b}\dots\mathcal{A}(\vec{R}_{j_s}-\vec{r}\,')\Big)_{00} \\ &+ \left(\frac{\varepsilon_1}{\varepsilon_2}-1\right) \sum_j \Theta(a-|\vec{r}-\vec{R}_j|)\,\Theta(a-|\vec{R}_j-\vec{r}\,'|)\,\Big\{\underline{A}^{(0,0)}(\vec{r}-\vec{r}\,') - 1 \\ &- \sum_{\ell=1}^{\infty} \frac{a^{-\ell}}{\ell!}\,\overline{(\vec{r}-\vec{R}_j)^{\ell}} \odot^{\ell}\, \underline{A}^{(\ell,0)}(\vec{R}_j-\vec{r}\,')\Big\}\,. \end{aligned} \tag{6.1}$$

In eq. (3.11) we replaced the sums over particle positions by integrals over the microscopic density, for which in turn the average density n_0 was substituted in lowest order of the fluctuation expansion. Thereby not only the mutual impenetrability of the spheres was neglected, but also the fact that two or more j-indices in eq. (6.1) may be identical. The self correlation contributions in the higher orders of the fluctuation expansion correct for the latter approximation.

We introduce for the matrix of renormalized connector fields

$$\mathcal{R}(\vec{r}-\vec{r}') = \mathcal{A}(\vec{r}-\vec{r}') + \int d\vec{r}_1\, \mathcal{A}(\vec{r}-\vec{r}_1)\, \mathcal{B}\, n_o \mathcal{A}(\vec{r}_1-\vec{r}') +$$

$$+ \int d\vec{r}_1 \int d\vec{r}_2\, \mathcal{A}(\vec{r}-\vec{r}_1)\, \mathcal{B}\, n_o \mathcal{A}(\vec{r}_1-\vec{r}_2)\, \mathcal{B}\, n_o \mathcal{A}(\vec{r}_2-\vec{r}') + \ldots \quad (6.2)$$

the symbolic notation

$$\mathcal{R}(\vec{r}-\vec{r}') = (r)\!-\!(r') + (r)\!-\!(1)\!-\!(r') + (r)\!-\!(1)\!-\!(2)\!-\!(r') + \ldots \quad (6.3)$$

A line stands for a connector field, a circle (j) for an integration over an intermediate variable $\vec{r}_j$. The cases in which some of the j-indices in (6.1) are identical corresponds in this symbolic notation to netted diagrams as given in fig. 3. The example (a) of this figure corresponds to

$$\int d\vec{r}_1 \int d\vec{r}_2 \int d\vec{r}_3 \int d\vec{r}_4 \int d\vec{r}_6\, \mathcal{A}(\vec{r}-\vec{r}_1)\, \mathcal{B}\, n_o \mathcal{A}(\vec{r}_1-\vec{r}_2)\, \mathcal{B}\, n_o \mathcal{A}(\vec{r}_2-\vec{r}_3)$$

$$\mathcal{B}\, n_o \mathcal{A}(\vec{r}_3-\vec{r}_4)\, \mathcal{B}\, n_o \mathcal{A}(\vec{r}_4-\vec{r}_2)\, \mathcal{B}\, \mathcal{A}(\vec{r}_2-\vec{r}_6)\, \mathcal{B}\, n_o \mathcal{A}(\vec{r}_6-\vec{r}')$$

$$= \int d\vec{r}_1 \int d\vec{r}_2 \int d\vec{r}_6\, \mathcal{A}(\vec{r}-\vec{r}_1)\, \mathcal{B}\, n_o \mathcal{A}(\vec{r}_1-\vec{r}_2)\, \mathcal{B}\, n_o\, [\int d\vec{r}_3 \int d\vec{r}_4\, \mathcal{A}(-\vec{r}_3)$$

$$\mathcal{B}\, n_o \mathcal{A}(\vec{r}_3-\vec{r}_4)\, \mathcal{B}\, n_o \mathcal{A}(\vec{r}_4)]\, \mathcal{B} \mathcal{A}(\vec{r}_2-\vec{r}_6)\, \mathcal{B}\, n_o \mathcal{A}(\vec{r}_6-\vec{r}') \ . \quad (6.4)$$

In the term between square brackets one recognizes a summand of the expansion of $\mathcal{R}(\vec{r}=0)$. Simple rings as in fig. 3(a),(b) can thus be included in the renormalized connector fields by substituting in (6.2) for $\mathcal{B}$ the matrix

$$\mathcal{B} + \mathcal{B}\mathcal{R}(\vec{r}=0)\mathcal{B} + \mathcal{B}\mathcal{R}(\vec{r}=0)\mathcal{B}\mathcal{R}(\vec{r}=0)\mathcal{B} + \ldots$$

$$= \mathcal{B}(1 - \mathcal{R}(\vec{r}=0)\mathcal{B})^{-1} \ . \quad (6.5)$$

Since $\underline{R}^{(\ell,p)}(\vec{r}=0)$ is an isotropic tensor irreducible in its first ℓ and its last p indices, it is proportional to $\delta_{\ell p}\, \underline{\Delta}^{(\ell,\ell)}$ (see theorem 4 of

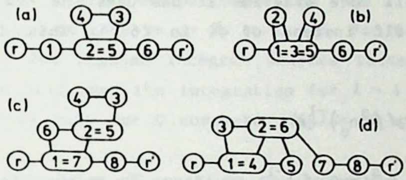


Fig. 3: Diagrammatic representation of some terms occurring in formula (6.1).

L	ℓ	β^s_ℓ for C connector fields at $\phi=0.1$	$\phi=0.2$	$\phi=0.3$	$\phi=0.4$	$\phi=0.5$
1	1	1.040	1.084	1.135	1.201	1.303
2	1	1.040	1.085	1.137	1.204	1.312
	2	1.012	1.025	1.039	1.053	1.071
L	ℓ	β^s_ℓ for F connector fields at $\phi=0.1$	$\phi=0.2$	$\phi=0.3$	$\phi=0.4$	$\phi=0.5$
2	1	1.193	1.420	1.678	1.962	2.262
	2	1.126	1.264	1.412	1.567	1.727
5	1	1.195	1.432	1.711	2.027	2.374
	2	1.130	1.280	1.448	1.634	1.832
	3	1.092	1.194	1.306	1.427	1.555
	4	1.070	1.146	1.227	1.313	1.403
	5	1.056	1.115	1.177	1.242	1.308

L	1	2	3	4	5
β^s_1 at $\phi=0.5$ for F connect.	2.092	2.262	2.326	2.356	2.374

Table 6: The polarizabilities of conducting spheres renormalized by resummation of ring self correlations. L is the number of equations of the system (6.10) used in the calculation.

ref. 19) Therefore the matrix $\mathcal{R}(\vec{r}=0)$ in the expression (6.5) is diagonal.

One can resum still more diagrams if one uses the new renormalized connector field itself instead of $\mathcal{R}$ in (6.5). This leads to the connector field

$$\mathcal{R}^{s} = (1 - \mathcal{A}\mathcal{B}^{s} n_{o})^{-1}\mathcal{A} \tag{6.6}$$

with

$$\mathcal{B}^{s} = \mathcal{B}(1 - \mathcal{R}^{s}(\vec{r}=0)\mathcal{B})^{-1} \; . \tag{6.7}$$

We also introduce renormalized reduced polarizabilities β_{ℓ}^{s} by

$$\frac{\beta_{\ell}^{s}}{\beta_{\ell}} \mathcal{B}_{\ell p} = (\mathcal{B}^{s})_{\ell p} \quad ; \tag{6.8}$$

they satisfy the equation

$$\beta_{\ell}^{s} \, \underline{\Delta}^{(\ell,\ell)} = \left(\underline{\Delta}^{(\ell,\ell)} + \frac{\beta_{\ell}}{\ell!(2\ell-1)!!} \underline{R}^{s(\ell,\ell)}(\vec{r}=0)\right)^{-1} \odot^{\ell} \beta_{\ell} \, \underline{\Delta}^{(\ell,\ell)} . \tag{6.9}$$

The connector field $\mathcal{R}^{s}$ contains also diagrams with nested rings as e.g. in fig. 3(c). Not included are more complicated diagrams of the type indicated in fig. 3(d), in which two rings share a line.

6.2 Evaluation of the renormalized polarizabilities

The renormalized connector field $\underline{R}^{s(\ell,p)}$ for $\ell,p \leqq 1$ can be obtained from the results of sects. 4 and 5; one just has to replace the β_{ℓ} by the β_{ℓ}^{s}. The latter, however, still have to be calculated. From the relations (6.7) - (6.9) we get an infinite system of coupled nonlinear equations for these quantities:

$$(1/\beta_{\ell}^{s} - 1/\beta_{\ell}) \, \underline{\Delta}^{(\ell,\ell)} = \frac{1}{\ell!(2\ell-1)!!(2\pi)^{3}} \int_{0}^{\infty} dk \, k^{2} \int d\hat{k} \; \underline{R}^{s(\ell,\ell)}(\vec{k}) \; . \tag{6.10}$$

Before this set of equations can be solved numerically, the angular integration on the r.h.s. has to be performed, yielding a set of scalar nonlinear equations. Of course, we have to truncate this system, which we do by considering only the first L equations and setting in the r.h.s. $\beta^s_\ell = \beta_\ell$ for $\ell > L$. For F connector fields the angular integration can easily be performed for all ℓ (cf. eqs. (5.1) and (5.8)), and in this case we go up to L = 5. For C connector fields the evaluation of the angular integral becomes increasingly tedious with growing ℓ. We performed the integration for $\ell = 1$ and $\ell = 2$ only (see appendix C), so that for C connector fields we cannot take L greater than 2.

The truncated system of equations can be solved by standard numerical methods *). As starting point in the search for the solution we use $\beta^s_\ell = \beta_\ell$ for all ℓ. In the case of C connector fields we retain only 6 multipoles; it was checked that the results for β^s_1 and β^s_2 change by less than 0.5% if more multipoles are taken into account. The results of the calculations for conducting spheres are listed in table 6. Note that the renormalization of the reduced polarizabilities has a greater effect with F than with C connector fields.

We now turn to the fluctuation expansion of the reciprocal dielectric constant λ with the $\mathcal{R}^s$ connector fields. It is shown in appendix E that (neglecting terms which vanish together with δ)

$$\{(1 - \mathcal{A}\mathcal{B}\, n)^{-1}\mathcal{A}\}_{00} = \{(1 - \mathcal{R}^s_\delta\, \mathcal{B}^s\, \delta n)^{-1}\, \mathcal{R}^s\}_{00} \tag{6.11}$$

holds, with the matrix $\mathcal{R}^s_\delta$ given by

$$\mathcal{R}^s_\delta(\vec{r}) = \Theta(r-\delta)\,\mathcal{R}^s(\vec{r}) \quad . \tag{6.12}$$

For the fluctuation expansion we find from eq. (6.11) (cf. also eqs. (3.20)-(3.22))

$$\lambda(k) = \lambda^{s(0)}(k) + \lambda^{s(2)}(k) + \ldots \tag{6.13}$$

$$\lambda^{s(0)}(k)\delta(\vec{k}-\vec{k}') = \frac{k^2}{4\pi a}\, \mathcal{R}^s_{00}(\vec{k},\vec{k}') \quad + \mathcal{O}(k) \,, \tag{6.14}$$

$$\lambda^{s(2)}(k)\delta(\vec{k}-\vec{k}') = \frac{k^2}{4\pi a}(\mathcal{R}^s_\delta\, \mathcal{B}^s \langle\delta n\, \mathcal{R}^s_\delta\, \delta n\rangle\, \mathcal{B}^s \mathcal{R}^s)_{00}(\vec{k},\vec{k}'). \tag{6.15}$$

*) We used the routines D01AMF and C05NBF of the NAG library.

ϕ	$\lambda_C^{s(0)}$	$\lambda_C^{s(2)}$	$\lambda_F^{s(0)}$	$\lambda_F^{s(2)}$	$\lambda_F^{s(0)}$	$\lambda_F^{s(2)}$
	2 renormal. β		2 renormal. β		5 renormal. β	
0.1	0.742	0.002	0.736	-0.017	0.736	-0.017
0.2	0.546	0.011	0.540	-0.040	0.538	-0.040
0.3	0.392	0.027	0.398	-0.052	0.394	-0.052
0.4	0.264	0.048	0.298	-0.055	0.291	-0.055
0.5	0.149	0.081	0.228	-0.053	0.219	-0.053

Table 7: Zeroth and second order of the fluctuation expansion for conducting spheres with resummation of ring self correlations as function of the volume fraction ϕ (infinite wavelength)

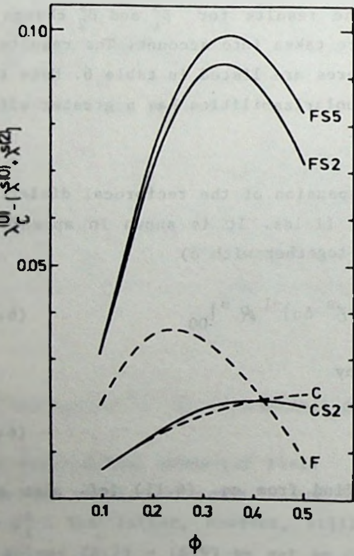


Fig. 4: The sum of the first two orders of the fluctuation expansion (conducting spheres, infinite wavelength). C and F indicate the connector fields used, S2 and S5 mean resummation of ring self correlations with the first 2 respectively the first 5 polarizabilities renormalized. All results are subtracted from the zeroth order of the fluctuation expansion with C connector fields, in order to make the small difference between the curves C and CS2 visible. The dashed lines indicate the results obtained without renormalization of the polarizabilities.

The evaluations of $\lambda^{s(0)}$ and $\lambda^{s(2)}$ are nearly identical to those of the corresponding quantities in sections 4 and 5: one just has to replace β by β^s and omit the contribution of the self correlation term in the second order, since $\mathcal{R}^s_\delta(\vec{r}=0) = 0$. In the calculation with C connector fields we retained 6 multipoles and used for β_1^s and β_2^s the values given in table 6; for $3 \leq \ell \leq 6$ we approximated β_ℓ^s by $\beta_\ell = 1$. For F connector fields we retained all multipoles and employed two different approximations for the β_ℓ^s. On the one hand we used the same approximation as in the C case, i.e. β_1^s and β_2^s calculated with the first two equations of the system (6.10) and β_ℓ^s set equal to $\beta_\ell = 1$ for $\ell \geq 3$. On the other hand we also used $\beta_1^s,\ldots,\beta_5^s$ calculated with the first five equations of (6.10) and set $\beta_\ell^s = 1$ for $\ell > 5$. The results of the calculations are listed in table 7, and are plotted with respect to $\lambda_C^{(0)}$ in fig. 4. Note that in the F-case the difference between the curves corresponding to 2 respectively 5 renormalized polarizabilities is rather small, indicating that the renormalization of higher-order polarizabilities has little influence on the result of the fluctuation expansion; we expect the same to be true in the C-case, where only the first two polarizabilities have been renormalized.

The striking feature of the renormalization of the polarizabilities is the fact that the resummation of ring self correlations has very little effect if C connector fields are used, whereas for F connector fields it leads to a considerable increase of the result for the effective dielectric constant.

7. Conclusions

7.1 Discussion of the results and comparison with the density expansion

In the preceding sections we have employed four different methods for the fluctuation expansion of $\lambda = 1/\varepsilon_e$: we used C and F connector fields with and without resummation of ring self correlations. Only two results, viz. those obtained with C connector fields, lie very close to each other. We now have to discuss which method is most trustworthy, or in other words, for which method we expect the fastest convergence of the fluctuation expansion.

On the basis of the results obtained in this chapter we conclude that the C connector fields should be preferred, because

1) they include more information about the configuration of spheres than the F connector fields,

2) $\lambda_C^{(2)}/\lambda_C^{(0)}$ is much smaller than $\lambda_F^{(2)}/\lambda_F^{(0)}$,
3) the result for $\lambda_C^{(0)} + \lambda_C^{(2)}$ is almost not affected by the resummation of ring self correlations.

Because of the last point the resummation of ring self correlations may as well be omitted for C connector fields. This is gratifying, since it reduces the amount of numerical work to a minimum. Furthermore, there is no real good reason to assume that the ring self correlations resummed in section 6 are much more important than other correlations which cannot be resummed algebraically.

In fig. 5 we plotted the relative deviation of the effective dielectric constant ε_e from the Clausius-Mossotti value ε_{CM} in the extreme case $\varepsilon_2/\varepsilon_1 \to \infty$. Our result $\varepsilon_e = (\lambda_C^{(0)} + \lambda_C^{(2)})^{-1}\varepsilon_1$ obtained with cut-out connector fields (curve C) gives a monotonically increasing but small correction, that even at $\phi = 0.5$ does not exceed 10%. The calculation with factorizing connector fields $\varepsilon_e = (\lambda_F^{(0)} + \lambda_F^{(2)})^{-1}\varepsilon_1$ (curve F) yields a contribution which is of the same order of magnitude, but decreases as ϕ becomes larger than 1/3 and crosses a lower bound (curve L) derived by Beran*), Felderhof[8] and Torquato[25] at $\phi = 0.47$. A closer discussion of the bounds will be given below.

Comparison of the curve C with its dipole version (CD) shows that higher-order multipoles account for about half of the correction on the Clausius-Mossotti dielectric constant (see also table 2). The line CD lies close to the evaluation of the Kirkwood-Yvon theory by Stell and Rushbrooke[4] (curve SR); below we shall return to this point, too.

At low volume fractions the fluctuation expansion with C connector fields coincides with the truncated density expansion $\varepsilon_e/\varepsilon_1 = 1 + 3\phi + 4.51\phi^2$ (curve D2). The first-order coefficient was calculated already by Maxwell[26], the second-order coefficient by Jeffrey[16] and by Felderhof, Ford and Cohen[12] (in the case $\varepsilon_2/\varepsilon_1 \to \infty$ under consideration the second-order coefficient can also be obtained from a calculation of Levine and McQuarrie[27]). The third-order coefficient is not yet known exactly, but an approximate value 2.66, in which only the dominant dipole contributions are taken into account, can be found from a result

*) Beran derived general formulas for the bounds, but he did not evaluate them for the special case of a hard-sphere fluid. This was done by Beasley and Torquato (cf. ref. 25).

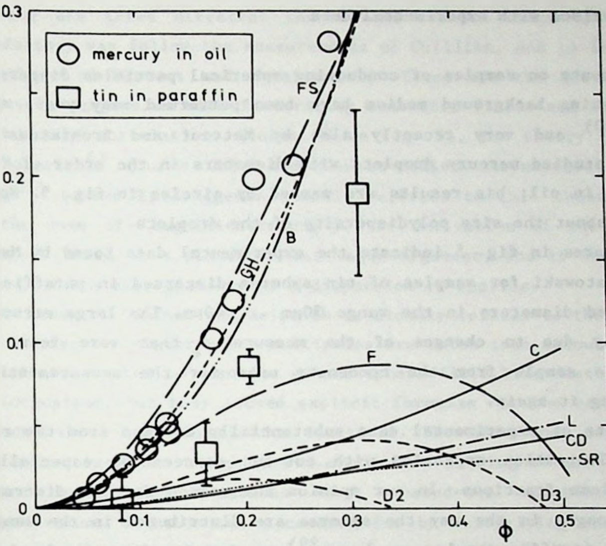


Fig. 5: Comparison of various theories and experiments in the case $\varepsilon_2/\varepsilon_1 \to \infty$. See text for explanations.

of de Boer, van der Maesen and ten Seldam[3]. Comparison of the analogous approximation for the second-order coefficient with its exact value suggests that the error made in this approximation is not larger than 20%. The curve corresponding to $\varepsilon_e/\varepsilon_1 = 1 + 3\phi + 4.51\phi^2 + 2.66\phi^3$ (marked D3 in fig. 5) follows the result of the fluctuation expansion with C connector fields up to $\phi \approx 0.3$, while the curve D2 already deviates at $\phi \approx 0.2$.

In view of the good agreement between the density expansion (D2, D3) and the fluctuation expansion (C) at low volume fractions on the one hand, and the agreement of the result of Stell and Rushbrooke (SR) with the dipole version (CD) of the fluctuation expansion on the other hand, there can be little doubt that the fluctuation expansion with cut-out connector fields describes the effective dielectric constant of a hard-sphere fluid like dispersion of spheres correctly.

7.2 Comparison with experimental data

Experiments on samples of conducting spherical particles dispersed in an insulating background medium have been performed many years ago by Guillien[20] and very recently also by Mettout and Broniatowski[28]. Guillien studied mercury droplets with diameters in the order of 0.5 mm suspended in oil; his results are marked by circles in fig. 5. Nothing is known about the size polydispersity of the droplets.

The squares in fig. 5 indicate the experimental data found by Mettout and Broniatowski for samples of tin spheres dispersed in paraffin. The spheres had diameters in the range 30μm ... 40μm. The large error bars are mainly due to changes of the measured ε_e that were found upon removing a sample from the condensor used for the measurements and reinserting it again.

Both sets of experimental data substantially deviate from the result of the fluctuation expansion with cut-out connectors, especially at higher volume fractions. In our opinion the reason for the discrepancy must be sought in the way the spheres are distributed in the samples. The tin-in-paraffin samples are known[29] to contain clusters of spheres. In order to dissolve these, Mettout and Broniatowski subjected the samples to 'baker transformations'*), i.e. the dispersions were repeatedly stretched and folded. The effective dielectric constant was measured as a function of the number of performed baker transformations. After ca. five transformations ε_e reached a stationary value, while a structure of lighter and darker layers could still be seen in the sample even by the naked eye. This might indicate that the baker transformation did not destroy those clusters which give rise to the enhanced effective dielectric constant.

In the experiments of Guillien the mercury-in-oil emulsion was continuously pumped through the condensor used for the electrical measurements, in order to avoid sedimentation. It seems plausible that the distribution of the spheres in the flow field deviated from a hard-sphere fluid's equilibrium distribution.

*) This type of samples as well as the baker transformation method were used earlier by G.Waysand et al. for experiments on dispersions of superheated superconducting particles (cf. chapter II of this thesis).

There are three different theoretical results which in a rather satisfactory way follow the measurements of Guillien, and to less extent also those of Mettout and Broniatowski. These are the result of the fluctuation expansion with factorizing connector fields and resummation of ring self correlations (curve FS in fig. 5), the theory of Günther and Heinrich[6)] (curve GH), and the so-called unsymmetric Bruggeman theory[21)] (curve B; Bruggeman himself referred to this theory as that for the case of "Kugeleinstreuung"). The derivation of the Bruggeman theory is based on a plausible but vague argument, and it is not quite clear to which microgeometry of a dispersion it applies.

The theory of Günther and Heinrich is closely related to the Kirkwood-Yvon theory, but higher order multipoles are taken into account. Günther and Heinrich wanted to describe a hard-sphere fluid like distribution of the inclusions, but they lacked explicit formulas for the corresponding two- and three-body correlation functions. Therefore they used instead expressions based on those of a f.c.c. close packing of spheres. These lattice correlation functions were smeared-out rotationally; the correct volume fraction was accounted for by multiplying the two- and three-particle densities by appropriate powers of $\phi/0.7405$ (0.7405 is the volume fraction corresponding to close packing). It is quite clear that the correlation functions obtained this way are markedly different from those of a hard-sphere fluid; geometrical contact of the spheres is e.g. always present in the lattice functions, whereas it occurs in a hard-sphere fluid with probability zero only. Günther and Heinrich concluded from the good agreement of their theory with the measurements of Guillien that "obviously the detailed form of the distribution functions has no essential influence". In view of our results this conclusion is not justified.

As for the result of the fluctuation expansion with factorizing connector fields and resummation of ring self correlations, its agreement with the measurements of Guillien is fortuitous in our opinion, as is its agreement with the theories of Bruggeman and of Günther and Heinrich. We do not see any reason why the resummation of a certain class of self correlations for hard-sphere fluid distribution functions should yield the same result as the use of the lattice distribution functions employed by Günther and Heinrich. From the large difference between the curves C and FS we rather conclude that the resummation of ring self correlations has a negative effect on the convergence of the fluctuation expansion.

It is very interesting to compare the various theories with recent measurements of the effective dielectric constants of water-in-oil microemulsions by van Dijk, Broekman, Joosten and Bedeaux[30]. The water droplets in these systems are spherical and mono-disperse to a good approximation, with diameters of ca 10 nm. They are stabilized by a

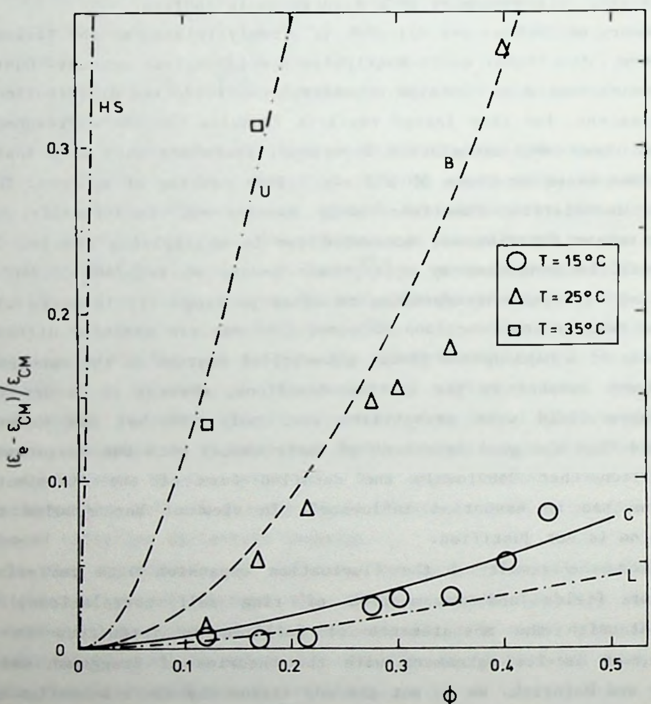


Fig. 6: Comparison of measurements of the effective dielectric constant of a microemulsion ($\varepsilon_2/\varepsilon_1 = 41.8$) with various theories. See text for explanations.

monomolecular layer of a surfactant. We compare the theories to the measurements on samples with a molar water/surfactant ratio of 35. Experiments on samples with smaller water/surfactant ratio have also been performed by van Dijk et al., but in these the influence of the surfactant on the dielectric properties can clearly not be neglected, since the one-particle contribution to ε_e (the term proportional to ϕ) was found to lie below that corresponding to pure water spheres in oil.

The droplets are known to form clusters when the temperature T of the emulsion is increased. The experimental data obtained at T = 15, 25 and 35 degrees centigrade are displayed in fig. 6. At T = 15°C the experimental data agree quite well with the result of the fluctuation expansion with cut-out connector fields (curve C). They also lie, within experimental accuracy, above the Beran-Felderhof-Torquato lower bound (curve L). When the temperature is increased the droplets form aggregates and the effective dielectric constant becomes larger. At T = 25°C the experimental results happen to lie close to Bruggeman's unsymmetrical theory (curve B), and at T = 35°C the measurements start to violate the upper Beran-Felderhof-Torquato bound (curve U) for a hard-sphere fluid like distribution of droplets*). The upper Hashin-Shtrikman bound (curve HS) is also shown in fig. 6, but clearly it is not very restrictive for the large ratio $\varepsilon_2/\varepsilon_1$ = 81.1/1.94 = 41.8 of the water-in-oil microemulsion.

7.3 Comparison with bounds and with the Kirkwood-Yvon theory

In fig. 7 the Beran-Felderhof-Torquato[8,25] upper (U) and lower (L) bounds are compared at ϕ = 0.2 with the C fluctuation expansion (C), the Hashin-Shtrikman bounds (HS) and the unsymmetric Bruggeman theory (B). Clearly the bounds are excellent for low dipole polarizability β_1 of the spheres. The Beran-Felderhof-Torquato bounds improve the Hashin-Shtrikman bounds for intermediate values of the polarizability, but the upper bound becomes useless in the limit $\beta_1 \to 1$. The result of the

*) A rather successful theory of the influence of clustering on the effective dielectric constant, based on a description of a cluster as a superposition of dimers, has been given by Bedeaux in ref. 30.

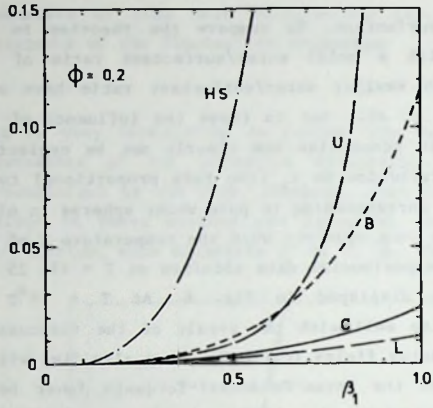


Fig. 7: Comparison of our result obtained with C connector fields with the upper (U) and lower (L) bound derived by Beran, Felderhof and Torquato. Plotted is the relative deviation from the Clausius-Mossotti dielectric constant as function of the reduced dipole polarizability, for a volume fraction of 20%. Also shown in the figure are the unsymmetric Bruggeman theory (B) and the upper bound (HS) derived by Hashin and Shtrikman; the lower Hashin-Shtrikman bound coincides with the β_1-axis.

fluctuation expansion lies rather close to the lower bound. It should be mentioned that for very low polarizabilities the curve C drops below the lower bound L (this cannot be resolved in fig. 7). This is due on the one hand to the contributions to the higher orders of the fluctuation expansion, and on the other hand also to an approximation made by Felderhof and Torquato in the evaluation of their exact expressions for the bounds.

We now return to a more detailed comparison of our result obtained with cut-out connector fields in dipole approximation and the result of the Kirkwood-Yvon theory. The latter yields the following formula[4] for S_2 (i.e. the part of S proportional to α^2, cf. also eq. (1.1); ε_1 is taken equal to unity):

$$S_2 = \alpha^2 \Big\{ 8\pi n_o \int_0^\infty g_2(r)\, r^{-4}\, dr + \\ + 2n_o^2 \int d\vec{r} \int d\vec{s}\, \big(g_3(\vec{r},\vec{s}) - g_2(r)g_2(s)\big)\, P_2(\hat{s}\cdot\hat{r})\, (rs)^{-3} \Big\} . \quad (7.1)$$

P_2 is the second Legendre polynomial. We report here without derivation the result of the fluctuation expansion for S_2 with C connector fields without the restriction to terms of second order in δn:

$$S_2 \underline{1} = \frac{\alpha^2}{a^6} \{\langle \delta n\ \underline{C}^{(1,1)} \cdot \underline{C}^{(1,1)} \delta n\rangle + \frac{1}{n_o} \langle \delta n\ \underline{C}^{(1,1)} \cdot (\delta n\ \underline{C}^{(1,1)} \delta n)\rangle\} . \quad (7.2)$$

In this formula δn is interpreted as a function rather than a multiplication operator; more explicitly one has

$$\langle \delta n\ \underline{C}^{(1,1)} \cdot \underline{C}^{(1,1)} \delta n\rangle = n_o \int d\vec{r}\ \underline{C}(\vec{r})^{(1,1)} \cdot \underline{C}^{(1,1)}(\vec{r}) +$$

$$+ n_o^2 \int d\vec{r} \int d\vec{s}\ \underline{C}^{(1,1)}(\vec{r}-\vec{s}) \cdot \underline{C}^{(1,1)}(\vec{s})\ (g_2(r)-1)\ , \quad (7.3)$$

$$\frac{1}{n_o} \langle \delta n\ \underline{C}^{(1,1)} \cdot \delta n\ \underline{C}^{(1,1)} \delta n\rangle = n_o \int d\vec{r}\ \underline{C}^{(1,1)}(\vec{r}) \cdot \underline{C}^{(1,1)}(\vec{r})\ (g_2(r)-1)$$

$$- n_o^2 \int d\vec{r} \int d\vec{s}\ \underline{C}^{(1,1)}(\vec{r}-\vec{s}) \cdot \underline{C}^{(1,1)}(\vec{s})\ (g_2(r)-1)$$

$$+ n_o^2 \int d\vec{r} \int d\vec{s}\ \underline{C}^{(1,1)}(\vec{r}) \cdot \underline{C}^{(1,1)}(\vec{s})\ (g_3(\vec{r},\vec{s})-1)\ . \quad (7.4)$$

One easily convinces oneself, recalling that $\underline{C}^{(1,1)}(\vec{r}) = (a/r)^3\ (\underline{1} - 3\hat{r}^2)\ \Theta(r-2a)$ (cf. eqs. (2.20) and (3.25)), that both expressions for S_2 are identical, as they should be*). They correspond, however, to entirely different decompositions of S_2: The first integral in eq. (7.1) results from combination of the first integrals in eqs. (7.3) and (7.4); the second integrals in eqs. (7.3) and (7.4) cancel, and the third integral in eq. (7.4) is equal to the second integral in eq. (7.1).

In fig. 8 we plotted results of different approximations for S_2. The curve SA was obtained by Stell and Rushbrooke[4], using the Percus-Yevick pair correlation function and the superposition approximation

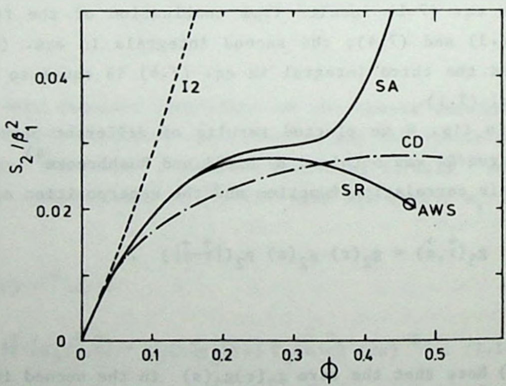
$$g_3(\vec{r},\vec{s}) = g_2(r)\ g_2(s)\ g_2(|\vec{r}-\vec{s}|)\ . \quad (7.5)$$

*) Note that the term $g_2(r)g_2(s)$ in the second integral of (7.1) may be replaced by one, since it gives no contribution for integration over finite spherical domains as $\int dr\ P_2(\hat{r}\cdot\hat{s}) = 0$, and since $g_2(r)$ tends to unity for large r. The term only serves to make the integral absolutely convergent.

With increasing volume fraction this approximation is less and less reliable. The superposition approximation can be avoided in a direct Monte-Carlo calculation of the second integral in (7.1), which was performed by Alder et al.[5] for one single value of ϕ (point marked AWS). The interpolation SR between SA and AWS is, according to Stell and Rushbrooke, the "best prediction available for S_2".

The curve CD shows our second order fluctuation expansion result (7.3); the difference between CD and SR must be attributed to the third order of the fluctuation expansion. The fact that this difference is quite small below $\phi = 0.4$ may be taken as an indication of a reasonable convergence of the fluctuation expansion. The curve I2 in fig. 8 gives the contribution of the first integral in eq. (7.1), also evaluated with the Percus-Yevick g_2. Clearly, it is a very poor approximation to the result SR. This observation once more underscores the advantage of the fluctuation expansion: while with this method one may obtain a satisfactory approximation to S_2 without knowledge of the three body correlation function g_3, this is not the case for the KY theory in its usual form.

Fig. 8: The quantity S_2 of the Kirkwood-Yvon theory. SA = KY theory with Percus-Yevick g_2 and superposition approximation for g_3, I2 = idem but with g_3 set equal to zero, AWS = Monte-Carlo result of Alder, Weis and Strauss, SR = interpolation of Stell and Rushbrooke, CD = dipole version of fluctuation expansion with cut-out connector fields.



Appendix A

In this appendix we sketch a potential-theory approach to the theory of irreducible tensors. A more general group-theoretical approach can be found in ref. 19.

We define the tensor $\overline{\vec{r}^{\,\ell}}$ of rank ℓ by

$$\overline{\vec{r}^{\,\ell}} = (-1)^{\ell} \frac{r^{2\ell+1}}{(2\ell-1)!!} \left(\frac{\partial}{\partial \vec{r}}\right)^{\ell} \frac{1}{r} \quad . \tag{A.1}$$

Obviously it is symmetric in all pairs of its indices. For $\ell = 1, 2, 3$ one has e.g.

$$\overline{\vec{r}^{\,1}} = \vec{r} \,, \qquad \overline{\vec{r}^{\,2}} = \vec{r}\vec{r} - \frac{r^2}{3}\,\underline{1} \,,$$

$$\left(\overline{\vec{r}^{\,3}}\right)_{\alpha\beta\gamma} = x_\alpha x_\beta x_\gamma - \frac{1}{5}\left(x_\alpha \delta_{\beta,\gamma} + x_\beta \delta_{\alpha,\gamma} + x_\gamma \delta_{\alpha,\beta}\right) r^2 \tag{A.2}$$

As one easily sees from the definition the $\overline{\vec{r}^{\,\ell}}$ are homogeneous in r of degree ℓ

$$\overline{\vec{r}^{\,\ell}} = r^{\ell}\, \overline{\hat{r}^{\,\ell}} \,. \tag{A.3}$$

Using this property one finds from eq. (A.1) the relations

$$\begin{aligned} \hat{r}\cdot \overline{\hat{r}^{\,\ell}} &= \hat{r}\cdot (-1)^{\ell} \frac{r^{\ell+1}}{(2\ell-1)!!} \left(\frac{\partial}{\partial \vec{r}}\right)^{\ell} \frac{1}{r} = \\ &= -\frac{r^{\ell+1}}{2\ell-1} \frac{\partial}{\partial r} \left(\frac{1}{r^{\ell}}\, \overline{\hat{r}^{\,\ell-1}} \right) = \frac{\ell}{2\ell-1}\, \overline{\hat{r}^{\,\ell-1}} \end{aligned} \tag{A.4}$$

and

$$\frac{\partial}{\partial \vec{r}} \frac{\overline{\hat{r}^{\,\ell}}}{r^{\ell+1}} = \frac{\partial}{\partial \vec{r}} \frac{\overline{\vec{r}^{\,\ell}}}{r^{2\ell+1}} = \frac{(-1)^{\ell}}{(2\ell-1)!!} \left(\frac{\partial}{\partial \vec{r}}\right)^{\ell+1} \frac{1}{r} = -(2\ell+1) \frac{\overline{\hat{r}^{\,\ell+1}}}{r^{\ell+2}} \quad . \tag{A.5}$$

With the aid of eq. (A.5) it is not difficult to prove by induction that for $\ell \geq 2$ there exist constant tensors $\underline{Q}^{(\ell,\ell-2)}$ of rank $2\ell-2$ with the property

$$\overline{\vec{r}^{\,\ell}} = \vec{r}^{\,\ell} + r^2\, \underline{Q}^{(\ell,\ell-2)} \odot^{\ell-2} \vec{r}^{\,\ell-2} \quad . \tag{A.6}$$

Repeated application of eq. (A.6) shows that one can also write

$$\hat{r}^{\ell} = \overline{\hat{r}^{\ell}} + \sum_{\substack{j > 0 \\ \ell-2j \geq 0}} \underline{T}^{(\ell,\ell-2j)} \odot^{\ell-2j} \overline{\hat{r}^{\ell-2j}} \tag{A.7}$$

with suitable constant tensors $\underline{T}^{(\ell,\ell-2j)}$ of rank $2(\ell-j)$. Using the well-known relation

$$\Delta \frac{1}{r} = - 4\pi \, \delta(\vec{r}) \tag{A.8}$$

it immediately follows from eq. (A.1) that $\overline{\vec{r}^{\ell}}$ is harmonic for $r>0$, i.e.

$$\Delta \, \overline{\vec{r}^{\ell}} = 0 \quad . \tag{A.9}$$

The latter equation also holds in the point $\vec{r} = 0$, since $\overline{\vec{r}^{\ell}}$ is in particular two times continuously differentiable (cf. eq. (A.6)).

We now turn to the orthogonality properties of the $\overline{\vec{r}^{\ell}}$ with respect to integration over the surface of the unit sphere. With the aid of Green's theorem as well as eqs. (A.3) and (A.9) one finds

$$\begin{aligned}
0 &= \int_{r<1} \Big\{ \big(\overline{\vec{r}^{\ell}} \big)_{\alpha_1,\alpha_2,\ldots,\alpha_\ell} \, \Delta \big(\overline{\vec{r}^{p}} \big)_{\beta_1,\beta_2,\ldots,\beta_p} \\
&\qquad - \big(\overline{\vec{r}^{p}} \big)_{\beta_1,\ldots,\beta_p} \, \Delta \big(\overline{\vec{r}^{\ell}} \big)_{\alpha_1,\ldots,\alpha_\ell} \Big\} \, d\vec{r} \\
&= \int_{r=1} \Big\{ \big(\overline{\vec{r}^{\ell}} \big)_{\alpha_1,\ldots,\alpha_\ell} \, \frac{\partial}{\partial r} \big(\overline{\vec{r}^{p}} \big)_{\beta_1,\ldots,\beta_p} \\
&\qquad - \big(\overline{\vec{r}^{p}} \big)_{\beta_1,\ldots,\beta_p} \, \frac{\partial}{\partial r} \big(\overline{\vec{r}^{\ell}} \big)_{\alpha_1,\ldots,\alpha_\ell} \Big\} \, d\hat{r} \\
&= (p-\ell) \int \big(\overline{\hat{r}^{\ell}} \big)_{\alpha_1,\ldots,\alpha_\ell} \big(\overline{\hat{r}^{p}} \big)_{\beta_1,\ldots,\beta_p} \, d\hat{r} \quad .
\end{aligned} \tag{A.10}$$

Eqs. (A.10) and (A.7) together yield

$$\int \overline{\hat{r}^{\ell}} \; \overline{\hat{r}^{\ell}} \; d\hat{r} = \int \overline{\hat{r}^{\ell}} \; \hat{r}^{\ell} \; d\hat{r} \tag{A.11}$$

and

$$\int \overline{\hat{r}^{\ell}} \; \overline{\hat{r}^{p}} \; d\hat{r} = 0 = \int \overline{\hat{r}^{\ell}} \; \hat{r}^{p} \; d\hat{r} \qquad \text{for } p < \ell \, . \tag{A.12}$$

The tensors $\underline{\Delta}^{(\ell,\ell)}$ defined by

$$\underline{\Delta}^{(\ell,\ell)} = \frac{1}{4\pi}\,\frac{(2\ell+1)!!}{\ell!}\int \overline{\hat{r}^{\ell}}\;\overline{\hat{r}^{\ell}}\;d\hat{r} \tag{A.13}$$

play an important role in the theory of irreducible tensors. They leave any irreducible tensor $\underline{A}^{(\ell)}$ of rank ℓ invariant under ℓ-fold contraction:

$$\underline{\Delta}^{(\ell,\ell)} \odot^{\ell} \underline{A}^{(\ell)} = \underline{A}^{(\ell)} . \tag{A.14}$$

In particular they are idempotent,

$$\underline{\Delta}^{(\ell,\ell)} \odot^{\ell} \underline{\Delta}^{(\ell,\ell)} = \underline{\Delta}^{(\ell,\ell)} , \tag{A.15}$$

and may therefore be called projectors. In order to prove the property (A.14) consider first an arbitrary solution $\Psi(\vec{r})$ of Laplace's equation. Applying again Green's theorem and expanding $1/|\vec{r}-\vec{r}\,'|$ in a Taylor series one finds for $r < 1$

$$\Psi(\vec{r}) = \int_{r'<1} \delta(\vec{r}-\vec{r}\,')\,\Psi(\vec{r}\,')\,d\vec{r}\,'$$

$$= \frac{-1}{4\pi}\int_{r'<1} \left\{ \Psi(\vec{r}\,')\,\Delta'\frac{1}{|\vec{r}-\vec{r}\,'|} - \frac{1}{|\vec{r}-\vec{r}\,'|}\,\Delta'\,\Psi(\vec{r}\,') \right\} d\vec{r}\,'$$

$$= \frac{-1}{4\pi}\sum_{\ell=0}^{\infty}\frac{(2\ell-1)!!}{\ell!}\int_{r'=1} \left\{\Psi(\vec{r}\,')\,\frac{\partial}{\partial r'}\,\vec{r}^{\,\ell}\odot^{\ell}\frac{\overline{\vec{r}\,'^{\ell}}}{r'^{\,2\ell+1}} - \vec{r}^{\,\ell}\odot^{\ell}\frac{\overline{\vec{r}\,'^{\ell}}}{r'^{\,2\ell+1}}\,\frac{\partial}{\partial r'}\,\Psi(\vec{r}\,')\right\} d\hat{r}\,'$$

$$= \sum_{\ell=0}^{\infty}\frac{1}{4\pi}\,\frac{(2\ell-1)!!}{\ell!}\,\vec{r}^{\,\ell}\odot^{\ell}\int_{r'=1}\overline{\hat{r}\,'^{\ell}}\left\{(\ell+1)\,\Psi(\vec{r}\,') + \frac{\partial}{\partial r'}\,\Psi(\vec{r}\,')\right\} d\hat{r}\,' \tag{A.16}$$

If one now chooses $\Psi(\vec{r}) = \vec{r}^{\,p}\odot^{p}\underline{A}^{(p)}$, where $\underline{A}^{(p)}$ is an arbitrary constant irreducible tensor of rank p, comparison of the coefficients of r^{ℓ} in (A.16) shows that

$$\vec{r}^{\,p}\odot^{p}\underline{A}^{(p)} = \vec{r}^{\,p}\odot^{p}\underline{\Delta}^{(p,p)}\odot^{p}\underline{A}^{(p)} , \tag{A.17}$$

and p-fold differentiation with respect to $\vec{r}$ yields the eq. (A.14). If one inserts $\Psi(\vec{r}) = \overline{\vec{r}^{\,p}}$ into eq. (A.16) one furthermore obtains

$$\overline{\vec{r}^{\,p}} = \vec{r}^{\,p} \odot^{p} \underline{\Delta}^{(p,p)} . \tag{A.18}$$

From eq. (A.18) one can calculate the gradient of $\overline{\vec{r}^{\,\ell}}$:

$$\frac{\partial}{\partial \vec{r}} \overline{\vec{r}^{\,\ell}} = \ell \, \vec{r}^{\,\ell-1} \odot^{\ell-1} \underline{\Delta}^{(\ell,\ell)} . \tag{A.19}$$

Combination of eqs. (A.19) and (A.5),

$$\frac{\partial}{\partial \vec{r}} \left(r \frac{\overline{\hat{r}^{\ell}}}{r^{\ell+1}} \right) = \hat{r} \frac{\overline{\hat{r}^{\ell}}}{r^{\ell+1}} - (2\ell+1) \frac{\overline{\hat{r}^{\ell+1}}}{r^{\ell+1}}$$

$$= \frac{\partial}{\partial \vec{r}} \left(r^{-2\ell} \, \overline{\vec{r}^{\,\ell}} \right) = -2\ell \, \hat{r} \frac{\overline{\hat{r}^{\ell}}}{r^{\ell+1}} + \frac{\ell}{r^{\ell+1}} \hat{r}^{\ell-1} \odot^{\ell-1} \underline{\Delta}^{(\ell,\ell)} , \tag{A.20}$$

gives the useful formula

$$\hat{r} \, \overline{\hat{r}^{\ell}} = \overline{\hat{r}^{\ell+1}} + \frac{\ell}{2\ell+1} \hat{r}^{\ell-1} \odot^{\ell-1} \underline{\Delta}^{(\ell,\ell)} . \tag{A.21}$$

We shall now derive some contraction formulae for the tensors $\underline{\Delta}^{(\ell,\ell)}$. For $p \leq \ell$ one finds from eqs. (A.11), (A.18) and (A.12)

$$\underline{\Delta}^{(\ell,\ell)} \odot^{p} \underline{\Delta}^{(p,p)} = \frac{(2\ell+1)!!}{4\pi \, \ell!} \int d\hat{r} \; \overline{\hat{r}^{\ell}} \; \hat{r}^{\ell-p} \; \overline{\hat{r}^{p}}$$

$$= \frac{(2\ell+1)!!}{4\pi \, \ell!} \int d\hat{r} \; \overline{\hat{r}^{\ell}} \; \hat{r}^{\ell-p} \left\{ \hat{r}^{p} + \underline{Q}^{(p,p-2)} \odot^{p-2} \hat{r}^{p-2} \right\} = \underline{\Delta}^{(\ell,\ell)} . \tag{A.22}$$

Use of this formula together with eqs. (A.18), (A.11) and (A.12) shows that for $\ell < p \leq 2\ell$

$$\underline{\Delta}^{(\ell,\ell)} \odot^{p} \underline{\Delta}^{(p,p)} = \frac{(2\ell+1)!!}{4\pi \, \ell!} \int d\hat{r} \left(\hat{r}^{\ell} \, \hat{r}^{\ell} \odot^{\ell} \underline{\Delta}^{(\ell,\ell)} \right) \odot^{p} \underline{\Delta}^{(p,p)}$$

$$= \frac{(2\ell+1)!!}{4\pi \, \ell!} \int d\hat{r} \; \hat{r}^{\ell} \odot^{p-\ell} \left(\hat{r}^{\ell} \odot^{\ell} \underline{\Delta}^{(\ell,\ell)} \odot^{\ell} \underline{\Delta}^{(p,p)} \right)$$

$$= \frac{(2\ell+1)!!}{4\pi \, \ell!} \int d\hat{r} \; \hat{r}^{2\ell-p} \; \overline{\hat{r}^{p}} = 0 \qquad (\ell < p \leq 2\ell) . \tag{A.23}$$

For the contraction of one of the first ℓ indices of $\underline{\Delta}^{(\ell,\ell)}$ with one of its last ℓ indices the formula

$$\sum_\beta \Delta^{(\ell,\ell)}_{\alpha_1,\dots,\alpha_{\ell-1},\beta,\beta,\gamma_1,\dots,\gamma_{\ell-1}} = \frac{2\ell+1}{2\ell-1}\,\Delta^{(\ell-1,\ell-1)}_{\alpha_1,\dots,\alpha_{\ell-1},\gamma_1,\dots,\gamma_{\ell-1}} \tag{A.24}$$

holds, as can readily be verified with the aid of eqs. (A.11) and (A.4). Repeated application of (A.24) yields

$$\sum_{\alpha_1,\dots,\alpha_\ell} \Delta^{(\ell,\ell)}_{\alpha_1,\dots,\alpha_\ell,\alpha_1,\dots,\alpha_\ell} = 2\ell+1\ . \tag{A.25}$$

Using eqs. (A.11), (A.21) and (A.4) one can finally show that

$$\sum_{\beta_1,\dots,\beta_\ell} \Delta^{(\ell,\ell)}_{\alpha_1,\dots,\alpha_{\ell-1},\beta_\ell,\alpha_\ell,\beta_1,\dots,\beta_{\ell-1}} \Delta^{(\ell,\ell)}_{\beta_1,\dots,\beta_\ell,\gamma_1,\dots,\gamma_\ell}$$

$$= \frac{(2\ell+1)!!}{4\pi\ \ell!} \int d\hat{r}\,\left(\hat{r}\cdot\underline{\Delta}^{(\ell,\ell)} \odot^{\ell-1} \hat{r}^{\ell-1}\,\overline{\hat{r}^{\ell}}\right)_{\alpha_1,\dots,\alpha_\ell,\gamma_1,\dots,\gamma_\ell}$$

$$- \frac{(2\ell+1)!!}{4\pi\ \ell!} \int d\hat{r}\,\left(\frac{2\ell+1}{\ell}\,\hat{r}\cdot\{\overline{\hat{r}^{\ell}}\,\hat{r} - \overline{\hat{r}^{\ell+1}}\}\,\overline{\hat{r}^{\ell}}\right)_{\alpha_1,\dots,\alpha_\ell,\gamma_1,\dots,\gamma_\ell}$$

$$= \frac{1}{\ell(2\ell-1)}\,\Delta^{(\ell,\ell)}_{\alpha_1,\dots,\alpha_\ell,\gamma_1,\dots,\gamma_\ell}\ . \tag{A.26}$$

We conclude this appendix with a discussion of the connection between irreducible tensors and spherical harmonics. By comparison of the Taylor expansion of $1/|\vec{r}-\vec{r}\,'|$,

$$\frac{1}{|\vec{r}-\vec{r}\,'|} = \sum_{\ell=0}^{\infty} \frac{r'^{\ell}}{r^{\ell+1}}\,\frac{(2\ell-1)!!}{\ell!}\,\overline{\hat{r}'^{\ell}} \odot^{\ell} \overline{\hat{r}^{\ell}} \qquad (r' < r)\ , \tag{A.27}$$

with the well-known (cf. ref. 22, eqs. (3.38) and (3.70)) expansion of $1/|\vec{r}-\vec{r}\,'|$ in terms of spherical harmonics and Legendre-polynomials respectively,

$$\frac{1}{|\vec{r}-\vec{r}\,'|} = \sum_{\ell=0}^{\infty} \frac{r'^{\ell}}{r^{\ell+1}} \sum_{m=-\ell}^{+\ell} \frac{4\pi}{2\ell+1}\,Y_\ell^{m*}(\hat{r}')Y_\ell^m(\hat{r}) = \sum_{\ell=0}^{\infty} \frac{r'^{\ell}}{r^{\ell+1}}\,P_\ell(\hat{r}'\cdot\hat{r}), \tag{A.28}$$

one finds the two relations

$$\frac{(2\ell+1)!!}{4\pi\ \ell!}\,\overline{\hat{r}'^{\ell}} \odot^{\ell} \overline{\hat{r}^{\ell}} = \sum_{m=-\ell}^{\ell} Y_\ell^{m*}(\hat{r}')\,Y_\ell^m(\hat{r})\ , \tag{A.29}$$

$$\frac{(2\ell-1)!!}{\ell!}\,\overline{\hat{r}'^{\ell}} \odot^{\ell} \overline{\hat{r}^{\ell}} = P_\ell(\hat{r}'\cdot\hat{r})\ , \tag{A.30}$$

and, using eq. (A.12) as well as $\int Y_\ell^{m*}(\hat{r})\, Y_\lambda^\mu(\hat{r})\, d\hat{r} = \delta_{\ell,\lambda}\delta_{m,\mu}$, also

$$Y_\ell^m(\hat{r}) = \frac{(2\ell+1)!!}{4\pi\ \ell!} \int d\hat{r}'\ Y_\ell^m(\hat{r}')\ \overline{\hat{r}'^{\ell}} \odot^\ell \overline{\hat{r}^{\ell}} \quad , \tag{A.31}$$

$$\overline{\hat{r}^{\ell}} = \sum_{m=-\ell}^{+\ell} Y_\ell^m(\hat{r}) \int d\hat{r}'\ \overline{\hat{r}'^{\ell}}\ Y_\ell^{m*}(\hat{r}') \quad . \tag{A.32}$$

Eqs. (A.29) – (A.32) allow to translate familiar formulae for the spherical harmonics into the language of irreducible tensors, e.g. Rayleigh's expansion of the plane wave:

$$e^{i\vec{k}\cdot\vec{r}} = \sum_{\ell=0}^{\infty} i^\ell (2\ell+1)\ j_\ell(kr)\ P_\ell(\hat{k}\cdot\hat{r})$$

$$= \sum_{\ell=0}^{\infty} i^\ell \frac{(2\ell+1)!!}{\ell!}\ j_\ell(kr)\ \overline{\hat{r}^{\ell}} \odot^\ell \overline{\hat{k}^{\ell}} \quad . \tag{A.33}$$

The spherical harmonics form a complete set of functions on the surface of the unit sphere. For an arbitrary function $f(\hat{r})$ one therefore has the expansion

$$f(\hat{r}) = \sum_{\ell=0}^{\infty} \sum_{m=-\ell}^{\ell} Y_\ell^m(\hat{r}) \int d\hat{r}'\ Y_\ell^{m*}(\hat{r}')\ f(\hat{r}') \tag{A.34}$$

Upon insertion of the relation (A.29) this expansion takes the form

$$f(\hat{r}) = \sum_{\ell=0}^{\infty} \frac{(2\ell+1)!!}{4\pi\ \ell!}\ \overline{\hat{r}^{\ell}} \odot^\ell \int d\hat{r}'\ \overline{\hat{r}'^{\ell}}\ f(\hat{r}') \quad , \tag{A.35}$$

expressing a completeness property of the tensors $\overline{\hat{r}^{\ell}}$.

Appendix B

We shall calculate here the Fourier transforms of the cut-out connector fields $\underline{C}^{(\ell,p)}(\vec{r})$ given in eq. (3.25) and of the function $K(\vec{r})$ defined in eq. (3.17).

Consider first the Fourier transform of $\underline{C}^{(\ell,p)}(\vec{r})$ in the case $\ell, p \geq 1$. Using the expansion (A.33) and the formulae (A.13) and (A.14) one finds

$$\underline{C}^{(\ell,p)}(\vec{k}) = \int_{r>2a} d\vec{r}\; e^{-i\vec{k}\cdot\vec{r}}\; \underline{C}^{(\ell,p)}(\vec{r}) = \sum_{m=0}^{\infty} (-i)^m \frac{(2m+1)!!}{m!} \overline{\hat{k}^m} \odot^m$$

$$\int \overline{\hat{r}^m}\; \overline{\hat{r}^{\ell+p}}\, d\hat{r} \quad (-1)^{\ell}\, a^{\ell+p+1}\, (2\ell+2p-1)!! \int_{2a}^{\infty} j_m(kr)\, r^{1-\ell-p}\, dr$$

$$= 4\pi\, i^{\ell-p}\, a^{\ell+p+1}\, (2\ell+2p-1)!! \int_{2a}^{\infty} j_{\ell+p}(kr)\, r^{1-\ell-p}\, dr\; \overline{\hat{k}^{\ell+p}} \,. \qquad \text{(B.1)}$$

With aid of the formula (cf. ref. 13, eq. 10.1.25)

$$j_m(x) = (-x)^m \left(\frac{1}{x}\frac{d}{dx}\right)^m \frac{\sin x}{x} \qquad \text{(B.2)}$$

the scalar integral can readily be performed,

$$\int_{2a}^{\infty} j_{\ell+p}(kr)\, r^{1-\ell-p}\, dr = k^{\ell+p-2} \int_{2ka}^{\infty} x^{1-\ell-p}\, (-x)^{\ell+p} \left(\frac{1}{x}\frac{d}{dx}\right)^{\ell+p} \frac{\sin x}{x}\, dx$$

$$= (2a)^{2-\ell-p}\; \frac{j_{\ell+p-1}(ka)}{2ka} \,, \qquad \text{(B.3)}$$

and one obtains

$$\underline{C}^{(\ell,p)}(\vec{k}) = i^{\ell-p}\, 4\pi a^3\, (2\ell+2p-1)!!\; 2^{2-\ell-p}\; \frac{j_{\ell+p-1}(2ka)}{2ka}\; \overline{\hat{k}^{\ell+p}} \,. \qquad \text{(B.4)}$$

In the case $\ell = 0$, $p \neq 0$ the angular integration can be done as above:

$$\underline{C}^{(0,p)}(\vec{k}) = 4\pi\, i^{-p}\, (2p-1)!!\, \overline{\hat{k}^p}\, \Big\{ a^{p+1} \int_a^{\infty} j_p(kr)\, r^{1-p} dr$$

$$+ a^{-p} \int_0^a j_p(kr)\, r^{p+2}\, dr \Big\} \,. \qquad \text{(B.5)}$$

The first of the two scalar integrals may again be evaluated with aid of formula (B.2),

$$a^{p+1} \int_a^{\infty} j_p(kr)\, r^{1-p}\, dr = a^3\, j_{p-1}(ka)/(ka) \,. \qquad \text{(B.6)}$$

In order to work out the second one we note that the spherical Bessel function j_p is related to the Bessel function $J_{p+1/2}$ by

$$j_p(x) = \left(\frac{\pi}{2x}\right)^{1/2} J_{p+1/2}(x) \quad . \tag{B.7}$$

We can therefore use formula (6.561.5) of ref. 23 to obtain

$$a^{-p} \int_0^a j_p(kr)\, r^{p+2}\, dr = a^3\, j_{p+1}(ka)/(ka) \ . \tag{B.8}$$

With the relation (cf. ref. 13, eq. 10.1.19)

$$j_{p+1}(x) + j_{p-1}(x) = (2p+1)\, \frac{j_p(x)}{x} \tag{B.9}$$

one finds from eqs. (B.5), (B.6) and (B.8)

$$\underline{c}^{(0,p)}(\vec{k}) = i^{-p}\, 4\pi a^3\, (2p+1)!!\, \frac{j_p(ka)}{(ka)^2}\, \overline{\hat{k}^p} \qquad (p \geq 1). \tag{B.10}$$

Since $\underline{c}^{(0,p)}(\vec{r}) = \underline{c}^{(p,0)}(-\vec{r})$ (cf. eqs. (2.15) and (2.21)), one also has

$$\underline{c}^{(p,0)}(\vec{k}) = \underline{c}^{(0,p)}(-\vec{k}) \quad . \tag{B.11}$$

The Fourier transform of $\underline{c}^{(0,0)}(\vec{r})$, finally, is well-known

$$\underline{c}^{(0,0)}(\vec{k}) = \int e^{-i\vec{k}\cdot\vec{r}}\, \frac{a}{r}\, d\vec{r} = 4\pi\, \frac{a^3}{(ka)^2} \quad . \tag{B.12}$$

Combination of eqs. (B.4) and (B.10) - (B.12) yields the formulae (4.2) and (4.3).

We now turn to the Fourier transformation of $K(\vec{r})$:

$$\begin{aligned} K(\vec{k}) = {} & \frac{3}{4\pi a^3} \int d\vec{r}\, e^{-i\vec{k}\cdot\vec{r}} \left[\int d\vec{r}''\, \Theta(a-|\vec{r}-\vec{r}''|)\Theta(a-r'')\right]\{\underline{c}^{(0,0)}(\vec{r}) - 1\} \\ & - \frac{3}{4\pi a^3} \sum_{\ell=1}^{\infty} \frac{1}{\ell!(2\ell-1)!!} \int_{r''<a} d\vec{r}'' \int_{|\vec{r}-\vec{r}''|<a} d\vec{r}\, \{e^{-i\vec{k}\cdot(\vec{r}-\vec{r}'')}\, \underline{c}^{(0,\ell)}(\vec{r}-\vec{r}'') \\ & \qquad \odot^{\ell}\, \underline{c}^{(\ell,0)}(\vec{r}'')\, e^{-i\vec{k}\cdot\vec{r}''}\} \end{aligned}$$

$$= \frac{3}{a^3} \int_0^\infty \frac{\sin kr}{kr} \left[\frac{2\pi}{3}\, \Theta(2a-r)\left(a - \frac{r}{2}\right)^2 \left(2a + \frac{r}{2}\right)\right] \left(\frac{a}{r} - 1\right) r^2\, dr$$

$$- \frac{3}{4\pi a^3} \sum_{\ell=1}^{\infty} \frac{1}{\ell!(2\ell-1)!!} \left(\int_{r<a} d\vec{r}\, e^{-i\vec{k}\cdot\vec{r}}\, \underline{C}^{(0,\ell)}(\vec{r}) \right) \odot^{\ell}$$

$$\left(\int_{r<a} d\vec{r}\, e^{-i\vec{k}\cdot\vec{r}}\, \underline{C}^{(\ell,0)}(\vec{r}) \right) . \qquad (B.13)$$

The integral between square brackets in the second member of this equation was evaluated using the well-known formula for the volume of a sphere's segment. The integrals containing $\underline{C}^{(0,\ell)}$ and $\underline{C}^{(\ell,0)}$ in the last member of eq. (B.13) were already evaluated earlier (see eqs. (B.5) and (B.8)). Substitution of the results obtained there and evaluation of the remaining integrals in eq. (B.13) leads to

$$K(\vec{k}) = \frac{4\pi a^3}{(ka)^2} \left(1 - 3\frac{j_1(2ka)}{2ka} - 3 j_1^2(ka)\right) - \frac{4\pi a^3}{(ka)^2}\, 3 \sum_{\ell=1}^{\infty} j_{\ell+1}^2(ka) \, . \qquad (B.14)$$

With aid of the formula (see § 116 of ref. 24)

$$\sum_{n=0}^{\infty} J_{n+\nu}(x)\, J_{n+\mu}(x) = x^{\mu-\nu} \int_0^x t^{\nu-\mu}\, J_{\nu-1}(t)\, J_{\mu}(t)\, dt \qquad (B.15)$$

the sum over the squared spherical Bessel functions can be performed:

$$\sum_{\ell=1}^{\infty} j_{\ell+1}^2(x) = \frac{\pi}{2x} \sum_{\ell=0}^{\infty} J_{\ell+1/2}^2(x) - j_1^2(x) - j_0^2(x)$$

$$= \frac{1}{2x} \int_0^{2x} \frac{\sin \tau}{\tau}\, d\tau - j_1^2(x) - j_0^2(x) = \frac{Si(2x)}{2x} - j_1^2(x) - j_0^2(x) \, . \qquad (B.16)$$

Eventually we thus find

$$K(\vec{k}) = \frac{4\pi a}{k^2} \left(1 - 3\,\frac{j_1(2ka)}{2ka} + 3\, j_0^2(ka) - 3\,\frac{Si(2ka)}{2ka}\right) \, . \qquad (B.17)$$

Appendix C

This appendix deals with the evaluation of the integral $\int \underline{R}_C^{(\ell,\ell)}(\vec{k})\, d\hat{k}$ for $\ell = 1$ and $\ell = 2$. Consider first the case $\ell = 1$:

$$\int \underline{R}_C^{(1,1)}(\vec{k})\, d\hat{k} = \int \{r_0^{11}(k)\, \hat{k}\hat{k} + r_1^{11}(k)\, \underline{1}\}\, d\hat{k}$$

$$= 4\pi\, \underline{1}\, \{\tfrac{1}{3}\, r_0^{11}(k) + r_1^{11}(k)\}\,. \tag{C.1}$$

In order to determine the coefficients r_0^{11} and r_1^{11} we substitute eq. (4.9) into eq. (4.6) with $p = 1$:

$$\{r_0^{\ell 1}\, \overline{\hat{k}^{\ell}}\, \hat{k} + r_1^{\ell 1}\, \overline{\hat{k}^{\ell-1}\, \llcorner 1 \lrcorner}\} = i^{\ell-1}\, \frac{4\pi a^3}{3}\, c_{\ell 1} \frac{(2\ell+1)!!}{\ell+1} \{\overline{\hat{k}^{\ell}}\, \hat{k} - \frac{\ell}{2\ell+1}\, \overline{\hat{k}^{\ell-1}\, \llcorner 1 \lrcorner}\}$$

$$- \phi \sum_{m=1}^{\infty} i^{\ell-m}\, \frac{(2\ell+2m-1)!!\,\ell!}{(\ell+m)!\,(2m-1)!!}\, c_{\ell m} \beta_m\, \overline{\hat{k}^{\ell+m}} \odot^m \{r_0^{m1}\, \overline{\hat{k}^{m}}\, \hat{k} + r_1^{m1}\, \overline{\hat{k}^{m-1}\, \llcorner 1 \lrcorner}\}. \tag{C.2}$$

In the first term on the r.h.s. we used the decomposition (A.21). The first tensor contraction in the second term has already been worked out in eq. (4.11); for the other one we find

$$\overline{\hat{k}^{\ell+m}} \odot^m \overline{\hat{k}^{m-1}\, \llcorner 1 \lrcorner} = \overline{\hat{k}^{\ell+m}} \odot^{m-1} \hat{k}^{m-1} = \frac{(\ell+m)!}{(2\ell+2m-1)!!}\, \frac{(2\ell+1)!!}{(\ell+1)!}\, \overline{\hat{k}^{\ell+1}}$$

$$= \frac{(\ell+m)!}{(2\ell+2m-1)!!}\, \frac{(2\ell-1)!!}{\ell!}\, \{\frac{(2\ell+1)}{\ell+1}\, \overline{\hat{k}^{\ell}}\, \hat{k} - \frac{\ell}{\ell+1}\, \overline{\hat{k}^{\ell-1}\, \llcorner 1 \lrcorner}\}\,. \tag{C.3}$$

Upon substitution of eqs. (4.11) and (C.3) into eq. (C.2) we can extract from the latter two scalar equations by equating the coefficients of the linearly independent tensors $\overline{\hat{k}^{\ell}}\, \hat{k}$ and $\overline{\hat{k}^{\ell-1}\, \llcorner 1 \lrcorner}$,

$$r_0^{\ell 1} = i^{\ell-1}\, \frac{4\pi a^3}{3}\, c_{\ell 1} \frac{(2\ell+1)!!}{\ell+1} - \phi \sum_{m=1}^{\infty} i^{\ell-m}\, \frac{(2\ell-1)!!}{(2m-1)!!}\, c_{\ell m} \beta_m \{r_0^{\ell 1} + \frac{2\ell+1}{\ell+1}\, r_1^{m1}\} \tag{C.4}$$

$$r_1^{\ell 1} = -i^{\ell-1}\, \frac{4\pi a^3}{3}\, c_{\ell 1}\, \frac{(2\ell-1)!!\,\ell}{\ell+1} + \phi \sum_{m=1}^{\infty} i^{\ell-m}\, \frac{(2\ell-1)!!}{(2m-1)!!}\, c_{\ell m} \beta_m\, \frac{\ell}{\ell+1}\, r_1^{m1}\ . \tag{C.5}$$

Dividing both equations by $i^{\ell+1}(2\ell-1)!!$ and adding the second one to the first we arrive at two uncoupled equations

$$\left\{\frac{(-1)^{\ell+1}}{(2\ell-1)!!}\left(r_0^{\ell 1}(k)+r_1^{\ell 1}(k)\right)\right\} = -\frac{4\pi a^3}{3}\, c_{\ell 1}(ka)$$

$$-\ \phi \sum_{m=1}^{\infty} c_{\ell m}(ka)\ \beta_m \left\{\frac{(-1)^{m+1}}{(2m-1)!!}\left(r_0^{m1}(k)+r_1^{m1}(k)\right)\right\}\ , \qquad \text{(C.6)}$$

$$\left\{\frac{(-1)^{\ell+1}}{(2\ell-1)!!}\, r_1^{\ell 1}(k)\right\} = \frac{4\pi a^3}{3}\,\frac{\ell}{\ell+1}\, c_{\ell 1}(ka)$$

$$+\ \phi \sum_{m=1}^{\infty} \frac{\ell}{\ell+1}\, c_{\ell m}(ka)\ \beta_m \left\{\frac{(-1)^{m+1}}{(2m-1)!!}\, r_1^{m1}(k)\right\}\ . \qquad \text{(C.7)}$$

With the matrix f defined in eq. (4.29),

$$f_{\ell m} = \delta_{\ell,m}\,\frac{\ell}{\ell+1}\ , \qquad \text{(C.8)}$$

we may thus write in matrix notation

$$\left(r_0^{11}(k)+r_1^{11}(k)\right) = \frac{4\pi a^3}{3}\left\{\left(1+\phi c(ka)\cdot\beta\right)^{-1}\cdot c(ka)\right\}_{11}\ , \qquad \text{(C.9)}$$

$$r_1^{11}(k) = -\frac{4\pi a^3}{3}\left\{\left(1-\phi f\cdot c(ka)\cdot\beta\right)^{-1}\cdot f\cdot c(ka)\right\}_{11}\ . \qquad \text{(C.10)}$$

For the desired integral (C.1) we finally obtain

$$\int \underline{R}_C^{(1,1)}(\vec{k})\, d\hat{k} = -(2\pi)^3\,\frac{2a^3}{9\pi}\,\phi\,\left\{c(ka)\cdot\beta\cdot\left(1+\phi c(ka)\cdot\beta\right)^{-1}\cdot c(ka)\right.$$

$$\left.+\ c(ka)\cdot\beta\cdot\left(1-\phi f\cdot c(ka)\cdot\beta\right)^{-1}\cdot f\cdot c(ka)\right\}_{11}\ \underline{1}\ . \qquad \text{(C.11)}$$

The calculation of

$$\int d\hat{k}\ \underline{R}_C^{(2,2)}(\vec{k}) = \int d\hat{k}\ \left\{r_0^{22}(k)\ \overline{\hat{k}^2\ \hat{k}^2} + r_1^{22}(k)\ \overline{\hat{k}\ \underline{1}\ \hat{k}} + r_2^{22}(k)\ \underline{\Delta}^{(2,2)}\right\}$$

$$= 4\pi\left\{\frac{2}{15}\, r_0^{22}(k) + \frac{1}{3}\, r_1^{22}(k) + r_2^{22}(k)\right\}\ \underline{\Delta}^{(2,2)} \qquad \text{(C.12)}$$

(cf. eq. (A.13) for the angular integrations) proceeds analogously. From equations (4.6) and (4.9) we find

$$\left\{r_0^{\ell 2}\,\overline{\hat{k}^{\ell}}\,\overline{\hat{k}^{2}} + r_1^{\ell 2}\,\overline{\hat{k}^{\ell-1}}\llcorner 1 \lrcorner\,\overline{\hat{k}} + r_2^{\ell 2}\,\overline{\hat{k}^{\ell-2}}\llcorner 2 \lrcorner\right\} =$$

$$= -i^{\ell}\,\frac{4\pi a^3}{3}\,\frac{(2\ell+3)!!\;2}{(\ell+1)(\ell+2)}\,c_{\ell 2}\,\overline{\hat{k}^{\ell+2}} - \phi\sum_{m=1}^{\infty} i^{\ell-m}\,\frac{(2\ell+2m-1)!!\,\ell!}{(\ell+m)!(2m-1)!!}\,c_{\ell m}\,\beta_m\,\overline{\hat{k}^{\ell+m}}$$

$$\odot^m \left\{r_0^{m2}\,\overline{\hat{k}^{m}}\,\overline{\hat{k}^{2}} + r_1^{m2}\,\overline{\hat{k}^{m-1}}\llcorner 1 \lrcorner\,\overline{\hat{k}} + r_2^{m2}\,\overline{\hat{k}^{m-2}}\llcorner 2 \lrcorner\right\}\;. \qquad \text{(C.13)}$$

We now decompose $\overline{\hat{k}^{\ell+2}}$ in a sum of the tensors occurring on the l.h.s. of the last equation. We already know (cf. eqs. (4.7), (4.8)) that it has the form

$$\overline{\hat{k}^{\ell+2}} = \overline{\hat{k}^{\ell}}\,\overline{\hat{k}^{2}} + \xi\,\overline{\hat{k}^{\ell-1}}\llcorner 1 \lrcorner\,\overline{\hat{k}} + \eta\,\overline{\hat{k}^{\ell-2}}\llcorner 2 \lrcorner\;. \qquad \text{(C.14)}$$

In order to determine the scalar coefficients ξ and η we contract with $\hat{k}$ from the right, using formulae (A.4) and (A.21),

$$\overline{\hat{k}^{\ell+1}}\,\frac{\ell+2}{2\ell+3} = \overline{\hat{k}^{\ell}}\,\hat{k}\,\frac{2}{3} + \xi\,\left(\underline{\Delta}^{(\ell,\ell)}\odot^{\ell}\,\hat{k}^{\ell-1}\,\underline{1}\,\hat{k}\right)\odot^2\left\{\underline{\Delta}^{(2,2)}\cdot\hat{k}\right\}$$

$$+\,\eta\left(\underline{\Delta}^{(\ell,\ell)}\odot^{\ell}\,\hat{k}^{\ell-2}\llcorner 2 \lrcorner\odot^2\,\underline{\Delta}^{(2,2)}\right)\cdot\hat{k}$$

$$= \frac{2}{3}\,\overline{\hat{k}^{\ell}}\,\hat{k} + \xi\left(\underline{\Delta}^{(\ell,\ell)}\odot^{\ell}\,\hat{k}^{\ell-1}\,\underline{1}\,\hat{k}\right)\odot^2\left\{\overline{\hat{k}^{2}}\,\hat{k} - \overline{\hat{k}^{3}}\right\}\frac{5}{2} + \eta\left(\underline{\Delta}^{(\ell,\ell)}\odot^{\ell-2}\,\hat{k}^{\ell-2}\right)\cdot\hat{k}$$

$$= \frac{2}{3}\,\overline{\hat{k}^{\ell}}\,\hat{k} + \xi\,\underline{\Delta}^{(\ell,\ell)}\odot^{\ell}\,\hat{k}^{\ell-1}\left\{\frac{2}{3}\,\hat{k}\hat{k} - \frac{3}{5}\,\overline{\hat{k}^{2}}\right\}\frac{5}{2} + \eta\,\underline{\Delta}^{(\ell,\ell)}\odot^{\ell-1}\,\hat{k}^{\ell-1}$$

$$= \left(\frac{2}{3} + \frac{\xi}{6}\right)\overline{\hat{k}^{\ell}}\,\hat{k} + \left(\frac{\xi}{2} + \eta\right)\overline{\hat{k}^{\ell-1}}\llcorner 1 \lrcorner\;. \qquad \text{(C.15)}$$

Comparison with equation (A.21) shows that

$$\xi = -\,\frac{2\ell}{2\ell+3}\;, \qquad\qquad \eta = \frac{\ell(\ell-1)}{(2\ell+1)(2\ell+3)}\;. \qquad \text{(C.16)}$$

After the tensor contractions on the r.h.s of eq. (C.13) have been performed with the aid of formula (4.11) and the results (C.14), (C.16) have been substituted one finds

$$\{r_0^{\ell 2}\,\overline{\hat{k}^{\ell}}\,\overline{\hat{k}^{2}} + r_1^{\ell 2}\,\overline{\hat{k}^{\ell-1}\llcorner 1 \lrcorner}\,\overline{\hat{k}} + r_2^{\ell 2}\,\overline{\hat{k}^{\ell-2}\llcorner 2 \lrcorner}\,\} =$$

$$-i^{\ell}\,\frac{4\pi a^3(2\ell+3)!!2}{3(\ell+1)(\ell+2)}\,c_{\ell 2}\,\{\overline{\hat{k}^{\ell}}\,\overline{\hat{k}^{2}} - \frac{2\ell}{2\ell+3}\,\overline{\hat{k}^{\ell-1}\llcorner 1 \lrcorner}\,\overline{\hat{k}} + \frac{\ell(\ell-1)}{(2\ell+1)(2\ell+3)}\,\overline{\hat{k}^{\ell-2}\llcorner 2 \lrcorner}\}$$

$$-\phi\sum_{m=1}^{\infty} i^{\ell-m}\,\frac{(2\ell-1)!!}{(2m-1)!!}\,c_{\ell m}\,\beta_m\,\{\overline{\hat{k}^{\ell}}\,\overline{\hat{k}^{2}}\,(r_0^{m2} + \frac{2\ell+1}{\ell+1}\,r_1^{m2} + \frac{(2\ell+1)(2\ell+3)}{(\ell+1)(\ell+2)}\,r_2^{m2}) -$$

$$\overline{\hat{k}^{\ell-1}\llcorner 1 \lrcorner}\,\overline{\hat{k}}\,(\frac{\ell}{\ell+1}\,r_1^{m2} + \frac{2\ell(2\ell+1)}{(\ell+1)(\ell+2)}\,r_2^{m2}) + \overline{\hat{k}^{\ell-2}\llcorner 2 \lrcorner}\,\frac{(\ell-1)\ell}{(\ell+1)(\ell+2)}\,r_2^{m2}\}\ . \qquad (C.17)$$

By equating the coefficients of like tensors and taking suitable linear combinations of the $r_j^{\ell 2}$ we may derive from this set of tensor equations three sets of scalar equations. For the r_j^{22} we then obtain in matrix notation the following formulae:

$$r_0^{22} + r_1^{22} + \frac{3}{2}\,r_2^{22} = \frac{4\pi a^3}{3}\,9\,\left((1+\phi c\cdot\beta)^{-1}\cdot c\right)_{22}\ , \qquad (C.18)$$

$$r_1^{22} + 2\,r_2^{22} = \frac{4\pi a^3}{3}\,(-12)\,\left((1-\phi f\cdot c\cdot\beta)^{-1}\cdot f\cdot c\right)_{22}\ , \qquad (C.19)$$

$$r_2^{22} = \frac{4\pi a^3}{3}\,6\,\left((1+\phi f'\cdot c\cdot\beta)^{-1}\cdot f'\cdot c\right)_{22}\ . \qquad (C.20)$$

The matrix f' in the last equation is given by

$$f'_{\ell m} \equiv \delta_{\ell,m}\,\frac{\ell(\ell-1)}{(\ell+2)(\ell+1)}\ . \qquad (C.21)$$

Insertion of the eqs. (C.18) - (C.20) into eq. (C.12) finally yields

$$\int d\hat{k}\,\underline{\underline{R}}_C^{(2,2)}(\vec{k}) = -\,(2\pi)^3\,a^3\,\frac{4}{5\pi}\,\phi\,\{c(ka)\cdot\beta\cdot(1+\phi c(ka)\cdot\beta)^{-1}\cdot c(ka)$$

$$+\frac{4}{3}\,c(ka)\cdot\beta\cdot(1-\phi f\cdot c(ak)\cdot\beta)^{-1}\cdot f\cdot c(ka)$$

$$+\frac{1}{3}\,c(ka)\cdot\beta\cdot(1+\phi f'\cdot c(ka)\cdot\beta)^{-1}\cdot f'\cdot c(ka)\}_{22}\,\underline{\underline{\Delta}}^{(2,2)}\ . \qquad (C.22)$$

Appendix D

In this appendix the inverse Fourier transform of $\underline{F}^{(\ell,p)}(\vec{k})$ is evaluated for $\ell,p \geq 1$. Using eq. (A.33) we may write

$$(2\pi)^{-3} \int e^{i\vec{k}\cdot\vec{r}} \, \underline{F}^{(\ell,p)}(\vec{k}) \, d\vec{k} =$$

$$= \sum_{m=0}^{\infty} \Big(\overline{\hat{r}^m} \odot^m \frac{(2m+1)!!}{m!} \int \overline{\hat{k}^m} \, \overline{\hat{k}^\ell} \, \overline{\hat{k}^p} \, d\hat{k} \Big)$$

$$\times \Big(i^{m+\ell-p} \frac{(2\ell+1)!!(2p+1)!!}{(2\pi)^3} \, 4\pi \int_0^\infty dx \; j_m(x\tfrac{r}{a}) \; j_\ell(x) \; j_p(x) \Big) \; . \qquad (D.1)$$

According to eq. (A.6) the tensor $\overline{\hat{k}^\ell} \, \overline{\hat{k}^p}$ can be expanded in the following way:

$$\overline{\hat{k}^\ell} \, \overline{\hat{k}^p} = \hat{k}^{\ell+p} \; + \text{terms containing } \hat{k}^n \text{ with } n \leq \ell+p-2 \; . \qquad (D.2)$$

Due to the orthogonality relation (A.12) the angular integration in (D.1) therefore vanishes for $m > \ell+p$. It also vanishes if $\ell+p+m$ is odd, since $\overline{(-\hat{k})^m} = (-1)^m \overline{\hat{k}^m}$. This allows us to write

$$(2\pi)^{-3} \int e^{i\vec{k}\cdot\vec{r}} \, \underline{F}^{(\ell,p)}(\vec{k}) \, d\vec{k} =$$

$$= \sum_{\substack{m=0 \\ m+\ell+p \text{ even}}}^{\ell+p} \Big(\overline{\hat{r}^m} \odot^m \frac{(2m+1)!!}{4\pi \; m!} \int d\hat{k} \, \overline{\hat{k}^m} \, \overline{\hat{k}^\ell} \, \overline{\hat{k}^p} \Big)$$

$$\times \Big(i^{m+\ell-p} (2\ell+1)!!(2p+1)!! \, \frac{2}{\pi} \int_0^\infty dx \; j_m(x\tfrac{r}{a}) \; j_\ell(x) \; j_p(x) \Big) \; . \qquad (D.3)$$

We split the spherical Bessel function j_m in the sum of two spherical Hankel functions

$$j_m(x) = \frac{1}{2i} \left(h_m^+(x) - h_m^-(x) \right) \; . \qquad (D.4)$$

The functions j_m and $h_m^\pm$ are analytic in the complex plane and have the following properties:

$$j_m(x) = (-1)^m \; j_m(-x) \; , \qquad (D.5)$$

$$j_m(x) = \frac{x^m}{(2m+1)!!} + \mathcal{O}(x^{m-2}), \quad h^{\pm}_m(x) = \frac{(2m-1)!!}{x^{m+1}} + \mathcal{O}(x^{-m}) \quad (x \ll 1) \qquad \text{(D.6)}$$

$$j_m(x) < \text{const.}\ e^{|\mathrm{Im}\ x|}, \qquad h^{\pm}_m(x) < \text{const.}\ e^{\mp \mathrm{Im}\ x} . \qquad \text{(D.7)}$$

Using these properties one can for $r > 2a$ evaluate the scalar integral in eq. (D.3) with Cauchy's formula, closing the integration paths by infinite arcs:

$$\int_0^{\infty} j_m(x\tfrac{r}{a})\ j_\ell(x)\ j_p(x)\ dx = \frac{1}{4i} \int_{-\infty}^{+\infty} \left(h^+_m(x\tfrac{r}{a}) - h^-_m(x\tfrac{r}{a})\right) j_\ell(x)\ j_p(x)\ dx$$

$$= \lim_{\eta \downarrow 0} \frac{1}{4i} \int \frac{1}{x-i\eta}\ x\ h^+_m(x\tfrac{r}{a})\ j_\ell(x)\ j_p(x)\ dx$$

$$+ \lim_{\eta \downarrow 0} \frac{1}{4i} \int \frac{1}{x-i\eta}\ x\ h^-_m(x\tfrac{r}{a})\ j_\ell(x)\ j_p(x)\ dx$$

$$= \lim_{\eta \downarrow 0} \frac{\pi}{2}\ i\eta\ h^+_m(i\eta\tfrac{r}{a})\ j_\ell(i\eta)\ j_p(i\eta)$$

$$= \delta_{m,\ell+p}\ \frac{\pi}{2}\ \frac{(2\ell+2p-1)!!}{(2\ell+1)!!(2p+1)!!} \left(\frac{a}{r}\right)^{\ell+p+1} . \qquad \text{(D.8)}$$

Combination of eqs. (D.3), (D.8) and (A.13) finally leads to

$$(2\pi)^{-3} \int e^{i\vec{k}\cdot\vec{r}}\ \underline{F}^{(\ell,p)}(\vec{k})\ d\vec{k} = (-1)^{\ell}\ (2\ell+2p-1)!!\ \left(\frac{a}{r}\right)^{\ell+p+1} \overline{\hat{r}^{\ell+p}} . \qquad \text{(D.9)}$$

Appendix E

Here we shall prove the relation (6.11). We first derive the auxiliary formula

$$\mathcal{I}\mathcal{L}n\mathcal{A}\mathcal{L}n\mathcal{J} =$$

$$\mathcal{I}\mathcal{L}n\{\mathcal{R}^s(\vec{r}=0)\mathcal{L} + (1 + \mathcal{R}^s_\delta \mathcal{L}^s n_o)^{-1} \mathcal{R}^s_\delta \mathcal{L} n\}\mathcal{J} + \mathcal{O}(\delta^3) . \qquad \text{(E.1)}$$

for arbitrary matrices $\mathcal{I}$ and $\mathcal{J}$ of such integral operators, which are regular in the sense that their kernels are piecewise continuous functions. In what follows we shall not write down terms of order δ^3 and other terms which vanish as δ tends to zero (all equalities are meant to hold in this limit).

Solving eq. (6.6) for $\mathcal{A}$ we find (cf. also the discussion following eq. (5.5))

$$\mathcal{A} = (1 + \mathcal{R}^s \mathcal{L}^s n_o)^{-1} \mathcal{R}^s = (1 + \mathcal{R}^s_\delta \mathcal{L}^s n_o)^{-1} \mathcal{R}^s \ . \tag{E.2}$$

We insert this relation into the l.h.s. of eq. (E.1):

$$\begin{aligned}
(\mathcal{I}\mathcal{L} n \mathcal{A}\mathcal{L} n \mathcal{J})(\vec{r},\vec{r}\,') &= \sum_{i,j} \mathcal{I}(\vec{r},\vec{R}_i)\mathcal{L}\mathcal{A}(\vec{R}_i,\vec{R}_j)\mathcal{L}\mathcal{J}(\vec{R}_j,\vec{r}\,') \\
&= \sum_{i,j} \mathcal{I}(\vec{r},\vec{R}_i)\mathcal{L}\{\mathcal{R}^s - (1+\mathcal{R}^s_\delta\mathcal{L}^s n_o)^{-1}\mathcal{R}^s_\delta \mathcal{L}^s n_o \mathcal{R}^s_\delta\}(\vec{R}_i,\vec{R}_j)\mathcal{L}\mathcal{J}(\vec{R}_j,\vec{r}\,') \\
&= \sum_{i} \mathcal{I}(\vec{r},\vec{R}_i)\mathcal{L}\mathcal{R}^s(\vec{R}_i,\vec{R}_i)\mathcal{L}\mathcal{J}(\vec{R}_i,\vec{r}\,') + \sum_{i,j} \mathcal{I}(\vec{r},\vec{R}_i)\mathcal{L} \\
&\quad \times \{\mathcal{R}^s_\delta - (1+\mathcal{R}^s_\delta\mathcal{L}^s n_o)^{-1}\mathcal{R}^s_\delta \mathcal{L}^s n_o \mathcal{R}^s_\delta\}(\vec{R}_i,\vec{R}_j)\mathcal{L}\mathcal{J}(\vec{R}_j,\vec{r}\,') \ .
\end{aligned} \tag{E.3}$$

Rewriting this expression in terms of the operator n one gets the r.h.s. of eq. (E.1).

We now apply formula (E.1) repeatedly and obtain

$$\begin{aligned}
(1-\mathcal{A}\mathcal{L}n)^{-1}\mathcal{A} &= \mathcal{A} + \mathcal{A}\mathcal{L}n\mathcal{A} + \mathcal{A}\mathcal{L}n\mathcal{A}\mathcal{L}n\mathcal{A} + \mathcal{A}\mathcal{L}n\mathcal{A}\mathcal{L}n\mathcal{A}\mathcal{L}n\mathcal{A}\mathcal{L}n\mathcal{A} + \ldots \\
&= \mathcal{A} + \mathcal{A}\mathcal{L}n\mathcal{A} + \mathcal{A}\mathcal{L}n\{\mathcal{R}^s(\vec{r}=0)\mathcal{L} + (1+\mathcal{R}^s_\delta\mathcal{L}^s n_o)^{-1}\mathcal{R}^s_\delta\mathcal{L}n\}\mathcal{A} \\
&\qquad + \mathcal{A}\mathcal{L}n\{\mathcal{R}^s(\vec{r}=0)\mathcal{L} + (1+\mathcal{R}^s_\delta\mathcal{L}^s n_o)^{-1}\mathcal{R}^s_\delta\mathcal{L}n\}^2\mathcal{A} + \ldots \\
&= \mathcal{A} + \mathcal{A}\mathcal{L}n\{1 - \mathcal{R}^s(\vec{r}=0)\mathcal{L} - (1+\mathcal{R}^s_\delta\mathcal{L}^s n_o)^{-1}\mathcal{R}^s_\delta\mathcal{L}n\}^{-1}\mathcal{A} \ .
\end{aligned} \tag{E.4}$$

Next we split off a factor $1 - \mathcal{R}^s(\vec{r}=0)\mathcal{L}$ from the term between brackets, use the definition (6.7) of $\mathcal{L}^s$ and substitute for $\mathcal{A}$ formula (E.2)

$$(1-\mathcal{A}\mathcal{B}\,n)^{-1}\mathcal{A} = \mathcal{A} + \mathcal{A}\mathcal{B}^{s}n\,\{1-(1+\mathcal{R}^{s}_{\delta}\mathcal{B}^{s}n_{o})^{-1}\mathcal{R}^{s}_{\delta}\mathcal{B}^{s}n\}^{-1}$$

$$= \mathcal{A} + \mathcal{A}\mathcal{B}^{s}n\,\{1+\mathcal{R}^{s}_{\delta}\mathcal{B}^{s}n_{o} - \mathcal{R}^{s}_{\delta}\mathcal{B}^{s}n\}^{-1}\,(1+\mathcal{R}^{s}_{\delta}\mathcal{B}^{s}n_{o})\mathcal{A}$$

$$= (1+\mathcal{R}^{s}_{\delta}\mathcal{B}^{s}n_{o})^{-1}\,(1+\mathcal{R}^{s}\mathcal{B}^{s}n\,\{1-\mathcal{R}^{s}_{\delta}\mathcal{B}^{s}\delta n\}^{-1})\mathcal{R}^{s}$$

$$= (1+\mathcal{R}^{s}_{\delta}\mathcal{B}^{s}n_{o})^{-1}\,(1-\mathcal{R}^{s}_{\delta}\mathcal{B}^{s}\delta n + \mathcal{R}^{s}\mathcal{B}^{s}n)\,\{1-\mathcal{R}^{s}_{\delta}\mathcal{B}^{s}\delta n\}^{-1}\,\mathcal{R}^{s}$$

$$= (1+(\mathcal{R}^{s}-\mathcal{R}^{s}_{\delta})\mathcal{B}^{s}\delta n)\,\{1-\mathcal{R}^{s}_{\delta}\mathcal{B}^{s}\delta n\}^{-1}\mathcal{R}^{s}\ . \qquad \text{(E.5)}$$

In the last step we used the fact that $\mathcal{R}^{s}_{\delta}\mathcal{B}^{s}n_{o}(\mathcal{R}^{s}-\mathcal{R}^{s}_{\delta}) = 0$. Since $\mathcal{R}^{s}(\vec{r}=0)$ is a diagonal matrix it commutes with $\mathcal{B}^{s}$, and we finally get

$$\{(1-\mathcal{A}\mathcal{B}\,n)^{-1}\mathcal{A}\}_{00} = \{(1+\mathcal{B}^{s}(\mathcal{R}^{s}-\mathcal{R}^{s}_{\delta})\delta n)\,(1-\mathcal{R}^{s}_{\delta}\mathcal{B}^{s}\delta n)^{-1}\mathcal{R}^{s}\}_{00}$$

$$= \{(1-\mathcal{R}^{s}_{\delta}\mathcal{B}^{s}\delta n)^{-1}\mathcal{R}^{s}\}_{00}\ , \qquad \text{(E.6)}$$

because $(\mathcal{B}^{s})_{0\ell} = 0$.

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CHAPTER II
DISPERSIONS OF SUPERHEATED SUPERCONDUCTING SPHERES

1. Introduction

Type I superconductors undergo a first order phase transition between the normal and superconducting states when an external magnetic field reaches the critical value B_c. As in other first-order phase transitions one can observe the phenomena of supercooling and superheating[1,2]. If the field strength is decreased below B_c, a normal conducting sample remains in a metastable normal conducting state until a certain value $B_{sc} < B_c$ is reached and the transition into the superconducting state occurs. Analogously, the magnetic field at the surface of a superconducting sample can be increased above B_c without phase transition, and only if the field strength exceeds a certain value $B_{sh} > B_c$ it becomes normal conducting. The phase diagram of tin (fig. 1) shows that the metastable regions can be quite large, with B_{sh} greater than twice the critical field.

Deposition of a tiny amount of energy in a superheated superconductor destroys the metastable state, for the resulting local increase of temperature suffices to initiate the transition into the thermodynamically stable normal state. This effect has been suggested to be used for the detection of elementary particles[4,5]: the change of magnetic flux through the sample, when the latter becomes normal conducting due to energy deposited by a passing elementary particle, can be registered as voltage pulse in an induction loop.

The superheated state is, however, also very sensitive to defects at the surface of the superconductor, which may act as nucleation centres for the transition into the normal conducting state. The phenomenon of superheating can therefore in general only be observed in a sample with an extremely carefully prepared surface[6], making the construction of a large detector consisting of one single piece of superconducting material unfeasible. A way out is the use of a large number of very small superconducting grains: Small grains are more likely to be free of

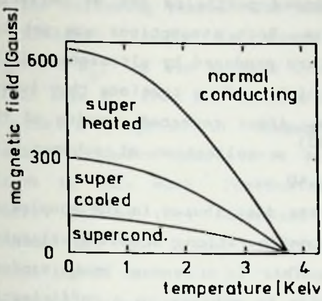


Fig. 1: The phase diagram of tin (cf. references 3 and 12)

defects, since the number of surface defects is roughly proportional to the surface area, and a phase nucleated in one grain cannot penetrate into another. Indeed superheating can easily be achieved[7] in tin or indium spheres of diameters smaller than ca. 40 µm.

One is thus led to consider dispersions of superconducting spheres. Due to the diamagnetic interactions in such a dispersion the maximum field strengths at the surfaces of the spheres are not equal, an effect that must be taken into account in the interpretation of experimental data.

Over a period of many years experimental studies of dispersions of superconducting spheres have been performed[7,8]. As an easily accessible quantity one measured in particular the fraction F of spheres which remain superconducting when the external field is increased from zero to a given value. For a collection of non-interacting, defect-free spheres F would be a step function. Due to defects and due to diamagnetic interactions, however, not all spheres transit at precisely the same external field, and the step of the function F is smeared out.

Theoretically little is known about the influence of the diamagnetic interactions[9], and it is our aim to help filling this gap. In order to keep the problem tractable, and also because experimental information about the detailed structure of the dispersions is lacking, we have to use a simplified model:

(1) We shall assume that the suspended particles are of perfectly spherical form and monodisperse in size. Both assumptions are not too unrealistic. In practice the particles are produced by ultrasonic mixing of molten metal[7] with oil, and due to high surface tensions they become spherical to a very good approximation. After repeated sieving of the thus prepared spheres one can obtain[10] a collection of spheres with diameters inside the range of ca. 35...40 μm.

(2) We shall assume that the spheres are distributed in the samples as in a hard-sphere fluid, i.e. that all configurations of non-overlapping spheres occur with equal probability. This in a sense 'most random' distribution is what experimentalists try to achieve to a sufficiently good approximation. Inspection by microscope, however, shows that the spheres tend to form aggregates. But no quantitative experimental information about the distribution of spheres in actual samples, on which a theory could be based, is currently available.

(3) We shall neglect the penetration of the magnetic field into the superconducting spheres. While this effect could probably be taken into account rather easily, it would not be worth-while to do so, since the radius of the spheres used in the experiments lies typically in the order of 10 μm and is much larger than the penetration depths, which are of order 0.05 μm. The field penetration should therefore not play an important rôle as long as the distance between the surfaces of the spheres is larger than ca. 5% of their radius.

(4) We shall assume that a superheated sphere becomes completely normal conducting as soon as anywhere at its surface the field strength reaches the value B_{sh}. This assumption is certainly correct if the external field strength B_{ex} is larger than B_c, since then the total volume of the sphere is in a metastable state even without amplification of the field by the demagnetization of the sphere itself or by diamagnetic interactions with other spheres. The situation is different for $B_{ex} < B_c$. In this case a superheated sphere, at the surface of which the field strength reaches the value B_{sh} due to diamagnetic interactions, can by partially transiting into the normal state reduce the field strength in the rest of its volume below B_c, so that this rest remains superconducting. The super- and normal conducting regions are then separated by a region which is in the intermediate state (cf. ref. 11, chpt. 44). The partial transition is excluded for an isolated sphere

for the following reason: The maximum field strength at the surface of an isolated sphere is equal to $1.5\ B_{ex}$ (cf. sect. 2), while $B_{sh} \approx 2.2\ B_c$, as can be seen from fig. 1. Therefore B_{ex} must always be larger than B_c when the maximum field strength exceeds B_{sh}.

The description of diamagnetic interactions between partially transited spheres constitutes a formidable problem that we shall not attack in this work. Fortunately the effect of partially transited spheres is not very important in dilute dispersions. Because these spheres are no longer metastable, they become completely normal conducting as soon as B_{ex} reaches $B_c \approx 0.45\ B_{sh}$. As will be shown in the following sections, for $B_{ex} < 0.45\ B_{sh}$ the maximum field strength reaches B_{sh} only on few spheres (less than 5%) if the volume fraction is small (< 10%). In dilute systems we therefore do not expect to make a serious error when neglecting the possibility of partial transitions, except for $B_{ex} < 0.45\ B_{sh}$. This may, however, no longer be true if defects of the surfaces of the spheres reduce the external field strength at which the spheres become normal conducting substantially below $0.45\ B_{sh}$.

Due to these simplifying assumptions one may not expect quantitative agreement between calculations based on our model and experimental data. The model should, however, provide a qualitatively correct description of the experiments; furthermore it can serve as a guideline for the construction of a more refined theory.

The outline of this chapter is as follows: Section 2 deals with the magnetostatic interactions between perfectly diamagnetic spheres, which are placed in an external magnetic field. In section 3 we introduce indicator functions describing the state of the spheres. In the following section these functions are used to derive a density expansion of the average fraction F of superconducting spheres. A density expansion of the probability distribution of the maximum field strength at the surface of a sphere is discussed in section 5. We conclude with a comparison of the theory with experimental data and with computer simulations.

2. Diamagnetic interactions between superconducting spheres

2.1 General relations

The magnetic field $\vec{B}$ in the space between the superconducting spheres is governed by the two Maxwell equations

$$\nabla \wedge \vec{B}(\vec{r}) = 0 \ , \tag{2.1}$$

$$\nabla \cdot \vec{B}(\vec{r}) = 0 \ . \tag{2.2}$$

Here we assumed that the medium between the spheres carries neither a current density nor a magnetization. Equation (2.1) allows us to write

$$\vec{B}(\vec{r}) = -\nabla U(\vec{r}) \tag{2.3}$$

outside the spheres, and eq. (2.2) then implies that the potential U satisfies Laplace's equation

$$\Delta U(\vec{r}) = 0 \ . \tag{2.4}$$

The boundary conditions for U at the surfaces of the superconducting spheres are given by

$$\frac{\partial}{\partial r} U(\vec{R}_i + \vec{r})\Big|_{r=a} = 0 \ , \tag{2.5}$$

with $\vec{R}_i$ the position of the centre of sphere i and a the radius of the spheres. These boundary conditions stem from the fact that the magnetic field vanishes inside a superconductor (Meissner-Ochsenfeld effect), and that the normal component of the magnetic field $\vec{B}$ is continuous at an interface. In writing down eq. (2.5) we have neglected the penetration of the field into the superconductor (cf. assumption 3 of the introduction). Far away from all spheres $\vec{B}$ becomes equal to the homogeneous applied field $\vec{B}_{ex}$,

$$-\nabla U(\vec{r}) \underset{(r\to\infty)}{\to} \vec{B}_{ex} \ . \tag{2.6}$$

The boundary value problem constituted by the equations (2.4)-(2.6) may be translated into the equivalent problem of electrostatic interactions between dielectric spheres, which has been solved in chapter I.2. To adapt the solution found there to the present problem one has to put the background dielectric constant ε_1 equal to unity and the dielectric constant ε_2 equal to zero (that this is an unphysical value does not affect the validity of the mathematical analysis). For the external potential of section I.2 the potential of a homogeneous external field must be substituted, i.e.

$$\int \frac{1}{|\vec{r}-\vec{r}\,'|}\, \rho_{ex}(\vec{r}\,')\, d\vec{r}\,' \quad \rightarrow \quad -\vec{r}\cdot\vec{B}_{ex} \;. \tag{2.7}$$

Using these rules one obtains from the results of section I.2 the relations

$$\vec{B}(\vec{r}) = \vec{B}_{ex} - \sum_i \sum_{\ell=1}^{\infty} \underline{A}^{(1,\ell)}(\vec{r}-\vec{R}_i) \odot^{\ell} \underline{m}_i^{(\ell)} \qquad (|\vec{r}-\vec{R}_i| > a) \tag{2.8}$$

and

$$\underline{m}_i^{(\ell)} = b_\ell \Big\{ -\delta_{\ell,1}\, \vec{B}_{ex} + \sum_{\substack{j \\ j\neq i}} \sum_{p=1}^{\infty} \underline{A}^{(\ell,p)}(\vec{R}_i - \vec{R}_j) \odot^{p} \underline{m}_j^{(p)} \Big\} \;, \tag{2.9}$$

with $b_\ell = \ell\,\big((\ell+1)!\,(2\ell-1)!!\big)^{-1}$. The quantity $\underline{m}_i^{(\ell)}$ is the magnetic 2^{ℓ}-pole moment of sphere i, generated by the induced currents flowing at its surface. It corresponds to the quantity $\underline{\rho}_i^{(\ell)}/a^2$ of section I.2. We defined $\underline{m}_i^{(\ell)}$ such that it has the same dimension as $\vec{B}$; the conventionally defined magnetic dipole moment is equal to $a^3\, \underline{m}_i^{(1)}$. The connector $\underline{A}^{(1,\ell)}(\vec{R})$ was in eq. (I.2.20) only defined for $R > 2a$; in this chapter we extend the definition (I.2.20) to $R \geq a$.

The total field at the surface of sphere i is the sum of the field which magnetizes the sphere and the field of the magnetic moments $\underline{m}_i^{(\ell)}$ it gives rise to. Since the magnetic moments are proportional to the multipole moments of the magnetizing field, we can express the total field in terms of the $\underline{m}_i^{(\ell)}$. By Taylor expansion of the magnetizing field we find, using relations (2.8) and (I.2.20),

$$\vec{B}(\vec{R}_i+a\hat{r}) = \vec{B}_{ex} - \sum_{\ell=1}^{\infty} \underline{A}^{(1,\ell)}(a\hat{r}) \odot^{\ell} \underline{m}_i^{(\ell)}$$

$$- \sum_{\substack{j \\ j\neq i}} \sum_{\ell,p=1}^{\infty} \frac{1}{(\ell-1)!} \hat{r}^{\ell-1} \odot^{\ell-1} \underline{A}^{(\ell,p)}(\vec{R}_i-\vec{R}_j) \odot^{p} \underline{m}_j^{(p)} \quad . \tag{2.10}$$

With the aid of eq. (2.9) the external field $\vec{B}_{ex}$ and the moments $\underline{m}_j^{(p)}$ on spheres $j\neq i$ may now be eliminated in favour of the $\underline{m}_i^{(\ell)}$. If we insert the explicit form of the connectors and also employ the formula

$$\overline{\hat{r}^{\ell+1}} - \frac{\ell+1}{2\ell+1} \hat{r}^{\ell-1} \odot^{\ell-1} \underline{\Delta}^{(\ell,\ell)} = \frac{2\ell+1}{\ell} (\underline{1}-\hat{r}^2) \cdot \overline{\hat{r}^{\ell+1}} , \tag{2.11}$$

which can be verified using eqs. (I.A.21) and (I.A.4), we obtain for the field on the surface of sphere i the expression

$$\vec{B}(\vec{R}_i+a\hat{r}) = \sum_{\ell=1}^{\infty} (2\ell+1)!! \, \frac{2\ell+1}{\ell} (\underline{1}-\hat{r}^2) \cdot \overline{\hat{r}^{\ell+1}} \odot^{\ell} \underline{m}_i^{(\ell)} \quad . \tag{2.12}$$

In view of the relation

$$r \frac{\partial}{\partial \vec{r}} \overline{\hat{r}^{\ell}} = -(2\ell+1) \, (\underline{1}-\hat{r}^2) \cdot \overline{\hat{r}^{\ell+1}} \tag{2.13}$$

(cf. eqs. (I.A.5) and (I.A.4)) we may alternatively write

$$\vec{B}(\vec{R}_i+a\hat{r}) = - \sum_{\ell=1}^{\infty} \frac{(2\ell+1)!!}{\ell} \, r \frac{\partial}{\partial \vec{r}} \overline{\hat{r}^{\ell}} \odot^{\ell} \underline{m}_i^{(\ell)} \quad . \tag{2.14}$$

2.2 The two sphere problem

This simplest case of diamagnetic interactions between spheres is important for the study of average properties of dilute dispersions of spheres, when pair interactions are expected to yield the dominant contribution. For two spheres eq. (2.9) takes the form

$$\underline{m}_1^{(\ell)} = b_\ell \left\{-\delta_{\ell,1}\vec{B}_{ex} + \sum_{p=1}^{\infty} \underline{A}^{(\ell,p)}(\vec{R}) \odot^p \underline{m}_2^{(p)}\right\} , \tag{2.15}$$

with $\vec{R} \equiv \vec{R}_1-\vec{R}_2$. The magnetic moments of sphere 2 may be eliminated in favour of those of sphere 1 with the aid of the obvious symmetry relation

$$\underline{m}_2^{(\ell)}(\vec{R},\vec{B}_{ex}) = \underline{m}_1^{(\ell)}(-\vec{R},\vec{B}_{ex}) . \tag{2.16}$$

In order to reduce the tensor equation (2.15) to scalar equations we make the ansatz

$$\underline{m}_1^{(\ell)} = \overline{\hat{R}^{\ell+1}} \cdot \left\{d_\ell^{\parallel}\ \hat{R}\hat{R}\cdot\vec{B}_{ex} + d_\ell^{\perp}\ (\underline{1}-\hat{R}^2)\cdot\vec{B}_{ex}\right\} \tag{2.17}$$

where $d_\ell^{\parallel}$ and $d_\ell^{\perp}$ are scalar coefficients depending on R. If one inserts this ansatz into eq. (2.15), uses relation (2.16) and repeatedly applies the tensor formulas (I.4.11) and (I.A.21) one finds

$$\begin{aligned}
\overline{\hat{R}^{\ell+1}} \cdot &\left\{d_\ell^{\parallel}\ \hat{R}\hat{R}\cdot\vec{B}_{ex} + d_\ell^{\perp}\ (\underline{1}-\hat{R}^2)\cdot\vec{B}_{ex}\right\} = \\
&= \delta_{\ell,1}\ \overline{\hat{R}^2} \cdot \left\{-\frac{3}{4}\ \hat{R}^2\cdot\vec{B}_{ex} + \frac{3}{2}\ (\underline{1}-\hat{R}^2)\cdot\vec{B}_{ex}\right\} \\
&- \sum_{p=1}^{\infty} (-1)^{\ell+p}\ \frac{(\ell+p)!\ (2\ell+1)\ell}{(\ell+1)!\ (\ell+1)!} \left(\frac{a}{R}\right)^{\ell+p+1}\ \overline{\hat{R}^{\ell+1}} \cdot \left\{\frac{p+1}{2p+1}\ d_p^{\parallel}\ \hat{R}^2\cdot\vec{B}_{ex}\right. \\
&\qquad\qquad \left. - \frac{p}{2p+1}\ d_p^{\perp}\ (\underline{1}-\hat{R}^2)\cdot\vec{B}_{ex}\right\} .
\end{aligned} \tag{2.18}$$

The fact that the tensorial structure on both sides of eq. (2.18) is equal justifies the ansatz (2.17). Eq. (2.18) holds for an arbitrary angle between $\vec{B}_{ex}$ and $\vec{R}$, so that we can extract from it two systems of linear equations for the $d_\ell^{\parallel}$ and the $d_\ell^{\perp}$. In terms of the variables

$$\tilde{d}_\ell^{\parallel} \equiv (-1)^\ell\ \sqrt{2(\ell+1)/\ell}\ \frac{(\ell+1)!}{2\ell+1}\ d_\ell^{\parallel} \tag{2.19a}$$

$$\tilde{d}_\ell^{\perp} \equiv (-1)^{\ell+1}\ \frac{(\ell+1)!}{2\ell+1}\ d_\ell^{\perp} \tag{2.19b}$$

these equations take the symmetric form

$$\tilde{d}^{\parallel}_{\ell} = \delta_{\ell,1} - \sum_{p=1}^{\infty} \frac{(\ell+p)!}{\ell!p!} \left\{\frac{\ell p}{(\ell+1)(p+1)}\right\}^{1/2} \left(\frac{a}{R}\right)^{\ell+p+1} \tilde{d}^{\parallel}_{p} \qquad (2.20a)$$

$$\tilde{d}^{\perp}_{\ell} = \delta_{\ell,1} + \sum_{p=1}^{\infty} \frac{(\ell+p)!}{\ell!p!} \frac{\ell p}{(\ell+1)(p+1)} \left(\frac{a}{R}\right)^{\ell+p+1} \tilde{d}^{\perp}_{p} \ . \qquad (2.20b)$$

The systems of equations (2.20) can be easily solved numerically if one cuts them off at a suitable multipole order.

The magnetic field at the surface of sphere 1 is obtained by inserting the expression (2.17) for the magnetic moments into formula (2.14). We first write the contracted tensors in terms of Legendre polynomials (cf. eqs. (2.13), (I.A.30) and (I.A.4))

$$\overline{\hat{r}^{\ell}} \odot^{\ell} \underline{m}_1^{(\ell)} = d^{\parallel}_{\ell} \frac{(\ell+1)!}{(2\ell+1)!!} P_{\ell}(\hat{r}\cdot\hat{R})\ \hat{R}\cdot\vec{B}_{ex}$$

$$- d^{\perp}_{\ell} \frac{\ell!}{(2\ell+1)!!} R \frac{\partial}{\partial\vec{R}} P_{\ell}(\hat{r}\cdot\hat{R}) \cdot\vec{B}_{ex} \ . \qquad (2.21)$$

Performing the differentiations with respect to $\vec{R}$ and $\vec{r}$ one then finds

$$\vec{B}(\vec{R}_1+a\hat{r}) = -\sum_{\ell=1}^{\infty} \frac{(2\ell+1)!!}{\ell} r \frac{\partial}{\partial\vec{r}} \overline{\hat{r}^{\ell}} \odot^{\ell} \underline{m}_1^{(\ell)}$$

$$= -\sum_{\ell=1}^{\infty} (\ell-1)!\ (\underline{1}-\hat{r}^2)\cdot\left\{d^{\parallel}_{\ell}\ (\ell+1)\ P'_{\ell}(\hat{r}\cdot\hat{R})\ \hat{R}^2 - d^{\perp}_{\ell}\ P'(\hat{r}\cdot\hat{R})\ (\underline{1}-\hat{R}^2)\right.$$

$$\left. - d^{\perp}_{\ell}\ P''_{\ell}(\hat{r}\cdot\hat{R})\ \hat{R}\hat{r}\cdot(\underline{1}-\hat{R}^2)\right\}\cdot\vec{B}_{ex} \ . \qquad (2.22)$$

At this point it is convenient to introduce spherical coordinates θ, ϕ on sphere 1. Polar axis and prime meridian are fixed by $\vec{R}$ and $\vec{B}_{ex}$:

$$\hat{r} = \begin{vmatrix} \cos\phi\ \sin\theta \\ \sin\phi\ \sin\theta \\ \cos\theta \end{vmatrix} , \quad \hat{R} = \begin{vmatrix} 0 \\ 0 \\ 1 \end{vmatrix} , \quad \hat{B}_{ex} = \begin{vmatrix} \sin\gamma \\ 0 \\ \cos\gamma \end{vmatrix} \ . \qquad (2.23)$$

γ denotes the angle between $\vec{R}$ and $\vec{B}_{ex}$. In these coordinates the field strength on the surface of sphere 1 is given by

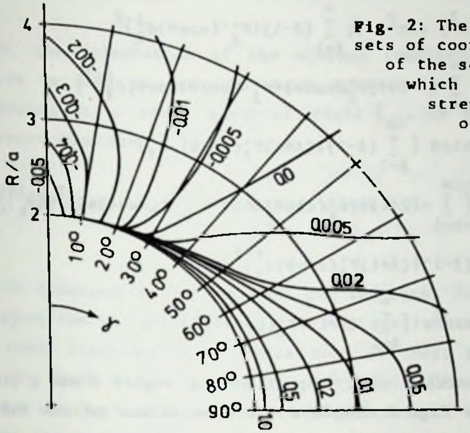
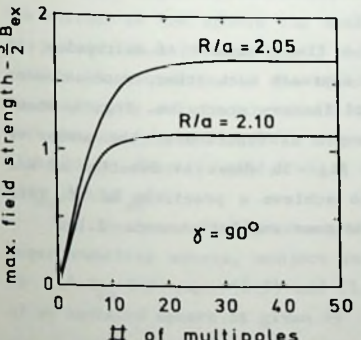


Fig. 2: The lines mark those sets of coordinates R, γ of the second sphere for which the maximum field strength at the surfaces of the spheres, divided by B_{ex}, differs from 3/2 by the value labeling the lines.



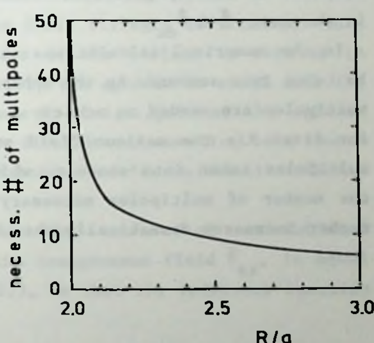


Fig. 3a: Variation of the result for the maximum field strength (measured in units of B_{ex}) with the number of multipoles taken into account.

Fig. 3b: The number of multipoles necessary in order to determine the maximum field strength at the surface of a sphere with a precision of 1%.

$$|\vec{B}(\vec{R}_1+a\hat{r})|^2 = \cos^2\phi\ \sin^2\gamma\ \sin^2\theta\ \{(\sum_{\ell=1}^{\infty}(\ell-1)!P_\ell''(\cos\theta)d_\ell^\perp)^2$$

$$-(\sum_{\ell=1}^{\infty}(\ell-1)![P_\ell'(\cos\theta)+P_\ell''(\cos\theta)\cos\theta]d_\ell^\perp)^2\}$$

$$+2\cos\phi\ \cos\gamma\ \sin\gamma\ \sin\theta\ (\sum_{\ell=1}^{\infty}(\ell-1)!(\ell+1)P_\ell'(\cos\theta)\ d_\ell^\parallel)$$

$$\times(\sum_{k=1}^{\infty}(k-1)![P_k'(\cos\theta)\cos\theta - P_k''(\cos\theta)\sin^2\theta]d_k^\perp)\}$$

$$+\{\cos^2\gamma\ \sin^2\theta\ (\sum_{\ell=1}^{\infty}(\ell-1)!(\ell+1)P_\ell'(\cos\theta)d_\ell^\parallel)^2$$

$$+\sin^2\gamma\ (\sum_{\ell=1}^{\infty}(\ell-1)!P_\ell'(\cos\theta)d_\ell^\perp)^2\}\ . \qquad (2.24)$$

The maximum of this function with respect to the angles θ and ϕ can be determined numerically. Fig. 2 displays for some values of the maximum field strength those positions of the second sphere (characterized by R and γ) which correspond to these values. When $\vec{R}$ lies parallel to $\vec{B}_{ex}$ the spheres screen each other slightly. This screening, however, is weak compared to the amplification of the maximum field strength which occurs in the case $\vec{R} \perp \vec{B}_{ex}$.

In the numerical calculations only a finite number of multipoles can be taken into account. As the spheres approach each other, more and more multipoles are needed to achieve a satisfactory precision. Fig. 3a shows for fixed R/a the maximum field strength as function of the number of multipoles taken into account, while fig. 3b shows as function of R/a the number of multipoles necessary to achieve a precision of 1%. This number increases dramatically when R becomes smaller than ca. 2.1a.

3. Indicator functions

For the calculation of the average fraction F of superconducting spheres we need to describe which spheres have already become normal conducting at a given external field $\vec{B}_{ex}$. To this end we introduce indicator functions $\chi_i^{(N)}$ by

$$\chi_i^{(N)}(\vec{R}_1,\vec{R}_2,\ldots,\vec{R}_N;\vec{B}_{ex}) \equiv \begin{cases} 1 & \text{if sphere } i \text{ is superconducting} \\ 0 & \text{if sphere } i \text{ is normal conducting} \end{cases} . \quad (3.1)$$

Due to diamagnetic interactions the indicator functions depend on the configuration of the N spheres. In this section we shall derive formulas for these functions and discuss some of their properties. One has to keep in mind, however, that the notion itself of indicator functions becomes meaningless when partial transitions of spheres can occur, i.e. for $B_{ex} < B_c = 0.45\ B_{ex}$.

Experiments conducted by Feder and McLachlan[12] on isolated superheated superconducting spheres showed that the threshold field strength at which a sphere becomes normal conducting depends on where on the surface of the sphere the maximum field strength is attained. This is probably due to very small defects of the surface as well as to anisotropic properties of the material in the sphere. We shall take the non-uniformity of the threshold values S_i $(i=1,\ldots,N)$ of the spheres into account by assuming that they are distributed according to a smooth probability density Q(S), which is zero outside a small interval $(B_{sh}[1-\Delta],B_{sh})$.

The maximum field strength at the surface of an isolated superconducting sphere, subject to the homogeneous field $\vec{B}_{ex}$, is equal to 1.5 B_{ex} (cf. eqs. (2.9) and (2.12)), so that the indicator function of an isolated sphere is given by

$$\chi_1^{(1)}(\vec{B}_{ex}) = \Theta(S_1 - \frac{3}{2} B_{ex}) . \quad (3.2)$$

Θ denotes the Heaviside function. Because of the hysteresis connected with the phenomenon of superheating and supercooling we have to specify the way in which the magnetic field reached its present value: it shall always be assumed that B_{ex} has been (slowly) increased from zero.

When two spheres are present the indicator function is given by

$$\chi_1^{(2)}(\vec{R}_1,\vec{R}_2;\vec{B}_{ex}) = \Theta\left(S_1-B_1^{(2)}(\vec{R}_1,\vec{R}_2;\vec{B}_{ex})\right)\,\Theta\left(S_2-B_2^{(2)}(\vec{R}_1,\vec{R}_2;\vec{B}_{ex})\right)$$
$$+\,\Theta\left(B_2^{(2)}(\vec{R}_1,\vec{R}_2;\vec{B}_{ex})-S_2\right)\,\Theta(S_1-S_2)\,\chi_1^{(1)}(\vec{B}_{ex})\ . \qquad (3.3)$$

Here $B_i^{(\ell+1)}(\vec{R}_i,\vec{R}_1,\ldots,\vec{R}_\ell;\vec{B}_{ex})$ denotes the maximum field strength at the surface of the perfectly diamagnetic sphere i, when ℓ other perfectly diamagnetic spheres are present at positions $\vec{R}_1,\ldots,\vec{R}_\ell$. The first term in eq. (3.3) corresponds to the case that both spheres still are superconducting. The second term accounts for the case that sphere 2 transited, as expressed by the factor $\Theta(B_2^{(2)}-S_2)$, prior to sphere 1. The latter condition is guaranteed by the factor $\Theta(S_1-S_2)$. The factor $\chi_1^{(1)}$ finally describes the state of sphere 1 after sphere 2 became normal conducting.

When $|\vec{R}_1-\vec{R}_2|$ becomes large compared to the spheres' radius the influence of the second sphere on the field strength at the surface of the first one decays as $\left(a/|\vec{R}_1-\vec{R}_2|\right)^3$ (cf. sec. 2). Therefore, if $1.5\ B_{ex} < B_{sh}(1-\Delta)$ or $1.5\ B_{ex} > B_{sh}$, there exists a certain distance of the spheres beyond which $\chi_1^{(2)} = \chi_1^{(1)}$ holds. How large this distance is depends on how far $1.5\ B_{ex}$ lies outside the interval $(B_{sh}[1-\Delta],B_{sh})$.

For the average of the indicator function with respect to the threshold values one finds from eq. (3.3), using the fact that $B_1^{(2)} = B_2^{(2)}$,

$$\bar{\chi}_1^{(2)}(\vec{R}_1,\vec{R}_2;\vec{B}_{ex}) \equiv \int dS_1 \int dS_2\ Q(S_1)\ Q(S_2)\ \chi_1^{(2)}(\vec{R}_1,\vec{R}_2;\vec{B}_{ex})$$
$$= \left(1-q(B_1^{(2)})\right)^2 + \Theta(B_1^{(2)}-B_1^{(1)})\left[\tfrac{1}{2}\,q^2(B_1^{(2)}) - \tfrac{1}{2}\,q^2(B_1^{(1)}) + q(B_1^{(2)})\left(1-q(B_1^{(2)})\right)\right]$$
$$+\,\Theta(B_1^{(1)}-B_1^{(2)})\left(1-q(B_1^{(1)})\right)q(B_1^{(2)})\ , \qquad (3.4)$$

with q denoting the primitive function of Q

$$q(S) \equiv \int_0^S Q(y)\ dy\ . \qquad (3.5)$$

In the limit $\Delta \to 0$ of a sharp distribution of threshold values q(S) becomes equal to $\Theta(S-B_{sh})$, and the expression (3.4) for the indicator function $\bar{\chi}_1^{(2)}$ then takes the simple form

$$\bar{\chi}_1^{(2)} = \Theta(B_{sh}-B_1^{(2)}) + \frac{1}{2}\,\Theta(B_1^{(2)}-B_{sh})\Theta(B_{sh}-B_1^{(1)}) \,. \tag{3.6}$$

Note that $\bar{\chi}_1^{(2)}$ would always vanish for $B_1^{(2)}>B_{sh}$ if we had assumed equal threshold values for both spheres right from the beginning, i.e. interchanged the limit $\Delta\to 0$ and the averaging over the threshold values.

For three spheres the indicator function is given by

$$\chi_1^{(3)}(\vec{R}_1,\vec{R}_2,\vec{R}_3;\vec{B}_{ex}) = \Theta(S_1-B_1^{(3)})\,\Theta(S_2-B_2^{(3)})\,\Theta(S_3-B_3^{(3)})$$

$$+\,\Theta(B_2^{(3)}-S_2)\,\Theta\!\left(\frac{S_1}{B_1^{(3)}}-\frac{S_2}{B_2^{(3)}}\right)\Theta\!\left(\frac{S_3}{B_3^{(3)}}-\frac{S_2}{B_2^{(3)}}\right)\chi_1^{(2)}(\vec{R}_1,\vec{R}_3;\vec{B}_{ex})$$

$$+\,\Theta(B_3^{(3)}-S_3)\,\Theta\!\left(\frac{S_1}{B_1^{(3)}}-\frac{S_3}{B_3^{(3)}}\right)\Theta\!\left(\frac{S_2}{B_2^{(3)}}-\frac{S_3}{B_3^{(3)}}\right)\chi_1^{(2)}(\vec{R}_1,\vec{R}_2;\vec{B}_{ex}) \,. \tag{3.7}$$

Three situations have now to be distinguished, corresponding respectively to the cases that all three spheres still are superconducting (first term), that sphere 2 (second term) transited prior to spheres 1 and 3, and that sphere 3 (third term) transited prior to spheres 1 and 2. We here have to write $\Theta(S_1/B_1^{(3)}-S_2/B_2^{(3)})$ where we wrote $\Theta(S_1-S_2)$ in eq. (3.3): This is necessary because with three spheres present the maximum field strengths at their surfaces are in general not equal.

For an arbitrary number N of spheres the indicator function can be constructed recursively:

$$\chi_1^{(N)}(\vec{R}_1,\ldots,\vec{R}_N;\vec{B}_{ex}) = \prod_{i=1}^{N}\Theta(S_i-B_i^{(N)}) + \sum_{j=2}^{N}\{\Theta(B_j^{(N)}-S_j)$$

$$\times\,[\prod_{\substack{i=1\\ i\neq j}}^{N}\Theta\!\left(\frac{S_i}{B_i^{(N)}}-\frac{S_j}{B_j^{(N)}}\right)]\,\chi_1^{(N-1)}(\vec{R}_1,\ldots,\vec{R}_{j-1},\vec{R}_{j+1},\ldots,\vec{R}_N;\vec{B}_{ex})\}. \tag{3.8}$$

4. Density expansion of the fraction F

4.1 The general scheme

The average fraction F of superconducting spheres is given by the configurational average <...> of $\overline{\chi}_1^{(N)}$:

$$F(B_{ex}) = \frac{1}{N} < \sum_{i=1}^{N} \overline{\chi}_i^{(N)} > = <\overline{\chi}_1^{(N)}>$$

$$= \int \overline{\chi}_1^{(N)}(\vec{R}_1,\ldots,\vec{R}_N;\vec{B}_{ex})\ P_N(\vec{R}_1,\ldots,\vec{R}_N)\ d\vec{R}_1\ldots d\vec{R}_N\ . \qquad (4.1)$$

In order to keep the notation simple, we shall from now on sometimes omit the sphere label when speaking of sphere 1 and write $\overline{\chi}^{(N)}$ instead of $\overline{\chi}_1^{(N)}$, $B^{(\ell)}$ instead of $B_1^{(\ell)}$ etc. P_N in eq. (4.1) denotes the probability density for the configurations of N spheres. It is clearly not feasible to evaluate the average of the complicated function $\overline{\chi}^{(N)}$ exactly, and approximations have to be made.

For low number density n_o, or equivalently low volume fraction $\phi = \frac{4\pi}{3} a^3 n_o$ of dispersed spheres, one may try to approximate F by the first terms of its Taylor series in ϕ. As is well-known, the Taylor coefficients can be calculated if on the one hand the reduced distribution functions belonging to P_N are analytic in ϕ, and if on the other hand $\overline{\chi}^{(N)}$ possesses a cluster expansion, i.e. if one can write

$$\overline{\chi}^{(N)}(\vec{R}_1,\ldots,\vec{R}_N;\vec{B}_{ex}) = \overline{\chi}^{[1]}(\vec{R}_1;\vec{B}_{ex}) + \sum_{i=2}^{N} \overline{\chi}^{[2]}(\vec{R}_1,\vec{R}_i;\vec{B}_{ex})$$

$$+ \sum_{\substack{i,j=2\\ j\neq i}}^{N} \overline{\chi}^{[3]}(\vec{R}_1,\vec{R}_i,\vec{R}_j;\vec{B}_{ex}) + \ldots, \qquad (4.2)$$

with 'cluster functions' $\overline{\chi}^{[\ell]}$, symmetrical with respect to their first ℓ arguments, which tend sufficiently fast to zero as the difference between any of these arguments becomes larger and larger. Taking the average of the ℓ^{th} term of the right member of eq. (4.2) one obtains

$$\int \sum_{\substack{i_2,\ldots,i_\ell=2 \\ i_k \neq i_j \text{ for } k\neq j}}^{N} \overline{\chi}^{[\ell]}(\vec{R}_1,\vec{R}_{i_2},\ldots,\vec{R}_{i_\ell};\vec{B}_{ex})\; P_N(\vec{R}_1,\ldots,\vec{R}_N)\; d\vec{R}_1\ldots d\vec{R}_N$$

$$= \frac{1}{N}\frac{N!}{(N-\ell)!}\int \overline{\chi}^{[\ell]}(\vec{R}_1,\vec{R}_2,\ldots,\vec{R}_\ell;\vec{B}_{ex})\; P_\ell(\vec{R}_1,\ldots,\vec{R}_\ell)\; d\vec{R}_1\ldots d\vec{R}_\ell$$

$$= n_o^{\ell-1}\int \overline{\chi}^{[\ell]}(\vec{R}_1,\ldots,\vec{R}_\ell;\vec{B}_{ex})\; g_\ell(\vec{R}_1,\ldots,\vec{R}_\ell)\; d\vec{R}_2\ldots d\vec{R}_\ell \quad . \tag{4.3}$$

Here P_N was assumed to be translationally invariant and symmetric in all pairs of its arguments. If the ℓ-particle correlation function g_ℓ is analytic in ϕ, and if the integral in eq. (4.3) converges for each ℓ, one can find from eqs. (4.1) - (4.3) the density expansion of F in powers of ϕ:

$$F(\phi,B_{ex}) = F_0(B_{ex}) + \phi F_1(B_{ex}) + \phi^2 F_2(B_{ex}) + \ldots \tag{4.4}$$

In particular, when one is only interested in the first ℓ terms of this series, it suffices to study the interactions between at most ℓ spheres.

The form which the functions $\chi^{[\ell]}$ must have, if a cluster expansion exists, can be determined by considering eq. (4.2) for different N. Thus we see from

$$\overline{\chi}^{(1)} = \overline{\chi}^{[1]} \quad , \tag{4.5}$$

$$\overline{\chi}^{(2)}(\vec{R}_1,\vec{R}_2) = \overline{\chi}^{[1]} + \{\overline{\chi}^{(2)}(\vec{R}_1,\vec{R}_2) - \overline{\chi}^{[1]}\} \tag{4.6}$$

that

$$\overline{\chi}^{[2]}(\vec{R}_1,\vec{R}_2) = \overline{\chi}^{(2)}(\vec{R}_1,\vec{R}_2) - \overline{\chi}^{(1)}. \tag{4.7}$$

Analogously one finds

$$\bar{\chi}^{[3]}(\vec{R}_1,\vec{R}_2,\vec{R}_3) = \frac{1}{2}\{\bar{\chi}^{(3)}(\vec{R}_1,\vec{R}_2,\vec{R}_3) - \bar{\chi}^{[2]}(\vec{R}_1,\vec{R}_2) - \bar{\chi}^{[2]}(\vec{R}_1,\vec{R}_3) - \bar{\chi}^{[1]}\} \tag{4.8}$$

and all higher $\bar{\chi}^{[\ell]}$.

We now turn to the question whether the integrals in eq. (4.3) converge. In the case $\ell=2$ we already saw in section 3 that $\bar{\chi}^{[2]}$ is of finite range as long as $1.5\ B_{ex} < (1-\Delta)B_{sh}$ or $1.5\ B_{ex} > B_{sh}$ holds. When the maximum field strength $1.5\ B_{ex}$ at the surface of an isolated sphere lies inside the interval $(B_{sh}[1-\Delta\ ], B_{sh})$, however, $\bar{\chi}^{[2]}(\vec{R}_1,\vec{R}_2;\vec{B}_{ex})$ becomes long-ranged. One then finds for widely separated spheres with $B^{(2)}(\vec{R}_1,\vec{R}_2) \approx B^{(1)}$ from eqs. (4.7), (3.2) and (3.4)

$$\begin{aligned}\bar{\chi}^{[2]}(\vec{R}_1,\vec{R}_2;\vec{B}_{ex}) &= \bar{\chi}^{(2)} - \bar{\chi}^{(1)} = \bar{\chi}^{(2)} - 1 + q(B^{(1)}) \\ &= \Theta(B^{(2)}-B^{(1)})\{\tfrac{1}{2}q^2(B^{(2)}) - q(B^{(2)}) - \tfrac{1}{2}q^2(B^{(1)}) + q(B^{(1)})\} \\ &\quad + \Theta(B^{(1)}-B^{(2)})(1 - q(B^{(2)}))(q(B^{(1)}) - q(B^{(2)})) \\ &= Q(B^{(1)})\ (q(B^{(1)})-1)\ \{B^{(2)} - B^{(1)}\} + \mathcal{O}(\{B^{(2)} - B^{(1)}\}^2)\ .\end{aligned} \tag{4.9}$$

The difference $B^{(2)}(\vec{R}_1,\vec{R}_2) - B^{(1)}$ is in leading order proportional to the dipole tensor, as can be seen using eqs. (2.9) and (2.12) ($\vec{R}$ again abbreviates $\vec{R}_1-\vec{R}_2$)

$$\begin{aligned}&B^{(2)}(\vec{R}_1,\vec{R}_2;\vec{B}_{ex}) - B^{(1)}(\vec{R}_1;\vec{B}_{ex}) = \\ &= \max_{\hat{r}} |3(\underline{1}-\hat{r}^2)\cdot\tfrac{1}{2}\{-\vec{B}_{ex} - \underline{A}^{(1,1)}(\vec{R})\cdot\tfrac{1}{2}\vec{B}_{ex} + \mathcal{O}(R^{-4})\}| - \tfrac{3}{2}B_{ex} \\ &= -\tfrac{9}{4}\hat{B}_{ex}\cdot(\tfrac{a}{R})^3\ \overline{\hat{R}^2}\cdot\vec{B}_{ex} + \mathcal{O}(R^{-4})\ .\end{aligned} \tag{4.10}$$

Thus for $B_{sh}(1-\Delta) < 1.5\ B_{ex} < B_{sh}$ the decay of $\bar{\chi}^{[2]}(\vec{R}_1,\vec{R}_2;\vec{B}_{ex})$ as $|\vec{R}_1-\vec{R}_2| \to \infty$ is too slow to make the integral (4.3) absolutely convergent. By virtue of the special properties of the dipole tensor, however, the integral converges conditionally and depends for a large sample only on the sample's shape. This is a familiar feature of magnetostatic interaction problems and mathematically related ones. A similar shape dependence occurs already if one calculates the magnetization of a simple diamagnetic medium as function of a homogeneous applied field.

We believe that also in the case $\ell \geq 3$ the integral in eq. (4.3) converges at least conditionally. Unfortunately, however, we did not succeed in providing a general proof.

4.2 The coefficient F_1

This subsection will be devoted to the discussion of the coefficient $F_1(B_{ex})$, which according to eqs. (4.1) - (4.4) and (4.7) as well as eq. (3.4) is given by

$$F_1(B_{ex}) = \frac{3}{4\pi a^3} \int_{|\vec{R}_1-\vec{R}_2|>2a} d\vec{R}_2 \quad \bar{\chi}^{[2]}(\vec{R}_1,\vec{R}_2;\vec{B}_{ex})$$

$$= 3 \int_{R=2a}^{\infty} d\frac{R}{a} \left(\frac{R}{a}\right)^2 \int_{\gamma=0}^{\pi/2} d\gamma \, \sin\gamma \, \{\Theta(B^{(2)}-B^{(1)})(\tfrac{1}{2}q^2(B^{(2)})-q(B^{(2)})-\tfrac{1}{2}q(B^{(1)})$$

$$+q(B^{(1)})) + \Theta(B^{(1)}-B^{(2)})(1-q(B^{(2)}))(q(B^{(1)})-q(B^{(2)}))\} \,. \qquad (4.11)$$

Here we assumed a hard-sphere fluid like distribution of spheres, using for the pair correlation function the expression

$$g_2 = \Theta(|\vec{R}_1-\vec{R}_2| - 2a) + \mathcal{O}(\phi) \,. \qquad (4.12)$$

The function q describing the distribution of threshold values has in principle to be determined experimentally, e.g. by measuring $F(B_{ex})$ in very dilute systems when

$$F(B_{ex}) = F_0(B_{ex}) = 1 - q(\tfrac{3}{2}B_{ex}) \,. \qquad (4.13)$$

Lacking suitable experimental data, however, we shall use a simple model distribution which is continuous and vanishes outside the interval $(B_{sh}[1-\Delta],B_{sh})$:

$$Q(S) = \begin{cases} 0 & \text{if } S < B_{sh}(1-\Delta) \text{ or } S > B_{sh}\,, \\ \frac{6}{\Delta^3}\left\{\frac{\Delta^2}{4} - \left(1-\frac{\Delta}{2} - \frac{S}{B_{sh}}\right)^2\right\} & \text{elsewhere.} \end{cases} \tag{4.14}$$

The evaluation of the integral in formula (4.11) was for $24a > |\vec{R}_1-\vec{R}_2|$ performed numerically, with the maximum field strength $B^{(2)}$ at the surface of sphere 1 calculated using eqs. (2.20) and (2.24). The contribution to the integral from configurations with $|\vec{R}_1-\vec{R}_2| > 24a$ was determined analytically with the aid of eqs. (4.9) and (4.10) (neglecting terms of order R^{-4} in the integrand) for a sample having the form of a flat slice perpendicular to $\vec{B}_{ex}$; this is the geometry used in the experiments. The results thus obtained for the coefficient $F_1(B_{ex})$ are listed in table I and displayed in fig. 4. The absolute numerical error made is estimated to be lower than 0.01 in the range $0.3 < B_{ex}/B_{sh} < 0.5$, while for $B_{ex}/B_{sh} > 0.5$ the relative numerical error is estimated lower than 2%.

If $1.5\ B_{ex} = B^{(1)} < B_{sh}(1-\Delta)$ or $B_{sh} < B^{(1)}$, there exists a distance of the spheres beyond which $\bar{\chi}^{[2]}$ vanishes, as discussed above. This range is plotted in fig. 5 as function of B_{ex}. We observe that for $B_{ex} \gtrsim 0.45\ B_{sh}$ the range greater than 2.2a, and consequently those configurations, in which the distance between the surfaces of the spheres is comparable to the field penetration depth, then do not essentially contribute to F_1 (cf. also sect. 1, assumption (3)). Not taking into account the field penetration therefore imposes no additional restriction on the validity of the theory, since due to the neglect of the possibility of partial transitions of spheres it is only reliable for $B_{ex} > 0.45\ B_{sh}$ anyway.

In order to understand the form of the function $F_1(B_{ex})$ let us have a look at fig. 6, where $\bar{\chi}^{[2]}$ is shown in dependence of $(B^{(2)} - B^{(1)})/B_{ex}$ for $\Delta = 0.2$ and different values of $B^{(1)}$. As long as $B^{(1)} < B_{sh}(1-\Delta) = 0.8\ B_{sh}$, only those configuratons of the spheres contribute to F_1 for which $B_1^{(2)} - B_1^{(1)} > (1-\Delta)B_{sh} - B_1^{(1)}$. For $B_1^{(1)}$ approaching 0.8 B_{sh} from below more and more of these field strength amplifying configuration contribute, and F_1 decreases. As $B^{(1)}$ increases above 0.8 B_{sh} the function $\bar{\chi}_1^{[2]}$ becomes positive for $B^{(2)} - B^{(1)} < 0$ and less negative for $B^{(2)} - B^{(1)} > 0$, implying that on the one hand also

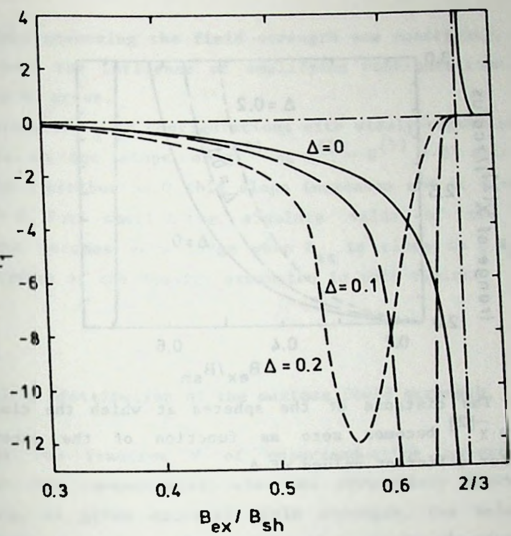


Fig. 4: The coefficient $F_1(B_{ex})$ for different widths Δ of the distribution of threshold values.

Table I: The coefficient $F_1(B_{ex})$

B_{ex}/B_{sh}	F_1 for Δ=0	Δ=0.1	Δ=0.2
0.30	-0.15	-0.18	-0.24
0.35	-0.26	-0.31	-0.42
0.40	-0.42	-0.53	-0.71
0.45	-0.67	-0.86	-1.21
0.50	-1.02	-1.40	-2.17
0.52	-1.24	-1.73	-2.97
0.54	-1.49	-2.17	-6.88
0.56	-1.82	-2.81	-11.6

B_{ex}/B_{sh}	F_1 for Δ=0.1	Δ=0.1	Δ=0.2
0.58	-2.24	-3.92	-11.5
0.60	-2.83	-7.75	-8.16
0.62	-3.83	-22.5	-3.88
0.64	-5.54	-9.45	-0.90
0.66	-16.8	-0.15	-0.02
0.68	0.26	0.00	0.00
0.70	0.00	0.00	0.00

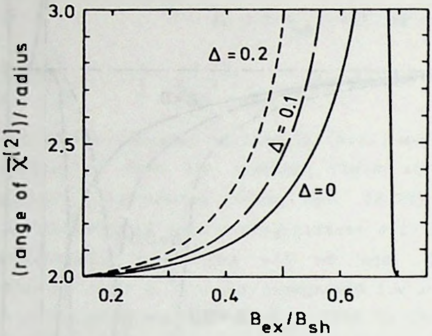


Fig. 5: The distance of the spheres at which the cluster function $\bar{\chi}^{[2]}$ becomes zero as function of the external field, for different values of Δ.

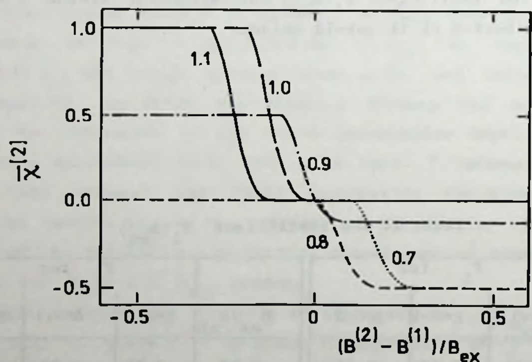


Fig. 6: The cluster function $\bar{\chi}^{[2]}$ as function of $B^{(2)}-B^{(1)}$, for Δ=0.2 . The numbers labeling the curves give the values of $B^{(1)}/B_{sh}$ to which they belong.

configurations screening the field strength now contribute, and that on the other hand the influence of amplifying configurations diminishes; consequently F_1 grows.

The influence on F_1 of configurations with widely separated spheres is proportional to the slope of $\bar{\chi}^{[2]}$ at $B^{(2)} - B^{(1)} = 0$; with decreasing width of the distribution Q this slope increases and it diverges in the limit $\Delta \to 0$. For small Δ the absolute value of the coefficient F_1 therefore becomes very large when B_{ex} is close to $\frac{2}{3} B_{sh}$, implying poor convergence of the density expansion in this region.

5. Probability distribution of the maximum field strength

Besides the fraction F of superconducting spheres, on which experiments have concentrated, also the probability distribution P(B) for finding, at given external field strength, the value B for the maximum field strength at the surface of a superconducting sphere is a quantity of interest. An elementary particle detector, as described in the introduction, would be run at an external field strength well below that at which an appreciable fraction of spheres is lost due to diamagnetic interaction induced transitions. In order to estimate the sensitivity of the detector, one needs to know how many spheres are how close to their transition points, and in this connection the distribution P(B) is important.

Rather than with the distribution function P itself we prefer to work with its integral p, given by

$$p(B) \equiv \int_0^B P(B')dB' = \frac{\text{average number of superconducting spheres with maximum field strength smaller than B}}{\text{average number of superconducting spheres}} \qquad (5.1)$$

Obviously P(B) vanishes for $B > B_{sh}$, and in what follows it shall always be understood that $B < B_{sh}$. In order to write down a formula for P(B) we need to introduce the new symbol $\tilde{B}_i^{(N)}$, denoting the actual maximum field strength at the surface of a superconducting sphere i. While in $B_i^{(N)}$ all N spheres are assumed to be perfectly diamagnetic, in the calculation of $\tilde{B}_i^{(N)}$ only those still superconducting are taken into account,

$$\tilde{B}_i^{(N)} = B_i^{(s+1)}(\vec{R}_i,\vec{R}_{j_1},\ldots,\vec{R}_{j_s};\vec{B}_{ex}) \qquad \text{(with } i,j_1,\ldots,j_s \text{ the indices of all still super-conducting spheres).} \tag{5.2}$$

Using the new notation we may write

$$p(B) = \frac{\langle \sum_{i=1}^{N} \overline{\chi_i^{(N)}\Theta(B-\tilde{B}_i^{(N)})}\rangle}{\langle \sum_{i=1}^{N} \overline{\chi}_i^{(N)} \rangle} = \frac{1}{F} \langle \overline{\chi^{(N)}\Theta(B-\tilde{B}^{(N)})} \rangle . \tag{5.3}$$

Analogously to the density expansion of $F(B_{ex})$ in section 4 we shall here calculate the interaction contribution to $p(B)$ to first order in the volume fraction. Under the assumption that a cluster expansion of $\overline{\chi^{(N)}\Theta(B-\tilde{B}^{(N)})}$ exists we find from eq. (5.3) for a hard-sphere fluid like distribution of spheres (cf. also eqs. (4.1)-(4.7))

$$\begin{aligned} p(B) = \{ & \overline{\chi^{(1)}\Theta(B-\tilde{B}^{(1)})} \\ & + \frac{3\phi}{4\pi a^3} \int_{|\vec{R}_1-\vec{R}_2|>2a} d\vec{R}_2 \, [\overline{\chi^{(2)}(\vec{R}_1,\vec{R}_2;\vec{B}_{ex})\Theta(B-\tilde{B}^{(2)})} - \overline{\chi^{(1)}\Theta(B-\tilde{B}^{(1)})}] \\ & + \mathcal{O}(\phi^2)\} \times \{F_0(B_{ex}) + \phi\, F_1(B_{ex}) + \mathcal{O}(\phi^2)\}^{-1} . \end{aligned} \tag{5.4}$$

To proceed the averages over the threshold values have to be performed. For a single superconducting sphere $\tilde{B}^{(1)}$ is obviously equal to $B^{(1)}$ when $\chi^{(1)} \neq 0$, so that

$$\overline{\chi^{(1)}\Theta(B-\tilde{B}^{(1)})} = \overline{\chi}^{(1)}\Theta(B-B^{(1)}) . \tag{5.5}$$

When two spheres are present $\tilde{B}^{(2)}$ is either equal to $B^{(2)}$ or to $B^{(1)}$, depending on whether sphere 2 still is superconducting. From eqs. (3.3) we find (remember that $B_2^{(2)} = B_1^{(2)} \equiv B^{(2)}$)

$$\chi^{(2)}\Theta(B-\tilde{B}^{(2)})=\{\Theta(S_1-B^{(2)})\Theta(S_2-B^{(2)})$$

$$+\Theta(B^{(2)}-S_2)\Theta(S_1-S_2)\Theta(S_1-B^{(1)})\}\Theta(B-\tilde{B}^{(2)})$$

$$=\Theta(S_1-B^{(2)})\Theta(S_2-B^{(2)})\Theta(B-B^{(2)})+\Theta(B^{(2)}-S_2)\Theta(S_1-S_2)\Theta(S_1-B^{(1)})\Theta(B-B^{(1)})$$

$$=\chi^{(2)}\Theta(B-B^{(1)})+\Theta(S_1-B^{(2)})\Theta(S_2-B^{(2)})\left(\Theta(B-B^{(2)})-\Theta(B-B^{(1)})\right), \quad (5.6)$$

yielding for the average over the threshold values

$$\overline{\chi^{(2)}\Theta(B-\tilde{B}^{(2)})}=\bar{\chi}^{(2)}\Theta(B-B^{(1)})+\{1-q(B^{(2)})\}^2\left(\Theta(B-B^{(2)})-\Theta(B-B^{(1)})\right). \quad (5.7)$$

By inserting formulae (5.5) and (5.7) into eq. (5.4) and expanding the denominator of the r.h.s. of that equation (which is of course only possible if $|\phi F_1| < F_0$) one arrives at the desired expression for the integral of the probability distribution:

$$p(B)=\{(F_0+\phi F_1)\Theta(B-B^{(1)})+\frac{3\phi}{4\pi a^3}\int_{|\vec{R}_1-\vec{R}_2|>2a} d\vec{R}_2\ [(1-q(B^{(2)}))^2$$

$$\times\left(\Theta(B-B^{(2)})-\Theta(B-B^{(1)})\right)]+\mathcal{O}(\phi^2)\}\ \{F_0+\phi F_1+\mathcal{O}(\phi^2)\}^{-1}$$

$$=p_0(B)+\phi p_1(B)+\mathcal{O}(\phi^2), \quad (5.8)$$

with

$$p_0(B)\equiv\Theta(B-B^{(1)}), \quad (5.9)$$

$$p_1(B)\equiv\frac{3}{F_0(B_{ex})4\pi a^3}\int_{|\vec{R}_1-\vec{R}_2|>2a} d\vec{R}_2\ \{1-q(B^{(2)})\}^2\left(\Theta(B-B^{(2)})-\Theta(B-B^{(1)})\right). \quad (5.10)$$

The first term p_0 in the last member of eq. (5.8) corresponds to the sharp probability distribution $\delta(B-1.5\ B_{ex})$ of the maximum field strength which one finds on non-interacting spheres. The second term ϕp_1 describes to lowest order the broadening of $P(B)$ due to diamagnetic interactions. One easily convinces oneself that p_1 is non-negative for $B < B^{(1)}$ and non-positive for $B > B^{(1)}$, as it must be because $p(B)$

on the l.h.s of eq. (5.8) satisfies the condition $0 \leq p(B) \leq 1$. The integrand in p_1 contains a factor $\{1-q(B^{(2)})\}^2$, which damps it for $B^{(2)}$ close to B_{sh}. This factor can be understood physically, if one realizes that spheres in configurations with high values of $B^{(2)}$ have already transited into the normal conducting state with enhanced probability. The broader the distribution Q of threshold values is, the smaller are the values of $B^{(2)}$ for which $\{1-q(B^{(2)})\}^2$ significantly deviates from unity, and the smaller is p_1: thus a broadening of Q will result in a sharpening of P(B). For $B^{(2)} > B_{sh}$ the factor $\{1-q(B^{(2)})\}^2$ vanishes, and when $B > B^{(1)}$ the integrand is therefore only non-zero if $B < B^{(2)} < B_{sh}$. Thus p_1 tends to zero as B approaches B_{sh} from below, in accordance with the normalization condition $p(B_{sh}) = 1$. The factor $1/F_0(B_{ex})$ contained in p_1 stems from the fact that p(B) gives the ratio of the number of superconducting spheres with maximum field strength smaller than B and the total number of **superconducting** spheres.

An interesting special situation is the limit $\Delta \to 0$ of a sharp distribution of threshold field strengths, when one has

$$(1 - q(B^{(2)}))^2 = \Theta(B_{sh} - B^{(2)}) \ . \tag{5.11}$$

One may then write , inserting a 'constructive zero' and recalling that $B < B_{sh}$,

$$\begin{aligned}
&(1-q(B^{(2)}))^2 \ \{\Theta(B-B^{(2)})-\Theta(B-B^{(1)})\} \\
&= \Theta(B-B^{(2)}) - \{\Theta(B-B^{(1)})-\Theta(B-B^{(1)})\Theta(B_{sh}-B^{(1)})\} - \Theta(B_{sh}-B^{(2)})\Theta(B_{sh}-B^{(1)}) \\
&= (\Theta(B-B^{(2)})-\Theta(B-B^{(1)})) - \Theta(B-B^{(1)})\{\Theta(B_{sh}-B^{(2)})-\Theta(B_{sh}-B^{(1)})\} \ ,
\end{aligned} \tag{5.12}$$

and the expression (5.10) for the coefficient p_1 takes the form

$$\begin{aligned}
p_1(B) = &- \Theta(B-B^{(1)}) \frac{3}{4\pi a^3} \int_{|\vec{R}_1-\vec{R}_2|>2a} d\vec{R}_2 \ (\Theta(B_{sh}-B^{(2)})-\Theta(B_{sh}-B^{(1)})) \\
&+ \frac{3}{4\pi a^3} \int_{|\vec{R}_1-\vec{R}_2|>2a} d\vec{R}_2 \ (\Theta(B-B^{(2)}) - \Theta(B-B^{(1)})) \ .
\end{aligned} \tag{5.13}$$

The integrals in eq. (5.13) are connected with the coefficient F_1 (also evaluated in the limit $\Delta \to 0$) in a simple manner; comparison with eqs. (3.6) and (4.11) shows that

$$p_1(B) = -\Theta(B-B^{(1)})2F_1(B_{ex}) + \left(\Theta(B^{(1)}-B)+2\Theta(B-B^{(1)})\right)F_1(B_{ex}\frac{B_{sh}}{B}). \quad (5.14)$$

For $\Delta \neq 0$ there is no such simple relation between p_1 and F_1.

In fig. 7 we plotted $p_0(B) + 0.1\, p_1(B)$, the result of the first order density expansion of p(B) at a volume fraction of 10%, for three different values of the external field strength and three different values of the width Δ of the distribution Q of threshold values. Apparently 10% volume fraction suffices for an appreciable broadening of P(B). For $B_{ex}/B_{sh} = 0.2$ the influence of finite Δ is too small to be resolved in the figure, but at larger external field strengths it is clearly visible that a positive Δ makes P(B) narrower. At $B=\frac{3}{2}B_{ex}$, where the lowest order p_0 of the expansion has a jump discontinuity, the density expansion converges poorly (cf. also the discussion at the end of section 4.2); therefore the two branches of the curves do not match at that point.

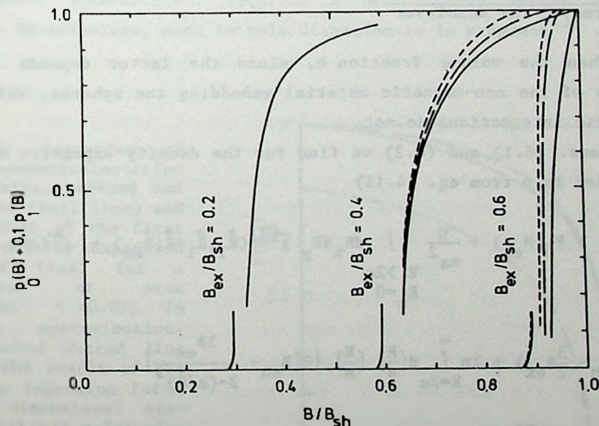


Fig. 7: The result of the first order density expansion for the integral p of the probability distribution P, at $\phi=0.1$. The full lines correspond to $\Delta=0$, the broken lines to $\Delta=0.1$ and the dashed lines to $\Delta=0.2$.

6. Comparison with other work

We shall first compare our results with those of a computer simulation carried out by Valette, Waysand and Stauffer[9]. In this simulation, as in our theory, the spheres were supposed to be monodisperse in size and distributed in a hard-sphere fluid like fashion. A sharp distribution of threshold values was assumed. In contrast to our work, however, only dipole interactions were taken into account, and only a two dimensional arrangement of spheres - a 'monolayer' perpendicular to the external field - was considered. Before a comparison with the simulation is possible, we have to restrict our theory to this case.

Retaining only dipoles in eqs. (2.12), (2.17) and (2.18) we find for the maximum field strength the simple expression

$$B^{(2)} = \frac{3}{2}\left\{\left(\frac{\cos\gamma}{1+(a/R)^3}\right)^2 + \left(\frac{\sin\gamma}{1-(a/R)^3/2}\right)^2\right\}^{1/2} B_{ex} \,. \tag{6.1}$$

In the assumed geometry γ is equal to 90 degrees. The appropriate parameter for the density expansion is the area fraction

$$\eta \equiv \frac{N\,\pi a^2}{\text{area of the monolayer}} \tag{6.2}$$

rather than the volume fraction ϕ, since the latter depends on the thickness of the non-magnetic material embedding the spheres, while the diamagnetic interactions do not.

Using eqs. (6.1) and (6.2) we find for the density expansion of F to first order in η from eq. (4.11)

$$F(B_{ex}) = F_0(B_{ex}) + \frac{\eta}{\pi a^2} \int_{\substack{R>2a \\ R_z=0}} dR_x dR_y\, \overline{\chi}^{[2]}(\vec{R}_1,\vec{R}_1+\vec{R};\vec{B}_{ex}) + \mathcal{O}(\eta^2)$$

$$= \Theta(B_{sh}-\tfrac{3}{2}B_{ex}) + 2\eta \int_{R=2a}^{\infty} d\left(\frac{R}{a}\right)\left(\frac{R}{a}\right)\Big\{\Theta\Big(B_{sh}-\frac{3B_{ex}}{2-(a/R)^3}\Big)$$

$$+\frac{1}{2}\,\Theta\Big(\frac{3B_{ex}}{2-(a/R)^3}-B_{sh}\Big)\Theta\big(B_{sh}-\tfrac{3}{2}B_{ex}\big) - \Theta\big(B_{sh}-\tfrac{3}{2}B_{ex}\big)\Big\} + \mathcal{O}(\eta^2)$$

$$= \Theta(B_{sh} - \tfrac{3}{2}B_{ex})\{1 - \eta \int_{\xi=2}^{\infty} d\xi\ \xi\ \Theta(\frac{3B_{ex}}{2-\xi^{-3}} - B_{sh})\} + \mathcal{O}(\eta^2)$$

$$= \Theta(B_{sh} - \tfrac{3}{2}B_{ex})\{1 - \frac{\eta}{2}\left((2-3\frac{B_{ex}}{B_{sh}})^{-2/3} - 4\right)\Theta(\frac{B_{ex}}{B_{sh}} - \frac{5}{8})\} + \mathcal{O}(\eta^2)\ . \qquad (6.3)$$

In fig. 8 the first order density expansion (6.3) of F is compared to the simulation of Valette, Waysand and Stauffer. The agreement of both curves is very satisfactory; the small difference between them could be due to higher orders in η. Only near $B_{ex}/B_{sh} = 2/3$, the point at which the density expansion diverges (cf. sect. 4.2), the discrepancy between the simple formula (6.3) and the simulation becomes appreciable.

The area fraction η=0.075 used in the simulation corresponds to a volume fraction ϕ=0.05, if one takes the thickness of the monolayer equal to the diameter of the spheres. For this volume fraction the result of the density expansion for a three dimensional system, with all multipoles taken into account, is also shown in fig. 8. As had to be expected, it substantially deviates from the two dimensional model in dipole approximation. The simulation of a three dimensional system, with as many multipoles retained as needed for a realistic description of the diamagnetic interactions, requires a dramatically higher numerical effort. Nevertheless, work in this direction is in progress[13).

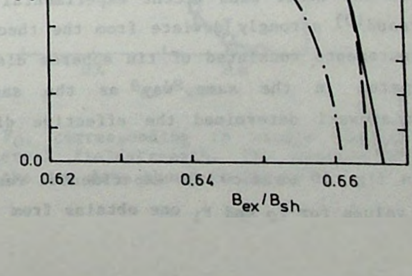


Fig. 8: Comparison of the computersimulation by Valette, Waysand and Stauffer (full line) and the result of the first order density expansion (dashed line) for a monolayer of area fraction η =0.075 in dipole approximation. The dashed dotted line marks the result of the density expansion for a three dimensional system, with all multipoles taken into account, at ϕ=0.05 .

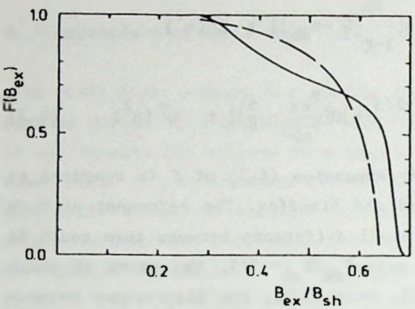


Fig. 9: Comparison of the experimental results of Feder and McLachlan (full line) with the first order density expansion at ϕ=0.16 and Δ=0 (dashed line).

Comparison of our results with real experiments is problematic, since the presently available data were obtained with samples which strongly deviate from the idealized system treated in this work.

Fig. 9 shows measurements conducted by Feder and McLachlan[12] on indium spheres mixed with plastic powder. The volume fraction of indium was about 1/6. The spheres were not at all monodisperse, but their radii varied from 5 to 25 µm. Since Feder and McLachlan did not use the pulse detection method mentioned in the introduction; they essentially measured the effective permeability of the sample, so that they could not distinguish between the transitions of one large sphere and those of several small ones. Keeping this in mind, it is not astonishing that the measurements of Feder and McLachlan do not quantitatively agree with the result of the first order density expansion, also drawn in fig. 9 for ϕ=0.17 and Δ=0 . We rather consider remarkable the extent to which the theoretical curve corresponding to a strongly idealized system correctly describes the global form of the experimental results.

On the other hand recent experimental data obtained by Mettout and Waysand[10] strongly deviate from the theory. The samples used in their measurements consisted of tin spheres dispersed in paraffin; they were prepared in the same way as the samples of which Mettout and Broniatowski determined the effective dielectric constant (cf. sect. I.7.2).

In fig. 10 we show the experimental results. Figs. 11 and 12 display the values for F_0 and F_1 one obtains from them by a least square fit of

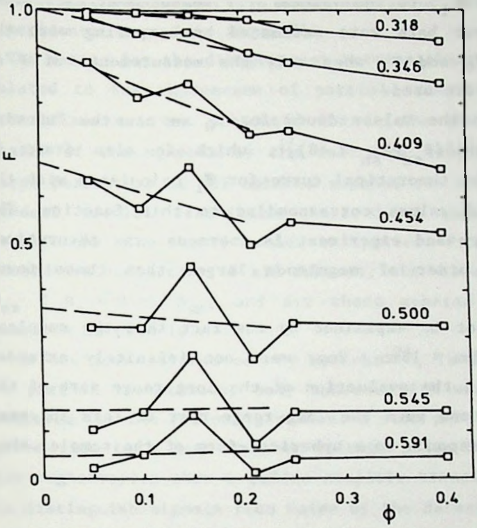


Fig. 10: The experimental results of Mettout and Waysand. Plotted is the fraction F versus the volume fraction ϕ; the numbers marking the curves give the value of the ratio B_{ex}/B_{sh} to which they belong. The dashed lines are the fits used to extract the values of F_0 and F_1 plotted in figs. 11 and 12.

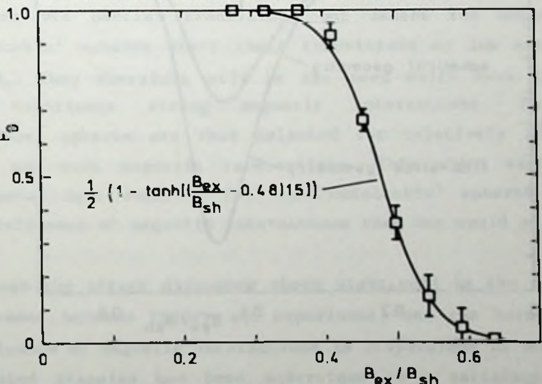


Fig. 11: The fraction F_0, corresponding to single particle effects, versus the external fieldstrength. The experimental points are obtained from the raw data shown in fig. 10.

the linear function $F_0 + \phi F_1$ to the values of F measured at $\phi = 0.05$, 0.1, 0.15 and 0.21. Error bars were estimated by comparing with the results one finds for F_0 and F_1 when only the measurements of F at $\phi = 0.05$ and $\phi = 0.1$ are used.

To interpolate between the values found for F_0 we use the function $F_0(B_{ex}) = (1/2)\{1 - \tanh(15(B_{ex}/B_{sh}-0.48))\}$, which is also drawn in fig. 11. Fig. 12 shows the theoretical curve for F_1 calculated with the distribution of threshold values corresponding to this function. The discrepancy between theory and experiment is enormous: the theoretical values for F_1 are one order of magnitude larger than those found experimentally.

This disagreement cannot be explained by the fact that the samples, which had dimensions 20mm × 15mm × 2mm, were not infinitely extended flat slices, as assumed in the evaluation of the long range part of the integral (4.11). Even if one puts the long range part of this integral equal to zero, which corresponds to a spherical form of the sample, the

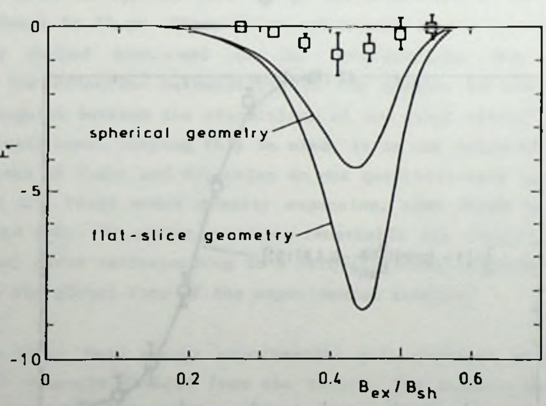


Fig. 12: Experimental results of Mettout and Waysand for the coefficient F_1 of the density expansion compared with the result of the theory, evaluated for two sample geometries. The distribution of threshold values corresponds to the values of F_0 displayed in fig. 11.

theoretical values for F_1 still are about five times larger than the experimental ones (see fig. 12).

The reason for the disagreement between theory and experiment might be related to the phenomenon of partial transitions of spheres. Partial transitions are not accounted for in the theory, which describes the states of the spheres by the indicator functions. Consequently, if a large percentage of all spheres reaches the normal conducting state via gradual partial transitions instead of quasi-instantaneous complete transitions, the theory cannot be applied. From fig. 11 one sees that a considerable fraction of all spheres, viz. about one third, transits for $B_{ex} < B_c \approx 0.45\ B_{sh}$, and for these spheres partial transitions are possible in principle.

As has been pointed out by Mettout[10], it is even possible that, due to partial transitions, only spheres with weak interactions have been detected for the following reason. A slow partial transition of a sphere gives rise to a much smaller voltage pulse in the induction loop used for registration than a sudden complete transition. In order to be able to distinguish signals from noise of the detection electronics, however, only voltage pulses above a certain threshold value can be accepted. Thus it is possible that there are many spheres which become normal conducting via partial transitions but escape the detection. These 'undetectable' spheres start their transitions at low external fields $B_{ex} < B_c$. They therefore will be the ones which have large defects and/or experience strong magnetic interactions. The remaining 'detectable' spheres are thus selected for relatively less important defects and weak magnetic interactions. This might explain why the experimental data obtained for the 'detectable' spheres show a much weaker influence of magnetic interactions than one would expect from the theory.

Although the effect discussed above might well be the reason for the disagreement between theory and experiment, one can hardly claim that the influence of magnetic interactions in dispersions of superconducting superheated granules has been understood in a satisfactory way. How could one improve on this situation from the theoretical side? The data shown in fig. 10 do not suggest that the linear approximation $F_0 + \phi F_1$ in the volume fraction is insufficient, so that efforts should concentrate on a better theory for F_1. In particular partial transitions of spheres should be taken into account. This, however, is extremely difficult. The problem of magnetostatic interactions between two diamagnetic spheres was rather easy to solve because of the simple geometry. Partially transited spheres will in general have normal conducting regions, regions being in the intermediate state and also perfectly diamagnetic superconducting regions. The geometry of these regions will be complicated and depend on the magnetic interactions. Therefore even the two-sphere problem is a formidable one when partial transitions are possible.

Another point on which the theory might be improved is the way in which the effect of defects is incorporated, but before trying this it seems to be advisable to first gather more empirical knowledge about the structure and distribution of defects.

On the experimental side progress could be made if it were possible to produce spheres with less defects, resulting in a narrow distribution of threshold values. In a dilute ($\phi < 10\%$), cluster-free dispersion of such spheres the theory predicts that only very few spheres start the transition into the normal conducting state for B_{ex} below the critical field, so that the problem of partial transitions would virtually be eliminated.

In view of the qualitative agreement between the theory and the measurements of Feder and McLachlan on indium spheres mixed with plastic powder (see fig. 9) it is tempting to infer that this system is more promising than the dispersions of tin spheres in paraffin. Such a conclusion would be premature, however, since the qualitative agreement might be fortuitous: after all there is only one measurement at one volume fraction available, while there are at least two parameters – F_0 and F_1 – present in the theory. Nevertheless a systematic experimental study of the indium/plastic samples would be very interesting.

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OVER ELECTRISCHE EN MAGNETISCHE EIGENSCHAPPEN VAN DISPERSIES VAN BOLVORMIGE DEELTJES

SAMENVATTING

In dit proefschrift worden twee aspecten van de fysica van dispersies behandeld.

Het eerste onderwerp is de effectieve diëlectrische constante van een dispersie. Deze constante beschrijft de diëlectrische eigenschappen van het materiaal op een lengteschaal, waarop de dispersie zich als een homogeen medium gedraagt.

De effectieve diëlectrische constante wordt al langer dan een eeuw bestudeerd en er zijn dan ook reeds diverse theorieën hiervoor voorgesteld. Deze kunnen echter slechts onder bepaalde restricties worden gebruikt. Met name voor het geval van hoogpolariseerbare inclusies in geconcentreerde dispersies ontbrak tot nu toe een systematische behandeling.

In hoofdstuk I wordt een theorie ontwikkeld die ook in dit moeilijke gebied toepasbaar is. Deze theorie verwaarloost in laagste orde correlaties tussen de posities van de deeltjes, die dan in de hogere ordes op een systematische manier in rekening worden gebracht.

In de theorie moet onder meer een veel-deeltjes electrostatisch interactieprobleem worden opgelost. Wegens de gecompliceerdheid van dit probleem kan slechts het geval van bolvormige inclusies worden behandeld.

De n^{de} orde van de theorie hangt af van de n-deeltjes correlatiefunctie van de verdeling van de bolletjes. Experimentele informatie is echter zelfs voor de paar-correlatiefunctie in een dispersie niet beschikbaar, zodat een modelfunctie gebruikt moet worden. Een vergelijking van diverse metingen met de theoretische resultaten toont aan, dat het veel gebruikte harde-bollen-gas model wel soms, maar lang niet altijd voor de beschrijving van reële dispersies deugt.

In hoofdstuk I wordt voorts nog een golfgetal afhankelijke generalisatie van de Clausius-Mossotti formule gegeven en worden de merites van een methode voor de hersommatie van een bepaalde klasse van zelfcorrelaties onderzocht.

Het onderwerp van hoofdstuk II vormen dispersies van supergeleidende bolletjes, die door een uitwendig magnetisch veld in een oververhitte metastabiele toestand gebracht zijn. Dit soort dispersies wordt al enige tijd experimenteel onderzocht, vooral met het oog op mogelijke toepassingen in detectoren voor elementaire deeltjes.

De magnetostatische interacties tussen de supergeleidende, perfect diamagnetische bollen zijn wiskundig equivalent met de in hoofdstuk I bestudeerde electrostatische interacties. Zij geven aanleiding tot verschillen in de maximale veldsterktes op de oppervlakken van de diverse bollen, waardoor deze bij verschillende waarden van het uitwendig veld normaalgeleidend worden.

De fractie van bollen die na een bepaalde verhoging van het uitwendig veld nog supergeleidend zijn is een gangbare meetgrootheid. Deze fractie wordt in hoofdstuk II voor verdunde dispersies in het kader van een dichtheidsontwikkeling berekend. Voorts wordt ook de waarschijnlijkheidsverdeling voor de maximale veldsterkte op de oppervlakken van de nog supergeleidende deeltjes bestudeerd.

In een speciaal geval kan de theorie met een computersimulatie worden vergeleken en komt met deze uitstekend overeen. De overeenstemming met echte experimenten is minder goed. Eén experiment komt kwalitatief redelijk met de theorie overeen, maar de resultaten van een ander experiment vertonen grote afwijkingen van wat op grond van de theorie te verwachten was. Hiervoor zijn verschillende redenen aanwijsbaar.

CURRICULUM VITAE

van Ulrich Geigenmüller
geboren te Rheydt (Duitsland) op 19 juli 1957

Na mijn Abitur aan de Schadow-Oberschule te Berlijn volgde ik in de winter van 1976 een werkplaatsopleiding bij de firma Siemens in Berlijn. In maart 1976 begon ik met mijn studie natuurkunde aan de Technische Universität Berlin. Na het Vordiplom examen vervolgde ik vanaf 1978 mijn studie aan de Rheinisch-Westfälische Technische Hochschule Aachen. In juni 1982 behaalde ik met lof het Diplom examen in natuurkunde met bijvak wiskunde. Voor mijn theoretische Diplomarbeit verrichtte ik o.l.v. Prof. Dr. B.U.Felderhof onderzoek naar de eliminatie van snelle variabelen in lineaire systemen.

Door beurzen van de 'Studienstiftung des Deutschen Volkes' en de 'Dr. Carl Duisberg Stiftung' werd ik in staat gesteld om in het academisch jaar 1982/83 een begin te maken met mijn promotieonderzoek aan het Instituut-Lorentz, o.l.v. Prof. Dr. P.Mazur. Vanaf oktober 1983 werd dit werk voortgezet in dienst van de 'Stichting voor Fundamenteel Onderzoek der Materie' (F.O.M.). Naast het in dit proefschrift beschreven onderzoek werkte ik ook aan o.m. een theorie van electrolytische frictie en aan een analyse van veel-deeltjes hydrodynamische interacties tussen druppels in een emulsie.

Aan het onderwijs droeg ik bij door in het academisch jaar 1983/84 Prof. Dr. D.Bedeaux te assisteren bij de organisatie van een studenten-seminarium over hydrodynamica. Voorts gaf ik gedurende drie semesters werkcolleges over statistische mechanica en hielp ik bij het afnemen van tentamens.

Dankzij financiële steun van de stichting F.O.M. kon ik in 1984 deelnemen aan de zomerschool 'Fundamental Problems in Statistical Mechanics VI' (Trondheim), in 1985 een werkbezoek brengen aan het laboratorium van Dr. G.Waysand (Parijs), en in 1986 deelnemen aan de '16th IUPAP International Conference on Thermodynamics and Statistical Mechanics' (Boston). Het C.N.R.S. (Frankrijk) maakte een tweede bezoek aan het laboratorium van Dr. Waysand mogelijk.

Leiden, januari 1987

LIST OF PUBLICATIONS

1) U.Geigenmüller, U.M.Titulaer and B.U.Felderhof: Systematic elimination of fast variables in linear systems.
Physica **119A** (1983) 41

2) U.Geigenmüller, U.M.Titulaer and B.U.Felderhof: The approximate nature of the Onsager-Casimir reciprocal relations.
Physica **119A** (1983) 53

3) U.Geigenmüller, B.U.Felderhof and U.M.Titulaer: Time-scaling in irreversible thermodynamics.
Physica **120A** (1983) 635

4) U.Geigenmüller: Comment on electrolytic friction.
Chem. Phys. Letters **110** (1984) 666

5) U.Geigenmüller and P.Mazur: The effective dielectric constant of a dispersion of spheres.
Physica **136A** (1986) 316

6) U.Geigenmüller and P.Mazur: Many-body hydrodynamic interactions between spherical drops in an emulsion.
Physica **138A** (1986) 269

7) U.Geigenmüller: On dispersions of superheated superconducting spheres.
To be submitted.

Apart from minor modifications the chapters I and II of this thesis are contained in the publications nos. 5 and 7, respectively.

STELLINGEN

1. De door Namiot gegeven theorie van een lange-dracht interactiepotentiaal tussen Brownse deeltjes ten gevolge van hydrodynamische fluctuaties is incorrect.

V.A. Namiot, Sov. Phys. J.E.T.P. 63 (1986) 706

2. De door Guillien waargenomen waarden van de effectieve diëlectrische constante van suspensies van kwik in olie liggen ook voor lage volumefractie van kwik hoger dan de waarden die door de theorie voor een harde-bollen-gas model van de suspensie voorspeld worden. Dit verschil kan niet alleen het gevolg zijn van polydispersiteit in de grootte van de kwikdruppels.

R. Guillien Ann. Physique 16 (1941) 201
B.U. Felderhof en R.B. Jones, Z. Phys. B 62 (1986) 231
Dit proefschrift, hoofdstuk I.7

3. Ten onrechte verwaarloost Schurr in zijn theorie van electrolytische frictie de hydroelectrische koppeling.

M.J. Schurr, Chem. Phys. 45 (1980) 119
F. Booth, J. Chem. Phys. 22 (1954) 1956
U. Geigenmüller, Chem. Phys. Lett. 110 (1984) 666

4. Het verdient aanbeveling, om de fluctuatieontwikkelingen van hydrodynamische transportcoëfficiënten in suspensies van harde bollen te herhalen met een anders gekozen voortzetting van de connectoren voor de virtuele situatie van elkaar overlappende bollen.

C.W.J. Beenakker en P. Mazur, Physica 126A (1984) 349
C.W.J. Beenakker, Physica 128A (1984) 48
Dit proefschrift, hoofdstukken I.5 - I.7

5. Uit het feit dat de door Rybczyński en Hadamard berekende mobiliteit van een enkele bolvormige druppel overeenkomt met de mobiliteit van één harde bol met geschikt gekozen slipparameter mag men niet concluderen dat er voor de veel-deeltjes-mobiliteiten een soortgelijke overeenkomst bestaat.

U. Geigenmüller en P. Mazur, Physica 138A (1986) 269

6. Beschouw een systeem uit de irreversibele thermodynamica, dat snelle en langzame variabelen bevat, en waarvan de beweging door een stelsel van lineaire differentiaalvergelijkingen beschreven wordt. Voor lange tijden kan men de beweging van de langzame variabelen door een slechts deze variabelen bevattend stelsel vergelijkingen van het zelfde type beschrijven; de coëfficienten van dit gereduceerd stelsel voldoen echter i.h.a. niet exact aan de Onsager relaties.

L. Onsager, Phys. Rev. 38 (1931) 2265
U. Geigenmüller, U.M. Titulaer en B.U. Felderhof, Physica 119A (1983) 53

7. Het effect van fluctuaties op de beweging van een gedempte Duffing-oscillator kan in plaats van de door Rodríguez en van Kampen toegepaste ontwikkeling van de Fokker-Planck vergelijking ook met behulp van de Langevin vergelijking op een systematische manier berekend worden.

R.F. Rodríguez en N.G. van Kampen, Physica 85A (1976) 347

8. Men kan eenvoudig inzien, dat tussen de isotrope tensoren

$$\Delta^{(\ell,\ell)}_{i_1 i_2 \ldots i_\ell, j_\ell j_{\ell-1} \ldots j_1} \qquad (\ell = 1, 2, 3, \ldots),$$

die totaal spoorloos en symmetrisch zijn in hun eerste ℓ en in hun laatste ℓ indices, voor $n > 1$ een samenhang van de vorm

$$\begin{aligned}\Delta^{(n,n)}_{i_1 \ldots i_{n-1} \beta, \alpha j_{n-1} \ldots j_1} &= a(n)\, \Delta^{(n,n)}_{i_1 \ldots i_{n-1} \alpha, \beta j_{n-1} \ldots j_1} \\ &+ b(n)\, \Delta^{(n-1,n-1)}_{i_1 \ldots i_{n-1}, j_{n-1} \ldots j_1} \delta_{\alpha,\beta} \\ + c(n)\, \Delta^{(n-1,n-1)}_{i_1 \ldots i_{n-1}, \alpha k_{n-2} \ldots k_1} & \Delta^{(n-1,n-1)}_{k_1 \ldots k_{n-2} \beta, j_{n-1} \ldots j_1}\end{aligned}$$

bestaat, waarbij $a(n)$, $b(n)$ en $c(n)$ scalaire coëfficiënten zijn.

J.A.R. Coope en R.F. Snider, J. Math. Phys. 11 (1970) 1003
S. Hess en W. Köhler, Formeln zur Tensorrechnung,
(Palm & Enke, Erlangen 1980)

9. Gemengde slip-stick randvoorwaarden zijn niet voor alle waarden van de slipparameter voldoende om de oplossing van de stationaire Stokes vergelijking voor de stroming van een incompressibele, visceuze vloeistof binnen een bolvormig vat eenduidig te bepalen.

10. De door Planck gebruikte indeling van de natuurkundigen in de metafysisch, de positivistisch en de axiomatisch ingestelden is tegenwoordig minder van toepassing.

M. Planck, voordracht gehouden te Leiden op 18 februari 1929,
(Max Planck, Vorträge und Erinnerungen, Wissenschaftliche Buchgesellschaft, Darmstadt 1975)

U. Geigenmüller

Leiden, 29 april 1987