cprt

DIELECTRIC PROPERTIES OF HETEROGENEOUS MIXTURES

PROEFSCHRIFT

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Stellingen

1. De geldigheid van de door O'Konski afgeleide formules ter beschrijving van de relaxatieverschijnselen in colloïdale mengsels kan slechts beperkt zijn.

   C. T. O'Konski: J. Chem. Phys. 23 (1955) 1559.

2. De gangbare mengrelaties voor heterogene mengsels, zoals ook in deze dissertatie beschreven, kunnen vaak niet zonder meer op colloidale systemen worden toegepast.

   C. J. F. Böttcher: Theory of Electric Polarization, § 64, Elsevier, Amsterdam 1952.
   A. Piekara: Koll. Ztschr. **59** (1932) 12.

3. De diëlectrische constante van een aantal vaste stoffen en heterogene mengsels wordt in sterke mate beïnvloed door de absorptie van vocht. De daarbij optredende verandering van de diëlectrische constante is veel groter dan volgens de gangbare mengrelaties zou mogen worden verwacht.

   C. T. O'Konski: J. Am. Chem. Soc. **73** (1951) 5093.
   A. R. von Hippel: Dielectric Materials and Applications, pag. 369/370, Wiley, New York 1954.

4. Bij een beschrijving van een ensemble van korrels van variabele afmetingen kan vaak met voordeel gebruik gemaakt worden van een log-normale verdelingsfunctie.

   J. H. Gaddum: Nature, **156** (1954) 463.
   F. Kottler: J. Frankl. Inst. **250** (1950) 339 en 419.

5. De wijze, waarop Henne en Fox de relatief hoge dissociatieconstante van δ, δ, δ-trifluor-valeriaanzuur ten opzichte van die der lagere homologen verklaren, is aanvechtbaar.

   A. L. Henne en C. J. Fox: J. Am. Chem. Soc. **75** (1953) 5750.

6. De diëlectrische metingen van van Vessem aan KCl poeder in CCl_4-CBr_4 en van Cumming aan sneeuw kunnen met behulp van verschillende mengwetten worden geïnterpreteerd.

   J. C. van Vessem: dissertatie, Utrecht 1947.
   W. A. Cumming: J. Appl. Phys. **23** (1952) 768.

7. De wijze waarop Voet in zijn metingen van de diëlectrische constanten van verschillende mengsels een agglomeratie-factor invoert is aan bedenkingen onderhevig.

   A. Voet: J. Phys. and Coll. Chem. **51** (1947) 1037.

8. Indien bij de injectie van electronen in een bêtatron de hoeveelheid ingevangen electronen afhangt van de verdwijnende ruimtelading, ware het te overwegen een tweede electronenkanon te gebruiken, hetwelk alleen dient om de torus snel met ruimtelading te vullen.

R. Wideroë: Ztschr. Angew. Physik, 5 (1953) 187.

9. Het gebruik van een meetcel als die beschreven door Voet en Guillien, waarbij door de snelle rotatie van het mengsel de deeltjes gericht worden, biedt het voordeel van een snelle bepaling van de vorm der gesuspendeerde deeltjes uit de metingen van de diëlectrische constante van het mengsel.

R. Guillien: Ann. Physique, 16 (1941) 205.
A. Voet: J. Phys. and Coll. Chem. 51 (1947) 1037.

10. Bij het gebruik van de formule van Kirchhoff voor het randeffect van condensatoren met cirkelvormige electroden

$$C_E = \frac{1,113\ D}{8\pi}\left(\log \frac{8\pi D}{d} + f(z) + k\right)$$

wordt vaak over het hoofd gezien, dat de constante k afhangt van de gebruikte opstelling.

A. M. Scott en L. Curtiss: J. Res. Nat. Bur. St. 22 (1939) 747.
Kohlrausch: Prakt. Physik, Bnd 2, s. 177, Rosenberg 1947.
W. von Guttenberg: Ann. Physik VI, 12 (1953) 321.

11. Ter vermijding van moeilijkheden, geïntroduceerd door een onbekende randcapaciteit, bij metingen van de diëlectrische constante van vaste stoffen met behulp van de condensatormethode, kan met voordeel gebruik gemaakt worden van proefstukjes die kleiner zijn dan de afmetingen van de condensator en die zich beperken tot dat gedeelte van de condensator waar het veld homogeen is.

12. De door Koryu Ishi voorgestelde opstelling, die in wezen slechts een vierpool is die uitsluitend is opgebouwd uit lineaire, passieve elementen en isotrope media, kan onmogelijk niet-reciprook zijn, zoals door hem wordt beweerd.

Koryu Ishi: Electronics, 28 (1955) Dec. no.
B. D. H. Tellegen: Tijdschrift N.R.G., 13 (1948) 73.
G. Goudet en H. Jassin: Onde Electrique, 30 (1950) 178 en 223.

13. Bij de bepaling van de diëlectrische eigenschappen van vaste stoffen met zeer hoge diëlectrische constante in het microgolf-gebied m.b.v. een impedantiebepaling naar de methode van von Hippel worden extreme eisen gesteld aan het nauwkeurig

passen van de proefstukjes in de golfgeleider. Daar aan deze eisen meestal mechanisch niet te voldoen is blijkt in dit geval verzilvering der proefstukjes een afdoende oplossing te bieden. Tevens kan bij deze metingen met voordeel gebruik gemaakt worden van een laagje materiaal, dat vlak voor het proefstukje aangebracht wordt, een kwart golflengte lang is en waarvan de diëlectrische constante gunstig ligt tussen die van het te onderzoeken materiaal en 1.

S. Roberts en A. R. von Hippel: J. Appl. Phys. **17** (1946) 610.
J. G. Powles en W. Jackson: Procs I. E. E. **96** III (1949) 383.

14. Het is aan te bevelen de uiterlijke vormgeving van het radiotoestel meer aan te passen aan zijn functie en de plaats die het in het interieur behoort in te nemen.

Aan mijn ouders
Aan mijn vrouw

ERRATUM

Page 11. By a typographical error the first line of the second paragraph is omitted. It is:
"For most dielectrics in a static field, there is also a con-"

Ir G. P. de Loor

Contents

List of symbols

d. c.	dielectric constant
ϵ_i	d. c. of the material of the granules
ϵ_o	d. c. of the continuum in which the granules are dispersed
ϵ_m	macroscopic d. c. of the mixture
ϵ^*	effective d. c. of the immediate surroundings of an average granule

These symbols can be used (Chapter VII) with the indices s or ∞. This means: s, the static d. c.; ∞, the d. c. when relaxation is finished.

v_i	volume filling factor of the dispersed granules
v_o	volume filling factor of the continuum; $v_o = 1 - v_i$
A_j	depolarization factor of an ellipsoidal granule in the j-direction
δ	shape factor; δ_{eff}: effective shape factor

$$S = \frac{1}{Q} = \frac{1}{3} \sum_{1}^{3} j \, \frac{1}{A_j}$$

$$T = \frac{1}{R} = \frac{1}{3} \sum_{1}^{3} j \, \frac{1}{1 - A_j}$$

$$S' = \frac{1}{3} \sum_{1}^{3} j \, \frac{1}{1 + (\frac{\epsilon_i}{\epsilon^*} - 1)A_j} \quad \text{for } \frac{\epsilon_i}{\epsilon_o} > 1, \text{ and } T' = \text{idem when } \frac{\epsilon_i}{\epsilon_o} < 1$$

S'_{ϵ_o}	idem with $\epsilon^* = \epsilon_o$
S'_{ϵ_m}	idem with $\epsilon^* = \epsilon_m$

$$S'' = \frac{1}{3} \sum_{1}^{3} j \, \frac{1}{1 + (\frac{\epsilon_o}{\epsilon^*} - 1) A_j}$$

q	a constant
k	a constant ("empirical factor")
α	polarizability of a granule
a	radius of a spherical granule
a, b, c	semi-axes of an ellipsoidal granule
e	eccentricity

τ_m	macroscopic relaxation time of the mixture (belonging to the maximum of the curve $\epsilon'_m = f(\epsilon''_m)$)
τ_i	idem for the material of the granules
τ_o	idem for the material of the continuum

Further symbols are indicated when used.

Introduction

Although many attempts have been made to relate the permittivity of a heterogeneous mixture to the permittivities of its components, the general theory of dielectrics is not yet sufficiently developed to explain the dielectric behaviour of such mixtures with sufficient accuracy.

There are many cases for which an accurate knowledge of this behaviour is wanted. An important example of such a case is the determination of the dielectric properties of a single crystal from the dielectric constant of the crystal powder 33): often no single crystal is available with dimensions large enough to enable a direct measurement of its dielectric properties. This problem also arises when the permittivity of the single crystal is too large for an accurate determination, a difficulty the author encountered with titanates at microwave frequencies. Still another example is the computation of the influence of porosity on the dielectric properties of ceramic samples.

Within the general theory, the methods for calculating the internal field at a molecule of a pure non-polar liquid can be extended to the study of foreign granules dispersed in a homogeneous and isotropic dielectric. Theoretical formulae thus derived are analogous to those for non-polar liquids. Of the models used to describe the dielectric behaviour of liquids, the first, which was proposed by Clausius and Mossotti and further developed by Lorentz and Lorenz, did not yield formulae for mixtures in good agreement with experiment.

Other derivations were made, based on more macroscopic considerations. In this connection, the study made by Maxwell 11) and Rayleigh 15) may be mentioned. Rayleigh extended his calculations to cylindrical granules imbedded in a homogeneous and isotropic dielectric, but his treatment only applies strictly when the spherical or cylindrical granules are arranged in cubic order.

A "form number", *u*, which later measurements 33) showed to be dependent on the volume-filling ratio, was introduced by Wiener 16). A further extension of the theory to mixtures containing non-spherical granules was given by Fricke 13), who assumed the granules to be ellipsoids and expressed the influence of the shape in terms of a shape factor, *A*. As this thesis will show, *A* relates satisfactorily with the actual shape of the granules and is also in agreement with the shape factor as used in other derivations. The derivations of Bruggeman [22] and the more empirical equation of Lichtenecker [24] should also be mentioned.

More recently, new derivations have been made by Böttcher [1][19] on the basis of the Onsager equations. Böttcher's theory was extended to mixtures containing non-spherical granules by Polder and van Santen [7]. The shape factor, A, used by Polder and van Santen is identical to that used by Niesel [23] in his recent derivations of Bruggeman's equations.

The results obtained with all these equations agree with experiment in varying degrees. Among other applications, the work of van Vessem [33], Guillien [29] and Cumming [52] may be mentioned.

The core of the problem would seem to lie in the fact that in the choice and application of a particular relation, the special assumptions made in deriving it are often overlooked, with the result that the present situation in this field is rather chaotic. This thesis will be an attempt at clarification. The task will be approached in the following way: In Chapter I, a theoretical treatment of the dielectric behaviour of mixtures is given, based on derivations given in the literature for non-polar liquids. Chapter II gives a survey of various mixture relations as discussed in the literature. Chapter III gives a method to determine the shape factor. In Chapter IV, the measurements are summarised, and in Chapter V the shape factor, determined from these experimental results, is related to the actual shape of the granules. Chapter VI contains a further analysis of the experimental results, together with some conclusions. The results of some calculations which were made in order to study the dielectric properties of a heterogeneous mixture when one of its constituents shows relaxation, are summarised in Chapter VII.

Chapter I

The calculation of the dielectric constant of heterogeneous mixtures

When a dielectric is introduced between the plates of an electrically charged condenser a voltage drop is observed. The ratio of the voltage between the plates without the dielectric, to the voltage with the dielectric inserted is denoted by the dielectric constant ϵ. An electric field **E** and a dielectric displacement **D** can then be defined in the dielectric, related *), in case of an isotropic dielectric, by $\mathbf{D} = \epsilon' \mathbf{E}$. For a more complete definition of the dielectric constant (d.c.) we can refer to the handbooks on dielectrics 1)2).
ductivity, σ, which is caused by charge displacements over distances which are large with respect to molecular dimensions. In a low-frequency alternating field, this corresponds to a phase difference between **D** and **E**, which manifests itself as a loss of energy in the dielectric. For this situation, a complex d.c. usually is introduced: $\epsilon = \epsilon' - j\epsilon''$, where ϵ' is the d.c. due to dielectric polarization and $\epsilon'' = \dfrac{4\pi\sigma}{\omega}$.

In polar substances at higher frequencies, an additional phase difference between **D** and **E** occurs due to a lag in the dipole orientation. Now two cases can be distinguished. In the first, σ has no influence in the region where the polar losses occur. Then ϵ'' is only dependent on dipole orientation. It will be denoted by ϵ''_μ. In the second case, losses due to the conductivity are also present, giving $\epsilon'' = \epsilon''_\mu + \epsilon''_\sigma = \epsilon''_\mu + \dfrac{4\pi\sigma}{\omega}$, and if σ is dependent on the frequency, it becomes impossible to distinguish between ϵ''_μ and ϵ''_σ. Only when σ is independent of frequency can a discrimination be made, based on a direct measurement of σ either in a static field or with the aid of a curve of ϵ'' *vs* $\log \omega$ measured at lower frequencies. The frequency dependence of ϵ' and ϵ''_μ has been studied extensively in the literature 1)59-67).

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*) As is usual in treating the theory of dielectrics, the c.g.s. system of units will be used throughout this thesis.

This formal treatment gives the difference between the relaxation phenomena related to ϵ''_μ and σ. To σ are related such low-frequency phenomena as the Maxwell-Wagner type of dispersion which is due to microscopic transient phenomena caused by actual charge displacements over distances large with respect to molecular dimensions. To ϵ''_μ are related the high-frequency phenomena due to dipole orientation.

§ 1. *For the description of the dielectric behaviour of a mixture*, relations can be derived which are analogous to those given by Onsager and Böttcher [1)3)4)], among others, for the electric behaviour of non-polar liquids. All these theories deal with a dielectric consisting of polarizable molecules in vacuo, with the object of deducing the macroscopic d.c. of the substance from the properties of the individual molecules. In order to make this analogy complete, a somewhat unusual approach to the problem will be given.

The dielectric displacement, **D**, and the electric field, **E**, were defined according to Maxwell's theory in which matter is considered as a continuum. Since matter consists of elementary particles, and thus in fact is not continuous, **D** and **E** are usually observed as an average over a macroscopic volume. This averaging process over a single specimen will be indicated by the symbol []. When dealing with mixtures consisting of granules imbedded in a homogeneous and isotropic dielectric, averages are taken over a group of specimens, each being of macroscopic dimensions. This averaging process will be indicated by the symbol <> [5)].

The average field at a granule is given by

$$\langle \mathbf{E}_i \rangle = \frac{1}{V_i} \int \mathbf{E}_i \, dV_i \qquad (\text{I}1.1)$$

where $\mathbf{E}_i$ is the field at a certain granule and V_i is the total volume occupied by the granules. The average macroscopic field in the mixture is given by

$$\langle \mathbf{E} \rangle = \frac{1}{V} \int \mathbf{E} \, dV \qquad (\text{I}1.2)$$

with V being the total volume of the mixture. In the case of a homogeneous field:

$$\langle \mathbf{E} \rangle = \mathbf{E}_m \qquad (\text{I}1.3)$$

where $\mathbf{E}_m$ is the external field applied to the mixture. Each component of the mixture is assumed to be homogeneous and isotropic. For a more thorough treatment of these definitions the reader is referred to a recent paper by W. F. Brown $^{5)}$.

§ 2. For vacuum

$$\mathbf{D} = \mathbf{E} \, . \tag{12.1}$$

When a non-polar liquid, *i.e.* a liquid consisting of polarizable molecules without a permanent dipole moment, is introduced, keeping the true charges on the electrodes of the condenser constant – *i.e.* keeping $\mathbf{D}$ constant –, $\mathbf{E}$ is altered. The relation (12.1) can then be written as

$$[\mathbf{D}] = [\mathbf{E}] + 4\pi [\mathbf{P}_1] \tag{12.2}$$

in which $[\mathbf{P}_1]$ is the polarization, being the total moment induced in the molecules per unit volume. The macroscopic behaviour of the homogeneous and isotropic liquid is also described (for moderate values of $\mathbf{E}$) by

$$[\mathbf{D}] = \epsilon \, [\mathbf{E}] \, , \tag{12.3}$$

which with (12.2), results in

$$(\epsilon - 1) \, [\mathbf{E}] = 4\pi [\mathbf{P}_1] \, . \tag{12.4}$$

In order to obtain more information about $[\mathbf{P}_1]$, we must examine more closely the average internal field, $[\mathbf{E}_i]$, acting on an individual molecule, which causes the polarization $[\mathbf{P}_1]$. When a polarizable molecule is subjected to the field $[\mathbf{E}_i]$, it is polarized, and the average induced molecular polarization, $[\mathbf{m}_p]$, is related to $[\mathbf{E}_i]$ by

$$[\mathbf{m}_p] = [\alpha_1] \, [\mathbf{E}_i] \, , \tag{12.5}$$

where $[\alpha_1]$ is the polarizability of the molecule (with respect to vacuo). With only one type of molecule present, and calling the number of molecules per unit volume N_1, the macroscopic polarization per unit volume can be written

$$[\mathbf{P}_1] = N_1 \, [\mathbf{m}_p] = N_1 \, [\alpha_1] \, [\mathbf{E}_i] \, . \tag{12.6}$$

If the volume occupied by one molecule of substance 1 is $\frac{4}{3}\pi \, abc$ (assuming the molecule to be ellipsoidal with semi-axes a, b and

c), and the macroscopic volume of the liquid is V, then the relative volume occupied by the molecules of the liquid is given by

$$\frac{N_1 \frac{4}{3} \pi \, abc}{V} = v_1 \quad {}^{*)}. \qquad (12.7)$$

Taking V equal to unity

$$[\mathbf{P}_1] = v_1 \frac{[\alpha_1] \; [\mathbf{E}_i]}{\frac{4}{3}\pi \, abc}. \qquad (12.8)$$

In order to calculate the average total field at an average particle, the interaction with the surroundings must be taken into account. This is done, according to Onsager, Böttcher, etc. 1)3)4), following Bell 6), by the introduction of the reaction field $[\mathbf{R}]$

$$[\mathbf{R}] = f[\mathbf{m}_p]. \qquad (12.9)$$

For a calculation of f, the particle is assumed to be located at the center of a cavity in the dielectric. Taking into account the cavity field, $[\mathbf{E}_h]$, and this reaction field, $[\mathbf{R}]$, $[\mathbf{m}_p]$ can be given as

$$[\mathbf{m}_p] = \frac{[\alpha_1] \; [\mathbf{E}_h]}{1 - [\alpha_1] f}. \qquad (12.10)$$

Because there are no permanent dipoles

$$[\mathbf{E}_i] = \frac{[\mathbf{E}_h]}{1 - [\alpha_1] f},$$

giving

$$(\epsilon - 1) \; [\mathbf{E}] = 4\pi \, N_1 \; [\alpha_1] \; [\mathbf{E}_i] \; . \qquad (12.11)$$

It is reasonable to assume that $[\alpha_1]$ is proportional to abc, and also that f is inversely proportional to abc 4)1), as further calculations will show. This means that

$$[\mathbf{P}_1] = v_1 \frac{[\alpha_1] \; [\mathbf{E}_h]}{1 - [\alpha_1] f} \cdot \frac{1}{\frac{4}{3}\pi \, abc}$$

is not dependent on the dimensions of the molecules.

§ 3. Analogous considerations can be applied to a mixture of a granular material with a d.c. ϵ_i, homogeneously dispersed in a continuous medium with a d.c. ϵ_o. If the continuous phase alone is present

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*) Onsager here assumes $N_1 \frac{4}{3} \pi \, abc = 1$, *vide* ref. 1.

$$[\mathbf{D}] = \epsilon_o \, [\mathbf{E}] \, . \tag{13.1}$$

When a certain quantity of granules is introduced into this continuous phase, while keeping the total amount of true charges on the electrodes of the condenser constant, – *i.e.* keeping $\langle \mathbf{D} \rangle$ constant – we can write formally

$$\langle \mathbf{D} \rangle = \epsilon_o \, \langle \mathbf{E} \rangle + 4\pi \, \langle \mathbf{P}_{im} \rangle \, . \tag{13.2}$$

Here this treatment deviates from the usual approach [1][7][8]. The quantity $\langle \mathbf{P}_{im} \rangle$ formally introduced in (13.2) is related to the macroscopic polarization per unit volume of the mixture $\langle \mathbf{P}_m \rangle$ because:

$$\langle \mathbf{D} \rangle = \langle \mathbf{E} \rangle + 4\pi \, \langle \mathbf{P}_m \rangle \, , \tag{13.3}$$

$\langle \mathbf{P}_{im} \rangle$ is thus given by

$$\langle \mathbf{P}_m \rangle = \langle \mathbf{P}_{im} \rangle + \frac{\epsilon_o - 1}{4\pi} \langle \mathbf{E} \rangle \tag{13.4a}$$

or

$$\langle \mathbf{P}_m \rangle = \langle \mathbf{P}_{im} \rangle + \langle \mathbf{P}_{om} \rangle \tag{13.4b}$$

provided we write:

$$(\epsilon_o - 1) \, \langle \mathbf{E} \rangle = 4\pi \, \langle \mathbf{P}_{om} \rangle \, .$$

The quantity $\langle \mathbf{P}_{im} \rangle$ is thus defined with regard to the continuous phase as the average *change* in the polarization per unit volume caused by the introduction of the granules while keeping the total amount of true charges on the electrodes of the condenser constant. Because no polarizable continuum was present in the derivations given in § 2, the increase of the average polarization per unit volume was immediately given by $[\mathbf{P}_1]$. If, in the case described in this connection, the granules were not brought into a continuous dielectric, but into vacuum ($\langle \mathbf{P}_{om} \rangle = 0$), (13.2) would be written as

$$\langle \mathbf{D} \rangle = \langle \mathbf{E} \rangle + 4\pi \, \langle \mathbf{P}_{im} \rangle \, . \tag{13.2a}$$

The more usual treatment of this case yields

$$\langle \mathbf{P}_m \rangle = v_i \, \langle \mathbf{P}_i \rangle + (1 - v_i) \, \langle \mathbf{P}_o \rangle \tag{13.5}$$

where $\langle \mathbf{P}_i \rangle$ and $\langle \mathbf{P}_o \rangle$ are defined from the equations

$$\langle \mathbf{D}_i \rangle = \langle \mathbf{E}_i \rangle + 4\pi \, \langle \mathbf{P}_i \rangle \tag{13.6a}$$

and

$$\langle \mathbf{D}_o \rangle = \langle \mathbf{E}_o \rangle + 4\pi \, \langle \mathbf{P}_o \rangle \tag{13.6b}$$

$\langle\mathbf{D}_i\rangle$, $\langle\mathbf{D}_o\rangle$, $\langle\mathbf{E}_i\rangle$, and $\langle\mathbf{E}_o\rangle$ being average values of the dielectric displacements and the electric fields in the granule and the continuous phase, respectively. It must of course be remembered that $\langle\mathbf{D}_i\rangle \neq \langle\mathbf{D}_o\rangle \neq \langle\mathbf{D}\rangle$ and $\langle\mathbf{E}_i\rangle \neq \langle\mathbf{E}_o\rangle \neq \langle\mathbf{E}\rangle$. Comparing equations (13.4b) and (13.5)

$$\langle\mathbf{P}_{im}\rangle = v_i \langle\mathbf{P}_i\rangle \tag{13.7a}$$

and

$$\langle\mathbf{P}_{om}\rangle = v_o \langle\mathbf{P}_o\rangle \ . \tag{13.7b}$$

By analogy with the molecular case treated in § 2 of this chapter, from equation (13.2) is obtained

$$(\epsilon_m - \epsilon_o)\ \langle\mathbf{E}\rangle = 4\pi \langle\mathbf{P}_{im}\rangle \tag{13.8}$$

with

$$\langle\mathbf{D}\rangle = \epsilon_m \langle\mathbf{E}\rangle \ . \tag{13.9}$$

Furthermore, $\langle\alpha_i\rangle$ can now be defined as the polarizability of one average granule with respect to the continuum. N_i can be identified with the number of granules per unit volume, $\langle\mathbf{E}\rangle$ with $\mathbf{E}_m$, the external field strength, and $\langle\mathbf{E}_i\rangle$ with the average field at a granule. Thus the average dipole moment, $\langle\mathbf{m}_p\rangle$, induced in one granule is given by

$$\langle\mathbf{m}_p\rangle = \langle\alpha_i\rangle \langle\mathbf{E}_i\rangle \ . \tag{13.10}$$

It must be remembered that this $\langle\alpha_i\rangle$ is the polarizability of one whole granule, which is different from the polarizability $[\alpha_i]$ defined with the aid of equation (13.6a) for one molecule of the material of the granules. $\langle\alpha_i\rangle$ can thus be related immediately to $\langle\mathbf{P}_{im}\rangle$ according to

$$\langle\mathbf{P}_{im}\rangle = N_i \langle\mathbf{m}_p\rangle = N_i \langle\alpha_i\rangle \langle\mathbf{E}_i\rangle \ . \tag{13.11}$$

Assuming the granules to be ellipsoidal with semi-axes a, b and c, the volume of one granule is $\frac{4}{3}\pi\ abc$. When the total volume of the mixture is V, the volume-filling ratio is given by

$$v_i = \frac{N_i \frac{4}{3}\pi\ abc}{V} \tag{13.12}$$

and thus

$$\langle\mathbf{P}_{im}\rangle = v_i \frac{\langle\alpha_i\rangle \langle\mathbf{E}_i\rangle}{\frac{4}{3}\pi\ abc} . \tag{13.13}$$

Considerations analogous to those given for the molecular case in § 1 lead to

$$(\epsilon_m - \epsilon_o)\ \mathbf{E}_m = 4\pi N_i \langle\alpha_i\rangle \langle\mathbf{E}_i\rangle \tag{13.14}$$

or
$$(\epsilon_m - \epsilon_o)\ \mathbf{E}_m = v_i \frac{<\alpha_i>\ <\mathbf{E}_i>}{abc/3}\ . \qquad (13.15)$$

§ 4. Before (13.14) can be utilized to calculate dielectric constants of mixtures, it is necessary to be able to determine $<\alpha_i>$ and $<\mathbf{E}_i>$. In order to do this, it is necessary to make certain definitions and assumptions.

a. In § 2 and § 3 of this chapter, the symbols for averages have been used with **D**, **E**, **P**, α, and **m**. Having thus defined the various quantities, these symbols will be omitted, and throughout this thesis the symbols for averages <> must be thought of as being used with **D**, **E**, **P**, α, and **m**.

b. In order to calculate the macroscopic d.c. of the mixture, ϵ_m, it is assumed that each granule i, with a d.c. ϵ_i, is surrounded by a homogeneous and isotropic substance with a d.c., ϵ^*, and with a field strength $\mathbf{E}^*$. This makes it possible to write

$$\mathbf{E}_{i,k} = \sum_1^3 T_{kl}\ \mathbf{E}^* \qquad (14.1)$$

in which the tensor T_{kl} depends on ϵ^*, ϵ_i, and the shape of the granules.

c. Concerning the mixture, it is assumed that the constituents do not influence each other's properties and boundary layers are assumed either to be absent or to have negligible effect on the calculations. All the granules are assumed to be:

1. ellipsoidal in shape,
2. uniformly distributed,
3. small with respect to the wavelength of the electric field, so that, when using an alternating field, quasi-static considerations can still be applied, and
4. large enough to exhibit the macroscopic properties of the material of which they are composed.

This enables the relation (14.1) to be specified 7)8). Assuming the granules to be orientated at random gives, on averaging,

$$\mathbf{E}_i = \frac{1}{3}\ (T_{11} + T_{22} + T_{33})\ \mathbf{E}^* \qquad (14.2)$$

with
$$T_{11} = T_a = \frac{1}{1 + (\frac{\epsilon_i}{\epsilon^*} - 1)\ A_a} \qquad (14.3)$$

in which A_a is the depolarization factor of the ellipsoidal granule in the direction of the a-axis. A_a can be determined from the well known relation 9)

$$A_a = \tfrac{1}{2}\, abc \int_0^{\infty} \frac{ds}{(a^2+s)^{\frac{3}{2}}\,(b^2+s)^{\frac{1}{2}}\,(c^2+s)^{\frac{1}{2}}}, \qquad (14.4)$$

Furthermore $$A_a + A_b + A_c = 1 \qquad (14.5)$$

For an ellipsoid of revolution about the c-axis, the three depolarization factors can be written: A_a, A_a, and $1 - 2\,A_a$, or δ, δ, and $1 - 2\,\delta$. δ denotes the shape factor. In Fig. I.1 $A_c = 1 - 2\,\delta$ is given as a function of the eccentricity e.

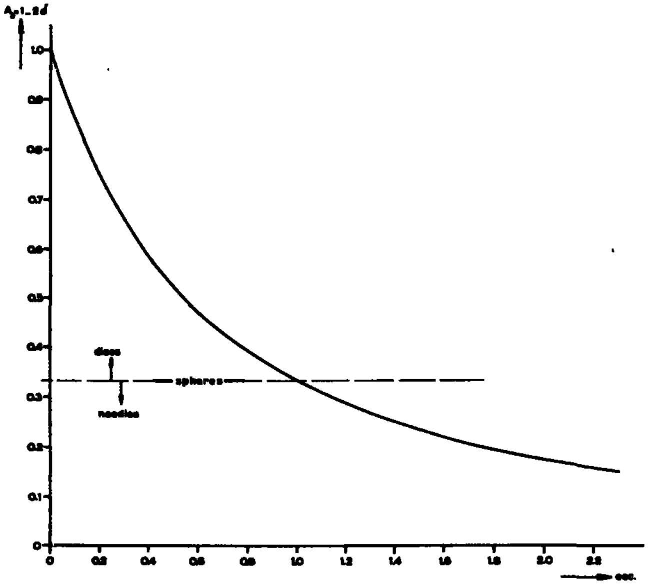

Figure I.1
The depolarization factor A_c as a function of the eccentricity e of an ellipsoid of rotational symmetry with semi-axes $a = b$ and c.

§ 5. Before the assumptions of § 4 can be used to determine the d.c. of the mixture, values must be given for ϵ^* and E^* [7)8)]. Following Böttcher [1)], Polder and van Santen [7)], and Scholte [4)], E^* is taken equal to E_m. In the literature, ϵ^* has been given two values $\epsilon^* = \epsilon_0$ (Maxwell, Rayleigh, Fricke), and $\epsilon^* = \epsilon_m$ (Böttcher, Polder and van Santen), but experimental results show poor agreement with these theories and for the present ϵ^* will be used in all theoretical relations.

In the following calculations, a procedure will be applied which is analogous to that given by Scholte [4] for molecular quantities. His derivations can be called sub-microscopic, because they deal with molecules which are treated as ellipsoidal particles in vacuo. The reaction field, **R**, is calculated by replacing the particle by a cavity which has as its centre, a dipole with the dipole moment of the particle. This treatment is similar to that given in § 2. However, the case of real particles or granules with a d.c. ϵ_i is being considered, and this can be called the microscopic case. The polarizability of a granule will be defined with respect to the medium in which the granules are dispersed. The reaction field is calculated by taking a granule out of the mixture, refilling the cavity with the material of the continuous phase, the cavity having at its centre a dipole with the dipole moment of the granule. These considerations are analogous to the treatment given in § 3. Then the calculation is as follows:

First, the polarizability of the granules must be defined. As previously mentioned, α_i must be defined with regard to the continuous phase in which the granules are dispersed. For this definition, the treatment given by Stratton (ref. 9, par. 3.24 and 3.25) will be used. The field $\mathbf{E}_{hac}$ in a particular granule consisting of a material with the d.c. ϵ_i, which is placed with its a-axis parallel to the field $\mathbf{E}_{ma}$ in a homogeneous and isotropic dielectric with a d.c. ϵ_o, is given by the relation

$$\mathbf{E}_{hac} = \frac{\epsilon_o}{\epsilon_o + (\epsilon_i - \epsilon_o)\, A_a}\, \mathbf{E}_{ma} \tag{15.1}$$

This field induces a polarization per unit volume in the granule, given by

$$\mathbf{P}_a = \frac{\epsilon_i - \epsilon_o}{4\pi}\, \mathbf{E}_{hac} \,. \tag{15.2}$$

The total moment induced in the granule with volume $\frac{4}{3}\pi\, abc$ is given by Stratton [9] as

$$\mathbf{m}_{ca} = \frac{abc}{3}\, \frac{\epsilon_o\, (\epsilon_i - \epsilon_o)}{\epsilon_o + (\epsilon_i - \epsilon_o)\, A_a}\, \mathbf{E}_{ma} \,. \tag{15.3}$$

The polarizability of the granule in the direction of the a-axis can thus be defined by

$$\frac{\mathbf{m}_{ca}}{\mathbf{E}_{ma}} = \alpha_a = \frac{1}{3}\, abc\, \frac{\epsilon_o\,(\epsilon_i - \epsilon_o)}{\epsilon_o + (\epsilon_i - \epsilon_o)\, A_a}$$

$$= \frac{1}{3}\, abc\, \epsilon_o \frac{(\epsilon_i/\epsilon_o - 1)}{1 + (\epsilon_i/\epsilon_o - 1)\, A_a} \qquad (15.4)$$

which yields $$\epsilon_i = \epsilon_o \frac{abc\ \epsilon_o + 3\, \alpha_a (1 - A_a)}{abc\ \epsilon_o - 3\, \alpha_a\, A_a}. \qquad (15.5)$$

Now the reaction field factor, f, must be determined. As already mentioned, the following procedure is closely analogous to that given by Scholte for non-polar liquids [4]. In the mixture, the granule is surrounded by a dielectric with a d. c. ϵ^* (*vide* § 4), the properties of which are determined by the other granules. When this granule is subjected to a field $\mathbf{E}_m$ along the a-axis,

$$\mathbf{E}_{ha} = \frac{\epsilon^*}{\epsilon^* + (\epsilon_i - \epsilon^*)\, A_a}\, \mathbf{E}_{ma} \qquad (15.6)$$

which equation, with the aid of (15.2), gives for $\mathbf{m}_a$ the dipole moment induced in the granule in the mixture for the a-direction

$$\mathbf{m}_a = \frac{4}{3}\pi\, abc\, \frac{\epsilon_i - \epsilon_o}{4\pi}\, \frac{\epsilon^*}{\epsilon^* + (\epsilon_i - \epsilon^*)\, A_a}\, \mathbf{E}_{ma} \qquad (15.7)$$

Substitution of (15.5) in this equation gives

$$\mathbf{m}_a = \frac{\epsilon^*\, \alpha_a}{\epsilon^* + (\epsilon_o - \epsilon^*)\, A_a}\, \frac{\epsilon_o}{\epsilon_o - \dfrac{3\, \alpha_a\, A_a(1 - A_a)(\epsilon^* - \epsilon_o)}{abc\ [\epsilon^* + A_a(\epsilon_o - \epsilon^*)]}}\, \mathbf{E}_{ma} \qquad (15.8)$$

The reaction field increases the dipole field by the factor $1/(1 - \alpha f)$. This means that for this case the reaction field factor f is

$$f_a = \frac{3}{abc}\, \frac{A_a\ (1 - A_a)(\epsilon^* - \epsilon_o)}{[\epsilon^* + A_a(\epsilon_o - \epsilon^*)]\epsilon_o}. \qquad (15.9)$$

Then, since $\mathbf{E}_i = \mathbf{E}_h/(1 - \alpha f)$ [1]

$$\mathbf{E}_{ia} = \frac{\epsilon^*}{\epsilon^* + (\epsilon_o - \epsilon^*)\, A_a}\, \frac{1}{1 - \alpha_a \dfrac{3\, A_a(1 - A_a)(\epsilon^* - \epsilon_o)}{abc[\epsilon^* + A_a(\epsilon_a - \epsilon^*)]\epsilon_o}}\, \mathbf{E}_{ma} \qquad (15.10)$$

Remembering that the granules are orientated at random, the contributions of the other axes must be taken into account, and, with the aid of (13.15), this results in

$$\epsilon_m - \epsilon_o = v_i(\epsilon_i - \epsilon_o)\ \tfrac{1}{3}\sum_1^3 j\ \frac{1}{1 + (\frac{\epsilon_i}{\epsilon^*} - 1)\,A_j} \qquad (15.11)$$

This formula is completely analogous to that derived by Polder and van Santen [7)] if ϵ^* is made equal to ϵ_m. Equation (15.11) can also be derived in a manner similar to that used by Polder and van Santen, as shown in § 8.

§ 6. When conducting granules are dispersed in a continuum with the d.c. ϵ_o, the polarizability of the granules for the a-direction is given by

$$\alpha_a = \frac{\epsilon_o}{A_a}\,\frac{abc}{3} \qquad (16.1)$$

according to ref. 1, pages 54 and 62, and ref. 9, par. 3.22 – 3.28. This result can also be obtained from equation (15.4), by writing $\epsilon_i = \infty$. Equation (16.1) thus also applies for the case $\frac{\epsilon_i}{\epsilon_o} \gg 1$. With the reaction field factor given by equation (15.9) and with the aid of (13.15),

$$\epsilon_m - \epsilon_o = \tfrac{1}{3}\sum_1^3 j\,\frac{v_i\ \epsilon^*}{A_j}. \qquad (16.2)$$

With $\epsilon^* = \epsilon_m$, this formula can be written for spherical granules ($A_j = \frac{1}{3}$) as

$$\epsilon_m = \frac{\epsilon_o}{1 - 3\ v_i}. \qquad (16.3)$$

In order to simplify calculation, (16.2) can be rewritten as

$$\epsilon_m - \epsilon_o = v_i\ \epsilon^*\ S \qquad (16.4)$$

with

$$S = \frac{1}{Q} = \tfrac{1}{3}\sum_1^3 j\ \frac{1}{A_j} \qquad (16.5)$$

§ 7. In the extreme case of a dielectric with a very high d.c. containing interstices with a low d.c., it can happen that $\frac{\epsilon_i}{\epsilon_o} \ll 1$. This occurs, for instance, in some ceramics with a very high d.c., *e.g.* $BaTiO_3$, where the material is fabricated by sintering and always contains air inclusions. For this case, where $\frac{\epsilon_i}{\epsilon_o} \to 0$

$$a_a = \frac{abc}{3} \frac{-\epsilon_o}{1 - A_a} \tag{17.1}$$

resulting in the formula

$$\epsilon_o - \epsilon_m = v_i \, \epsilon_o \, T \tag{17.2}$$

with

$$T = \frac{1}{R} = \frac{1}{3} \sum_1^3 j \frac{1}{1 - A_j} \, . \tag{17.3}$$

For spherical interstices, this leads to

$$\frac{\epsilon_m}{\epsilon_o} = 1 - 1.5 \, v_i \, . \tag{17.4}$$

It will be noted that ϵ_m in equation (17.2) is independent of the value of ϵ^*. In this case, the mutual interaction of the interstices seems not to be so important. This is reasonable, because the granules with a low d.c. are all surrounded by a dielectric with a very high d.c., which more or less shields them electromagnetically from each other.

§ 8. As stated above, equation (15.11) can also be derived in macroscopic terms. In analogy with the treatments given in ref. 7 and 8,

$$\langle \mathbf{D} \rangle = \frac{1}{V} \int \mathbf{D} \, dV = v_o \, \langle \mathbf{D}_o \rangle + v_i \, \langle \mathbf{D}_i \rangle = \epsilon_o \, \mathbf{E}_m + v_i \, (\epsilon_i - \epsilon_o) \, \langle \mathbf{E}_i \rangle \, .$$

Then,

$$\epsilon_m = \frac{\langle \mathbf{D} \rangle}{\mathbf{E}_m} = \epsilon_o + v_i \, (\epsilon_i - \epsilon_o) \frac{\langle \mathbf{E}_i \rangle}{\mathbf{E}_m} \, .$$

Then, with (14.1) and $\mathbf{E}^* = \mathbf{E}_m$, (15.11) is obtained.

The calculations given above lead to a general relation, (15.11), which connects the macroscopic d.c. of the mixture with the d.c. of its components. The ellipsoidal shape of the granules and the influence of surrounding granules (by the use of an effective d.c., ϵ^*) have both been taken into account. Because ϵ^* is not known, it is necessary to make some assumptions in order to be able to calculate ϵ_m from (15.11) or (16.4). At the present time, no method of calculating ϵ^* has been found which is universally valid, and the assumptions made in the literature are usually very inadequately discussed.

The introduction of an effective d.c., ϵ^*, of the immediate surroundings of an average granule can be thought of as being purely formal. The use of ϵ^* was suggested by the work of de

Vries [8) and Brown [10). If the depolarization factor, A, for a given powder can be determined, experimental observations of ϵ_m should yield a value of ϵ^* from which it may be possible to obtain some information on the mutual interaction of the granules. In Chapter III, a method of determining A will be given. The values of ϵ_m, ϵ_i, ϵ_o, and v_i are known from direct measurements.

The derivations given above can be extended to mixtures consisting of two kinds of granules dispersed in a continuous phase. In that case, it is necessary to use the same methods as those given in the literature for mixtures of two non-polar liquids.

Chapter II

Survey of mixture relations

A brief survey of some of the mixture relations mentioned in the literature will be given in this chapter. For a more thorough treatment, the reader is referred to the work of Lowry [44] and Reynolds [27].

§ 1. *Results obtained with the assumption $\epsilon^* = \epsilon_o$*

The formulae for this case were derived by Maxwell [11] for spherical granules. These first derivations in this field were all made for the analogous case of calculating the conductivity of a mixture [8]. They were later extended by Burger [12] and Fricke [13] to the case of ellipsoidal granules. By a different method, Ollendorff [14] derived the same formula for the permeability of a mixture consisting of a continuum with a permeability $\mu_o = 1$ and granules with a permeability μ_i. His derivations, however, are limited to the case of ellipsoidal granules in parallel alignment.

The formula finally obtained is

$$\epsilon_m - \epsilon_o = \frac{v_i}{1 - v_i} (\epsilon_i - \epsilon_m) \frac{1}{3} \sum_1^3 j \frac{1}{1 + (\frac{\epsilon_i}{\epsilon_o} - 1) A_j} \qquad \text{(III.1)}$$

or

$$\epsilon_m - \epsilon_o = \frac{v_i}{1 - v_i} (\epsilon_i - \epsilon_m) S'_{\epsilon_o} . \qquad \text{(III.1a)}$$

This gives, for spherical granules ($A_j = \frac{1}{3}$), the well known relation

$$\frac{\epsilon_m - \epsilon_o}{\epsilon_m + 2\,\epsilon_o} = v_i \frac{\epsilon_i - \epsilon_o}{\epsilon_i + 2\,\epsilon_o} . \qquad \text{(III.2)}$$

Rayleigh [15][8] showed that the above formula is a sufficiently accurate first order approximation for a regular arrangement of spheres. Similarly, he showed that the formula for a regular arrangement of cylinders, directed perpendicular to the field, would be

$$\frac{\epsilon_m - \epsilon_o}{\epsilon_m + \epsilon_o} = v_i \frac{\epsilon_i - \epsilon_o}{\epsilon_i + \epsilon_o} \qquad \text{(III.3)}$$

Wiener [16] introduced into his calculations a "Formzahl" (form number), u, and obtained the following formula, which resembles those given above,

$$\frac{\epsilon_m - \epsilon_o}{\epsilon_m + u} = v_i \frac{\epsilon_i - \epsilon_o}{\epsilon_i + u} \,. \qquad \text{(III.4)}$$

The name "Formzahl" indicates that, according to Wiener, u should depend only on the shape of the granules. Measurements, however, showed u to be dependent on v_i [33][27]. Comparison with equation (III.1) gives for u

$$u = \frac{\epsilon_i S'_{\epsilon_o} - \epsilon_o}{1 - S'_{\epsilon_o}} \,, \qquad \text{(III.5)}$$

thus showing u to be dependent on ϵ_i and ϵ_o, as Fricke [13] had already calculated. For spherical granules

$$u = 2\,\epsilon_o \,. \qquad \text{(III.6a)}$$

For the two extreme cases, needle-shaped granules (A_j = ½;½;0) and disc-shaped granules (A_j = 0;0;1)

$$u = 2\,\epsilon_i \quad \text{(discs)} \qquad \text{(III.6b)}$$

$$u = \tfrac{1}{2}\,(\epsilon_i + 3\,\epsilon_o) \quad \text{(needles)} \,. \qquad \text{(III.6c)}$$

Rayleigh's original formulae, with all their terms of higher order, are accurate for the case they describe, *i.e.* a regular arrangement of spheres or cylinders. The same formulae, however, are frequently applied to random arrangements, where they are no longer applicable. Recent model-measurements in an electrolytic trough show the validity of this statement [17]. Lewin [18] made calculations for high frequencies, using the same type of mixture as Rayleigh and arrived at the same formula (III.2), but with complex dielectric constants.

For the two extreme cases of conducting granules *) and $\epsilon_i/\epsilon_o \ll 1$, formula (III.1) can be written

$$\frac{\epsilon_m}{\epsilon_o} = 1 + \frac{S\,v_i}{1 - v_i} \qquad \text{(III.7)}$$

for the case of conducting granules, and

$$\frac{\epsilon_o}{\epsilon_m} = 1 + \frac{T\,v_i}{1 - v_i} \qquad \text{(III.8)}$$

for $\epsilon_i/\epsilon_o \ll 1$.

---

*) Together with the case $\epsilon_i/\epsilon_o \gg 1$; *vide* Chapter I, § 6.

In the two preceding formulae for spherical granules, $S = 3$ and $T = 1.5$. For $\frac{\epsilon_i}{\epsilon_o} << 1$, Fricke [13] gives the formula

$$\epsilon_o - \epsilon_m = \frac{T\, v_i}{1.- v_i} (\epsilon_m - \epsilon_i) \tag{II1.9}$$

which is accurate up to a higher value of v_i or for a lower ratio ϵ_o/ϵ_i. Fricke checked his formula for conductivities, and reports obtaining a reasonable agreement with his measurements [13].

§ 2. *Results obtained with the assumption $\epsilon^* = \epsilon_m$*

In analogy with the relevant derivations of Onsager [3] for non-polar liquids, Böttcher [19][1] provided the formulae: for spherical non-conducting granules

$$\frac{\epsilon_m - \epsilon_o}{\epsilon_m + 2\,\epsilon_m} = v_i \frac{\epsilon_i - \epsilon_o}{\epsilon_i + 2\,\epsilon_m} \tag{II2.1}$$

and for spherical conducting granules

$$\frac{\epsilon_m}{\epsilon_o} = 1 + \frac{3\, v_i}{1 - 3\, v_i}\,. \tag{II2.2}$$

The latter formula had already been used by Beaulard [20] (1899), following a treatment of Betti [21], for his measurements on mixtures containing copper dust (*vide* Chapter IV, § 2f).

The derivations for non-spherical granules were extended by Polder and van Santen [7]. They obtained a formula identical with equation (I5.11), in which $\epsilon^* = \epsilon_m$.

For the two extreme cases of conducting granules (and $\frac{\epsilon_i}{\epsilon_o} >> 1$) and $\frac{\epsilon_i}{\epsilon_o} << 1$, the following equations are found

$$\frac{\epsilon_m}{\epsilon_o} = 1 + \frac{S\, v_i}{1 - S\, v_i} \qquad (\epsilon_i/\epsilon_o >> 1) \tag{II2.3}$$

$$\frac{\epsilon_m}{\epsilon_o} = 1 - T\, v_i \qquad (\epsilon_i/\epsilon_o << 1)\,. \tag{II2.4}$$

The general assumption $\epsilon^* = \epsilon_m$ was also used by Bruggeman [22] in his treatment of statistical mixtures.

§ 3. *The Bruggeman-Niesel equations*

Bruggeman [22] derived his formulae in a manner different from that used in the previous paragraphs. For the case of $v_i \rightarrow 0$ the formula (I5.11) is accurate when $\epsilon^* = \epsilon_o$. In Bruggeman's procedure, small amounts of powder Δv_i are then added. This procedure is repeated until the volume filling factor becomes v_i, always assuming the dielectric in which the new granules are dispersed to remain homogeneous after each addition. Then Δv_i is allowed to approach zero.

Niesel [23], working along the same lines, used an integration procedure, and arrived at the same results as Bruggeman. For spherical-, disc- and needle-shaped granules, the following formulae are obtained

for spheres $$(1 - v_i) = \frac{\epsilon_i - \epsilon_m}{\epsilon_i - \epsilon_o} \sqrt[3]{\frac{\epsilon_o}{\epsilon_m}} \qquad \text{(II3.1)}$$

for discs $$(1 - v_i) = \frac{\epsilon_i - \epsilon_m}{\epsilon_i - \epsilon_o} \cdot \frac{2\,\epsilon_i + \epsilon_o}{2\,\epsilon_i + \epsilon_m} \qquad \text{(II3.2)}$$

for needles $$(1 - v_i) = \frac{\epsilon_i - \epsilon_m}{\epsilon_i - \epsilon_o} \cdot \left(\frac{\epsilon_i + 5\,\epsilon_o}{\epsilon_i + 5\,\epsilon_m}\right)^{\frac{2}{5}} . \qquad \text{(II3.3)}$$

Polder and van Santen [7] obtained a relation for disc-shaped granules with their treatment which is the same as relation (II3.2). With Niesel's treatment, however, it is difficult to determine the dielectric constant of a mixture having granules with shapes other than those used above, because of the complicated integrals involved. For the two extreme cases of conducting granules (and $\frac{\epsilon_i}{\epsilon_o} \gg 1$) and $\frac{\epsilon_i}{\epsilon_o} \ll 1$, the integrals are much simpler. By closely following Niesel's integration procedure, the following relations were derived.

For conducting granules (and $\frac{\epsilon_i}{\epsilon_o} \gg 1$)

$$\frac{\epsilon_m}{\epsilon_o} = (1 - v_i)^{-S} , \qquad \text{(II3.4)}$$

which for spherical granules can be cast into the form

$$\frac{\epsilon_m}{\epsilon_o} = 1 + \frac{3\,v_i}{1 - v_i\,q} \qquad \text{(II3.5)}$$

with $$q = 2 - \frac{1}{3}\,\frac{v_i\,(2 - v_i)}{1 - v_i + \frac{1}{3}\,v_i^2} .$$

For lower values of v_i, *i.e.* $v_i < 20\%$, $q = 2$ is a satisfactory approximation. For the case of $\epsilon_i/\epsilon_o \ll 1$, the formula is written

$$\frac{\epsilon_m}{\epsilon_o} = (1 - v_i)^T \tag{II3.6}$$

with
$$\frac{\epsilon_m}{\epsilon_o} = 1 - T\, v_i$$

as a first order approximation.

§ 4. Comparing the formulae for conducting granules: (II1.7), (II2.2), (II2.3), and (II3.5), it is seen that they can be given in one common form

$$\frac{\epsilon_m}{\epsilon_o} = 1 + \frac{S\, v_i}{1 - q\, v_i} \cdot \tag{II4.1}$$

where q is different in each of the relations used.

With the procedure given in Chapter I and using Kirkwood's formula for non-polar liquids, still another analogous formula can be found for a mixture containing conducting granules. Using from ref. 1 equation (7.74) together with (I2.7) and (I6.1), gives

$$\frac{\epsilon_m}{\epsilon_o} = 1 + 3\, v_i(1 + \tfrac{5}{4}\, v_i + \tfrac{25}{16}\, v_i^2 + \ldots) \ .$$

Assuming this to be an infinite geometrical progression

$$\frac{\epsilon_m}{\epsilon_o} = 1 + \frac{3\, v_i}{1 - \frac{5}{4}\, v_i}$$

which also has the form of (II4.1).

This analogy can be used up to $v_i = 20\%$. Then the second order approximation calculated by Rayleigh predicts higher values for ϵ_m than are found with (II1.7). For the same case, equation (II3.5) gives lower values than those given by (II4.1) with $q = 2$. The measurements show (*vide* Chapter IV), that q is a constant up to $v_i = 20\%$. This constant varies with each type of mixture. For a higher value of v_i, values for ϵ_m are found which are lower than predicted by (II4.1). Thus, for conducting granules, a comparison of (II4.1) and (I6.4) gives, for the d.c. of the immediate surroundings of an average granule,

$$\frac{\epsilon^*}{\epsilon_o} = \frac{1}{1 - q\, v_i} \tag{II4.2a}$$

or
$$\frac{\epsilon^*}{\epsilon_o} = 1 + q\, v_i + (q\, v_i)^2 + \ldots \tag{II4.2b}$$

For $\frac{\epsilon^*}{\epsilon_m}$, then, the formula

$$\frac{\epsilon^*}{\epsilon_m} = \frac{1}{1 + (S - q)\ v_i} \qquad (114.3)$$

is found.

§ 5. Some of the relations which are given in the literature have a more empirical nature. For example, the equation given by Lichtenecker [24])

$$\ln \epsilon_m = v_o \ln \epsilon_o + v_i \ln \epsilon_i \ , \qquad (115.1)$$

is widely used. Furthermore, the two extreme cases given by Wiener [16]), between which all possible mixture relations will be found, are often considered in the literature. These two cases are shown in Fig. II.1 a and b, and result in the formulae

$$\epsilon_m = \epsilon_o + v_i(\epsilon_i - \epsilon_o) \qquad (115.2)$$

$$\frac{1}{\epsilon_m} = \frac{v_i}{\epsilon_i} + \frac{v_o}{\epsilon_o}\ . \qquad (115.3)$$

As can be seen, both relations belong to the same highly anisotropic mixture, for which the d.c. is given in two mutually perpendicular directions.

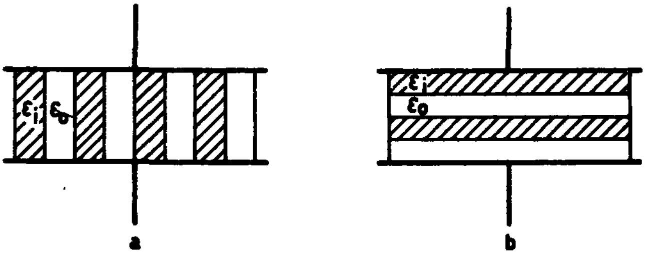

Figure II.1

Modifying Rayleigh's formula, Kamiyoshi [25]) gives the equation

$$\epsilon_m = \frac{2\ \epsilon_{m_I} \cdot \epsilon_{m_{II}}}{\epsilon_{m_I} + \epsilon_{m_{II}}} \qquad (115.4)$$

This formula was derived for the region $(1 - \frac{\pi}{6}) < v_i < \frac{\pi}{6}$. In this relation, ϵ_{m_I} is the d.c. calculated according to Rayleigh for the case of spheres consisting of a material with a d.c. ϵ_i imbedded in a continuum with a d.c. ϵ_o, and ϵ_{mII} is the d.c. calculated with Rayleigh's formula for the case of spheres with a d.c. ϵ_o imbedded in a continuum with a d.c. ϵ_i.

Modifying Bruggeman's equations, Pearce [26]) recently proposed the following formula

$$\frac{\epsilon_m - \epsilon_o}{\epsilon_i - \epsilon_o} = \epsilon' = \frac{(1 - k)\, v_i}{1 - k\, v_i} \qquad (115.5)$$

with k being a constant dependent only on the type of mixture used. Pearce defines k only in relation to experimental results, and calls it the "empirical factor".

Chapter III

The determination of the shape factor

As has been shown in Chapter I, for a determination of ϵ^* from direct measurements, the depolarization factor, *A*, must be known. For this purpose, the dispersed granules are assumed to be ellipsoids of revolution with depolarization factors $A_a = A_b = \delta$ and $A_c = 1 - 2\,\delta$, where δ is the shape factor. Using granules from a single sample for each series of measurements, it is reasonable to suppose the effective shape factor, δ_{eff}, to be constant over the entire volume-filling factor range. As $v_i \to 0$, then $\epsilon_m \to \epsilon_0$ and $\epsilon^* \to \epsilon_0$. Hence the values $\epsilon^* = \epsilon_0$ *) and $\epsilon^* = \epsilon_m$ are substituted in the appropriate formula (*e.g.* (15.11)), and the function $\delta = f(v_i)$ is calculated for these cases. The two curves

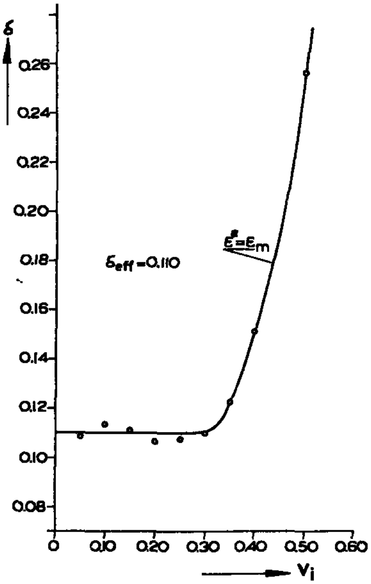

Figure III.1
$\delta = f(v_i)$ according to (15.11). NH_4Cl powder in CCl_4-CBr_4, measurements according to van Vessem 33).**)

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*) This gives the basic formula (3a) of W. Niesel 23).
**) Courtesy, Appl. Sci. Res.

obtained in this way must coincide when $\nu_i \to 0$, thus giving the actual value of δ_{eff} at $\nu_i = 0$. An example is given in Fig. III.1.

From an appropriate formula, e.g. (15.11), a quadratic function is obtained for δ. This procedure gives two values for δ_{eff}, one belonging to a disc-shaped type of granule ($\delta_{eff} < \frac{1}{3}$), the other to a needle-shaped type of granule ($\delta_{eff} > \frac{1}{3}$). Hence this method does not determine which kind of granules really are present. Reynolds [27] recently demonstrated by a second series of measurements on the same powder but with a different continuum that a choice is possible. Another possibility is to make a microphotograph of the granules.

As the measurements discussed in Chapter IV will show, the procedure is very effective in the determination of the sphericity of the granules. Both δ_{eff} and the eccentricity e can be determined fairly accurately. For the two extreme cases of conducting granules and $\epsilon_i/\epsilon_o << 1$, it is better to determine the

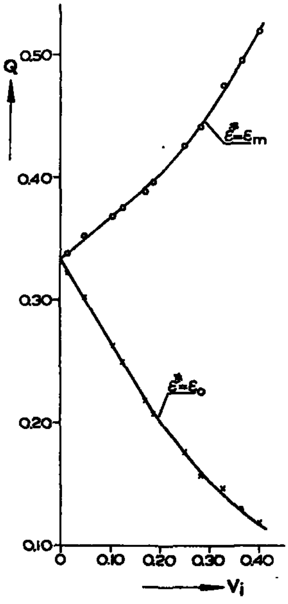

Figure III.2
$Q = f(\nu_i)$ according to (16.4). Hg in lubricating oil, measurements according to Guillien [29]: $Q_o = 0.333$, so $\delta_{eff} = \frac{1}{3}$, indicating spheres. *)

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*) Courtesy Appl.Sci.Res.

Q_0 and R_0 and to determine δ_{eff} and e with the aid of a graph of $Q_0 = f(\delta)$ or $R_0 = f(\delta)$. An example of such a determination of Q_0 is given in Fig. III.2. The functions $Q = f(\delta)$ and $R = f(\delta)$ are given in Fig. III.3.

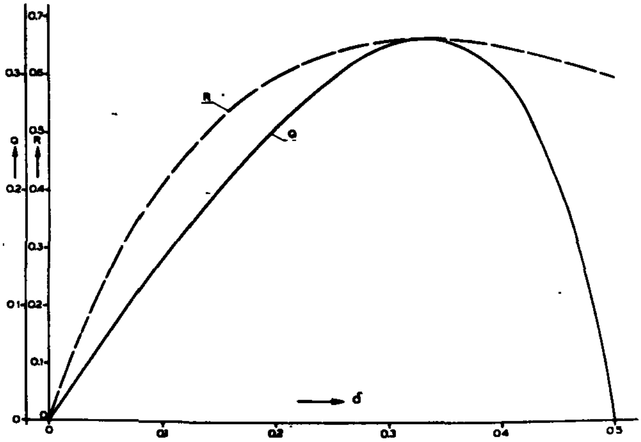

Figure III.3
$R = f(\delta)$ and $Q = f(\delta)$.

The method may also be applied to the formulae given in § 1, § 2, and § 3 of Chapter II, giving the same results for δ_{eff}. In Chapter IV, Q_0 will be determined for several series of measurements with the aid of formula (13.4), giving results analogous to those determined with equation (16.4) (Fig. IV.5). Curve I in Fig. IV.5 is for the same material as that of Fig. III.2, and gives the same result: $Q_0 = 0.333 \pm 0.003$, hence $\delta_{eff} = \frac{1}{3}$, indicating that the granules are spherical.

Having determined δ_{eff}, it is now possible to calculate the effective value of ϵ^* by means of either equation (15.11) or equation (16.4). This value can be compared with the values of ϵ_m or ϵ_0 in order to investigate the applicability of the assumptions about ϵ^* mentioned in Chapter II. As an example, in Fig. III.4, ϵ^*/ϵ_m is given as a function of v_i for the two mixtures of Fig. III.1 and III.2.

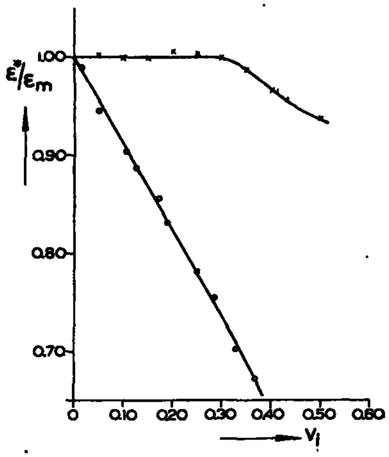

Figure III.4
$\epsilon^*/\epsilon_m = f(v_i)$. × NH_4Cl powder in CCl_4-CBr_4 33): $\delta_{eff} = 0.110$; ○ Hg in lubricating oil 29): $\delta_{eff} = 1/3$. *)

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*) Courtesy Appl.Sci.Res.

Chapter IV

Measurements

This chapter contains the author's measurements on materials of large dielectric constant dispersed in polyvinylchloride (p.v.c.), together with a summary of the data obtained by other investigators. All these results are then used to determine δ_{eff} and ϵ^* for the various systems considered.

The specimens used in our measurements were prepared by mixing the sample powder with the appropriate amount of p.v.c. powder. This mixture was heated under pressure till the p.v.c. melted and formed a continuum around the granules of the powder. In order to determine the properties of the substance serving as a continuum, specimens of pure p.v.c. were made by the same procedure. The specimens were 26 mm in diameter and 1.5 to 6.0 mm thick. They were very sensitive to moisture, and were therefore dried and held in a desiccator over P_2O_5.

The use of solid specimens for these measurements produced several difficulties. During manufacture a slight change in the density of the continuum may occur, and agglomeration of the granules is possible at the higher volume-filling ratio's. In making the measurements, an air gap between the specimen and the electrodes will give an incorrect value of ϵ_m, and the effect of the edge of the electrodes of the measuring condenser is also difficult to calculate.

The d.c. of the specimens was measured with the aid of a condensor consisting of two circular electrodes, 50 mm in diameter, whose capacity was determined with the specimen in position between the plates and with the specimen taken out, keeping the electrodes of the condenser at the same distance. Originally a measuring set designed by Hartshorn and Ward [28)] was used, but later measurements were made with an apparatus based on a heterodyne-beat method, to which the Hartshorn and Ward condenser was adapted. In the procedure described, difficulties arising from an unknown edge correction are avoided because the specimens are smaller in diameter than the electrodes and are confined to that part of the space between the electrodes where the field is parallel and uniform. To eliminate the influence of an air gap of unknown thickness between electrodes and specimen, secondary electrodes were pasted on the specimens by means of a silver paint. Measurements were made at six spot frequencies between 0.1 and 9 Mc/s. In Fig. IV.1 the results $\epsilon_m = f(v_i)$ are plotted at 100 Kc/s for the materials used by the author.

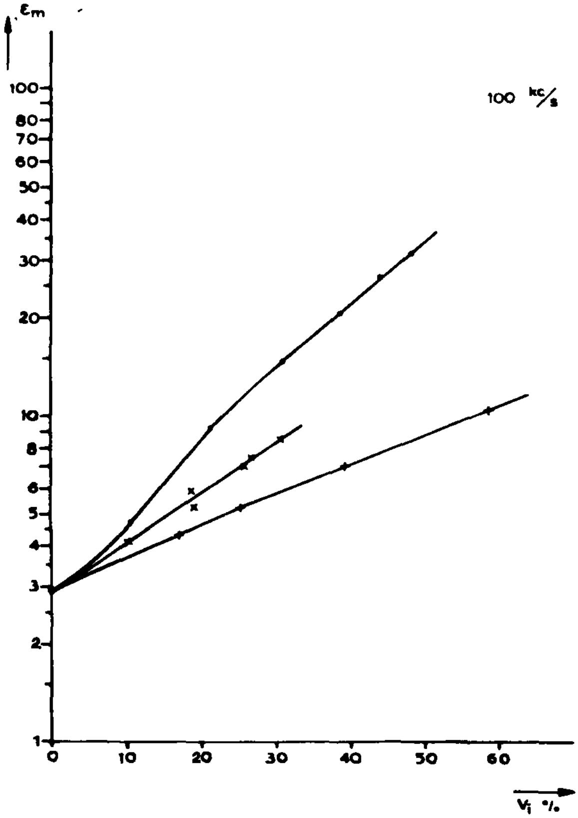

Figure IV.1
Experimental results: $\epsilon_m = f(v_i)$.
. $BaTiO_3$ powder in p.v.c.; × TiO_2 powder in p.v.c.; + Tellurite glass powder in p.v.c.

A measuring cell was also made in which the granules could be dispersed in a liquid. This permitted circulation during the measurements, and samples with large density discrepancies between granules and continuum could be studied. The cell was based on one designed by Guillien [29]. Many difficulties were encountered in eliminating the rotation of the liquid, which caused the granules to cluster together at the top of the cell, thus destroying the homogeneity of the mixture. The introduction of blades made a great improvement, and the final form of the cell is given in Fig. IV. 2.

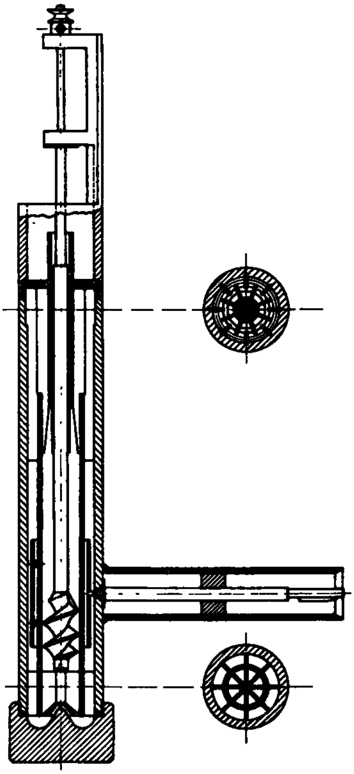

Figure IV. 2
Stirrer cell.

Of the specimens described above, some were machined for measurement in a waveguide. Here the measuring technique worked out by von Hippel [30][31] was employed (*vide* Chapter VII).

The results of many measurements are available in the literature. Many of them are given here together with those of the author, in the order of the ratio ϵ_i/ϵ_0 and with the reinterpretation now possible with the method described in the foregoing chapters.

§ 1. *Non-conducting granules*

a. NH_4Cl powder in CCl_4-CBr_4 (van Vessem [33])

$\epsilon_i/\epsilon_0 = 6.84/2.234 = 3.062$. The graph needed for the determination of δ_{eff} is given in Fig. III.1, and gives $\delta_{eff} = 0.110 \pm 0.004$ (thus $e = 0.17$). The other value obtained with the procedure given in Chapter III is improbable ($\delta > 0.5$). With the former value for δ_{eff} (0.110), the curve $\epsilon^*/\epsilon_m = f(v_i)$ was calculated, giving ϵ^*/ϵ_m constant = 1 between $v_i = 0$ and $v_i = 30\%$ (*vide* Fig. III.4 and Fig. IV.3).

b. Tellurite glass powder (B.T.H. [34]) in p.v.c. (author)

The d.c. ϵ_i was measured by the author between 0.06 and 68 Mc/s, giving $\epsilon_i = 26$, $\tan \partial = 0.002$. These results have already been reported by Poley [35]. Only four specimens could be made because of the very small amount of powder available. The results for 0.1 and 1 Mc/s are given in Table IV.I.

Table IV.I
Powder of Tellurite glass in p.v.c., $\epsilon_i = 26$.

v_i %	100 Kc/s ϵ_m	1 Mc/s ϵ_m
0	2.93	2.79
17.0	4.33	4.14
25.2	5.27	5.15
39.2	7.06	6.97
58.4	10.5	10.4

Due to the lack of specimens of lower v_i for the determination of δ_{eff}, the values for $v_i = 5\%$ and 10% were interpolated graphically (*vide* Fig. IV.1). Compiling the measurements on all frequencies gave $\delta_{eff,1} = 0,24 \pm 0.03$ and $\delta_{eff,2} = 0.42 \pm 0.02$, giving $e_1 = 0.5 + 0.1$ and $e_2 = 1.7 \pm 0.3$ respectively.

c. $PbCl_2$ powder in CCl_4 (Guillien [29])

$\epsilon_i/\epsilon_0 = 28/2.2252 = 12.58$.

The calculations according to Chapter III resulted in the following values:

$\delta_{eff,1} = 0.116$ ($e_1 = 0.18$) and $\delta_{eff,2} = 0.475$ ($e_2 = 5.3$).

d. TiO$_2$ powder in p.v.c. (author)

For the determination of v_i, the density of the powder was first determined with a pyknometer, giving ρ = 3.62. Measurements on sintered TiO$_2$ are available in the literature [36][37], and from them a value of ϵ_i = 81 was chosen. The influence of a variation in this value was determined, but proved to be of minor importance for the determination of δ_{eff}. $\epsilon_i/\epsilon_o \approx 29$. The results for 1 and 9 Mc/s are summarised in the Table IV.II. *Vide* also Fig. IV.1.

Table IV.II
TiO$_2$-powder in p.v.c.

v_i %	1 Mc/s ϵ_m	9 Mc/s ϵ_m
0	2.79	2.66
10.2	4.07	3.93
19.1	5.45	5.30
18.8	6.04	5.55
25.8	7.38	6.57
26.6	7.76	7.16
30.5	8.67	8.14

Lichtenecker [24] derived a formula for $\epsilon_m = f(v_i)$ which would give acceptable results in this particular case. Other authors have also used this approximation (*vide* eq. (115.1)) for TiO$_2$ powder with good success [36][38]. Compilation of all the available results shows:

$\delta_{eff,1}$ = 0.173 ± 0.006 resulting in $e_1 = 0.30^5 \pm 0.01^5$
$\delta_{eff,2}$ = 0.453 ± 0.004 resulting in $e_2 = 3.28 \pm 0.15$.

e. BaTiO$_3$ powder in p.v.c. (author)

The d.c., ϵ_i, of the BaTiO$_3$ powder was not known exactly, but, as our own measurements (*vide* Ch.VII) and measurements in the literature on sintered samples showed [32], ϵ_i must be in the region of ϵ_i = 1500 and the value of ϵ_i/ϵ_o is at least 400. Q_o was now determined with the equation (16.4), assuming $\epsilon_i/\epsilon_o \gg 1$. In § 3 of this chapter, it will be shown that this can be done. Many measurements were made on this material. The averaged values for 0.1 and 1 Mc/s are given here in Table IV.III.

Compiling the many available results, and including those of

Table IV.III
$BaTiO_3$ powder in p.v.c.

v_i %	100 Kc/s ϵ_m	1 Mc/s ϵ_m
0	2.93	2.79
10.6	4.74	4.59
21.3	9.23	8.96
30.9	14.7	14.3
38.6	20.8	20.4
43.8	26.7	26.2
47.9	31.9	31.1

the other frequencies used by the author, gives $Q_o = 0.26 \pm 0.02$;
giving: $\delta_{eff,1} = 0.21 \pm 0.02$ resulting in $e_1 = 0.40 \pm 0.06$
$\delta_{eff,2} = 0.42^5 \pm 0.01$ resulting in $e_2 = 2.3 \pm 0.4$.

f. ZnO powder in rolled rubber (Scott [39])

The rubber used for the specimens was rolled in one particular direction during manufacture. The d.c. was measured in three mutually perpendicular directions. Scott observed that in these specimens the granules were directed in the direction of major flow by the rolling procedure. This also influences the d.c. Two series of measurements are available: a series at 1 Kc/s and one at 100 Kc/s, with $\epsilon_i/\epsilon_o = 34/2.57 = 13.23$ and $\epsilon_i/\epsilon_o = 25.5/2.56 = 9.96$ respectively. The results of these measurements are given in Table IV.IV.

Table IV.IV
D.c. of ZnO powder in rolled rubber [39].

v_i %	1 Kc/s $\epsilon_i = 34$			100 Kc/s $\epsilon_i = 25.5$		
	Direction			Direction		
	a	b	c	a	b	c
0	2.56	2.57	2.58	2.55	2.55	2.57
10	3.04	3.28	3.38	3.01	3.02	3.29
20	3.67	4.05	4.26	3.60	3.92	4.12
28.3	4.09	-	5.12	4.01	-	4.84
33.6	4.36	5.00	5.65	4.35	4.79	5.28

The depolarization factor was calculated with the aid of the formula

$$\epsilon_m - \epsilon_o = v_i \ (\epsilon_i - \epsilon_o) \frac{1}{1 + (\epsilon_i/\epsilon^* - 1) A}$$

since the granules are directed by the rolling procedure *). Calculation of A gave $\sum_1^3 j \ A_j > 1$. Reducing to $\sum_1^3 j \ A_j = 1$ *) gives: $A_a = 0.44$, $A_b = 0.30$, and $A_c = 0.26$, which finally gives [40] for the axial ratios of the granules:

$$c/a = 1.56 \qquad \text{and} \qquad c/b = 1.12 \ .$$

The manufacturer's value for the eccentricity is $e = 1.8$. This is in fair agreement with the above values since the orientation of the granules is probably incomplete, which explains the fact that in the first calculations $\sum_1^3 j \ A_j > 1$. Scott remarks that X-ray examination of the samples revealed that there was considerable alignment of the granules.

g. Only recently a very interesting series of measurements became available; these were made by Reynolds [27][41][42] on granules of a well determined shape in various liquids with different d.c. His measurements on glass lamellae, glass rods and glass spheres give values for the shape factor δ_{eff} which are in excellent agreement with the actual shape of the granules [41] as determined from micro-photographs. These measurements also include results in which $\frac{\epsilon_i}{\epsilon_o} < 1$.

In the Fig. IV.3 the results of the calculation of ϵ^* are given for several mixtures by plotting $\epsilon^*/\epsilon_m = f(v_i)$. It is seen that $\epsilon^* < \epsilon_m$, and $\epsilon^* > \epsilon_o$. Thus for all the measurements given here, where $\frac{\epsilon_i}{\epsilon_o} > 1$, $\epsilon_o < \epsilon^* < \epsilon_m$. This is also concluded by Reynolds and Hough from the measurements mentioned under g. By including their measurements for which $\frac{\epsilon_i}{\epsilon_o} < 1$, the general conclusion can be drawn that ϵ^* lies in between ϵ_o and ϵ_m.

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*) ref. 4, pages 69 – 71.

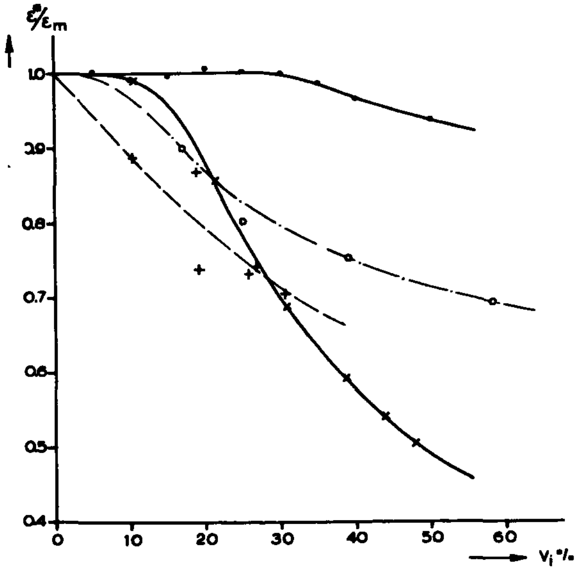

Figure IV.3
$\epsilon^*/\epsilon_m = f(v_i)$. • NH4Cl powder in CCl4-CBr4 [33]; o Telluriteglass powder in p.v.c. ; + TiO2 powder in p.v.c.; × BaTiO3 powder in p.v.c.

§ 2. *Conducting granules*

The available results of measurements on mixtures containing conducting granules are given in Fig. IV.4. The calculations were made with the aid of formula (16.4) which gives Q_0. To show that the method described in Chapter III can also be used with the other formulae discussed in Chapter II, Q_0 was determined with the aid of equation (113.4). The results of this determination are given in Fig. IV.5. With the aid of the graph of $Q = f(\delta)$ in Fig. III.3, δ_{eff} was determined. Formula (114.1) was checked by calculating q.

a. Spheres of Hg in lubricating oil (Guillien [29])

Measurements were made at two temperatures, $t = 17.8$ °C ($\epsilon_0 = 2.263$) and $t = 24$ °C ($\epsilon_0 = 2.210$).

Calculation gave (*vide* Fig. III.2 and IV.5) $Q_0 = 0.333 \pm 0.003$ a good test for the method. Calculation of q gave $q = 2.00 \pm 0.09$ until $v_i = 25\%$.

Good agreement was also observed with the formula of Bruggeman.

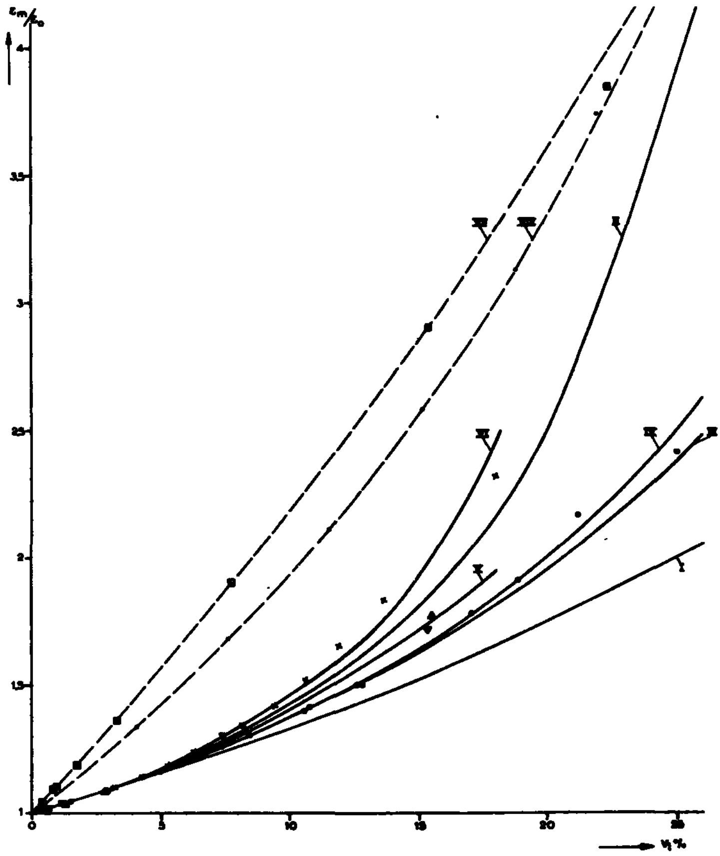

Figure IV.4
Conducting granules. $\epsilon_m/\epsilon_0 = f(v_i)$. Relation (II4.1). I – IV: $S = 3$, I: $q = 1$ (eq. (II1.7)), II: $q = 3$ (equation of Böttcher (II2.2)), III: equation of Niesel-Bruggeman (II3.4), IV: $q = 2$, V: $q = 2.5$, VI: $q = 3.45$. VII equation (II4.1): $S = 10.9$, $q = 0.80$; VIII idem: $S = 7.81$, $q = 1.69$.
Experimental results: according to Voet 43): ▽ carbonyliron powder in linseed oil, △ idem in mineral oil; according to Guillien 29): ○ Hg in lubricating oil, × granules of Wood's metal in lubricating oil, □ Mg powder in CCl_4, ⊠ idem in ether, . Fe powder in CCl_4.

b. Spheres of Wood's metal in lubricating oil (Guillien 29))

The calculations gave $Q_0 = 0.33$ with, however, the possibility of small deviations. This is nonetheless in agreement with Guillien's observations that the granules are a bit oblate. Calcula-

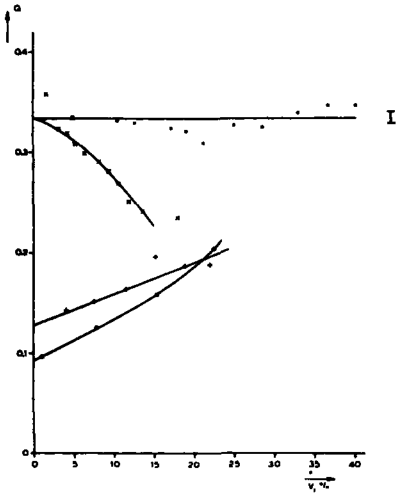

Figure IV. 5
Determination of Q_0. $Q = f(v_i)$ according to the equation of Niesel-Bruggeman (II3.4) from the experimental results of Guillien [29]: . Hg in lubricating oil, × Powder of Wood's metal in lubricating oil, ○ Mg powder in CCl_4, + Fe powder in CCl_4.

tion gave $q = 3.45 \pm 0.27$. That q becomes larger than $q = 3$ can be explained by the fact that the granules were crushed by the circulating mechanism during the measurements.

c. Spherical granules of iron in oil (Voet [43])

Two continua were used by Voet: linseed oil with $\epsilon_0 = 3.85$ and mineral oil with $\epsilon_0 = 2.39$. The measurements were not sufficiently accurate to show with absolute certainty that $Q_0 = \frac{1}{3}$, implying spherical granules, though the results suggest it. Voet concludes from his measurements that Bruggeman's formula would give the best results for this case. However, for these two series the Böttcher formula gives equally good results. Best agreement with the measurements was found for the value $q = 2.5$.

d. Mg-powder in CCl_4 ($\epsilon_0 = 2.221$) and ether ($\epsilon_0 = 4.398$) (Guillien [29])

Calculation here gave: $Q_0 = 0.092$ for both continua, thus $\delta_{eff,1} = 0.064$ and $\delta_{eff,2} = 0.482$, giving for the eccentricity $e_1 = 0.09$ and $e_2 = 6.9$ respectively. Further, $q = 0.80$.

e. Carbonyl-iron powder in CCl_4 (Guillien [29])

ϵ_o = 2.230. Here Q_o = 0.128, thus $\delta_{eff,1}$ = 0.090 and $\delta_{eff,2}$ = 0.474, giving for e: 0.13 and 5.2 respectively. For this case for v_i from 0 to 20%, q = 1.69.

f. It is now possible to analyse some older measurements which could not easily be fitted into the picture used when they were made [44].

1. In 1897, Millikan [45] made a series of measurements on emulsions of water in a mixture of benzene and carbontetrachloride having a density of one. A calculation of Q_o shows that Q_o = 0.358 instead of 0.333, probably because the assumption $\frac{\epsilon_i}{\epsilon_o} \gg 1$ does not fully apply for this case. Good agreement is observed with the Maxwell formula (II1.7).

2. F. Hwlati [46] (1901) also checked Maxwell's formula (II1.7), using spherical conducting granules. He prepared a series of salves containing Hg granules, with a volume-filling factor of between v_i = 0.2 and 3.5%. A calculation of Q_o gave $Q_o = \frac{1}{3}$ within the obtainable accuracy. Because the maximum v_i is only v_i = 3.55%, no definite choice can be made between the formulae of Maxwell (II1.7), Bruggeman (II3.4) and Böttcher (II2.3), though individual comparisons with the measurements gave best results with Bruggeman's formula. This formula, on the average, fitted within 0.1% while the other two fitted within 0.5%. This is in agreement with the measurements of Guillien [29] on Hg granules given above.

3. In 1899, F. Beaulard [20] made measurements on two specimens containing copper dust. The measurements did not fit well with the formulae used. An approximate calculation of Q_o, possible because of the low value of v_i of both specimens, gave Q_o = 0.295 or S = 3.39, thus giving e = 0.5 or e = 1.8. This demonstrates that it is not so remarkable that the measurements did not successfully fit into a picture based on spherical granules. Best agreement is obtained with formula (II4.1) with q = 2 giving:

v_i %	$\frac{\epsilon_m}{\epsilon_o}$ measured	$\frac{\epsilon_m}{\epsilon_o}$ calculated
1.607	1.056	1.056
6.904	1.270	1.272

4. John [47][44] (1918) studied some mixtures with granules of a well-determined shape (spheres and cylinders) in ordered arrange-

ments. However, the size of the granules was comparable to the dimensions of his measuring condenser: a size effect was to be expected [33] and was indeed observed. The values obtained are too low.

Using all the data given here, ϵ^* was also determined. With one exception $\epsilon_o < \epsilon^* < \epsilon_m$, the exception being the data on Wood's metal in lubricating oil [29] for higher values of v_i. This exception, however, is improbable, and the deviations can be explained, as already remarked, by the fact that at larger values of v_i the granules were crushed by the circulating mechanism [29] and were no longer spherical. The function $\epsilon^*/\epsilon_m = f(v_i)$ for Hg granules in lubricating oil is given in Fig. II.4.

§ 3. *Discussion*

This review of the experimental results demonstrates that none of the equations given in Chapter II satisfactorily describes the behaviour of heterogeneous mixtures over the entire volume-filling factor range, because in every instance ϵ^* lies between ϵ_o and ϵ_m. Agreement with one of the relations of Chapter II can be obtained only for a limited number of cases and for a small region of v_i. Reynolds and Hough [27][42] noted that the experimental curve $\epsilon^* = f(v_i)$ shows some analogy with the curve obtained by comparing the Bruggeman-Niesel relations (extended to all possible shapes) with equation (I5.11). This analogy, however, is far from complete.

In the measurements discussed above, a change of behaviour seems to occur around $v_i = 20\%$. This effect is especially pronounced with the $BaTiO_3$ powder. It also occurs with the TiO_2 powder and the Tellurite glass powder, although here the effect is less marked. This phenomenon is most clearly observed in the curves $\delta = f(v_i)$ and $Q = f(v_i)$, which are necessary for the determination of δ_{eff}. The measurements and calculations made by Reynolds [27] also suggest this. The same effect occurs with the mixtures containing conducting granules where q is no longer a constant for $v_i > 20\%$.

The literature contains measurements on water emulsions. C.A.R.Pearce [17] made measurements with emulsions of seawater in oil and found good agreement with the formula of Bruggeman (II3.5). This suggests $S = 3$ and therefore spherical granules, in agreement with the observations. The author also made some measurements of this kind, using the measuring condenser shown in

Fig. IV. 2 to circulate the emulsion. A slight deviation from the spherical shape was found ($Q_o < \frac{1}{3}$) and the results showed a tendency to differ depending upon whether the emulsion was circulated or static. The probable reason for this is that the high pumping speeds tend to elongate the granules somewhat and cause them to direct themselves in the direction of major flow. This is also suggested by Voet 43), who states that the granules are directed by stress. Scott's measurements (*vide* § 1f) 39) can also be referred to here. It also gives a possible explanation of the extreme values for the eccentricity found for $PbCl_2$ powder, Fe powder, and Mg powder, all of which were measured by Guillien 29) in a cell in which the mixture was circulated during the measurements. Assuming a total directing of the granules in the direction of major flow gives the results of Table IV.V.

Table IV. V
Measurements according to 29).
Determination of *e*, assuming parallel alignment of the granules.

powder	$Q_o = \delta_{eff}$	giving *e*	see §
$PbCl_2$	0.19	1.8	1 c
Fe	0.128	2.6	2 e
Mg	0.092	3.3	2 d

These values for *e* are reasonable, as the following Chapter will show. This suggests that the method adopted by Guillien is sufficiently accurate only for spherical granules, because no preferential direction is then present. For other types of granules, the method can be used when only the form of the granules is wanted, and also when the granules and the continuum are of equal density, so that no circulation is necessary during the actual measurement. However, under this condition care must be taken that the granules do not agglomerate 43). As Reynolds' measurements 27) suggest, his stirrer cell avoids an orientational effect, being of a design deviating slightly from that used by Guillien 29) and that used by the author.

The calculation of δ_{eff} for non-conducting granules according to the method described in Chapter III, is fairly complicated. The calculation of Q for conducting granules, on the other hand, is simple. Some calculations were made in order to determine to what extent the second method can be used as an approximation for non-conducting granules. The results are summarised in the Table IV.VI.

Table IV.VI
Results of approximative method
for the determination of *e*.

ϵ_i/ϵ_o	Q_o	gives δ_o	instead of δ_{eff}	see §
9.3	0.43	–	0.24 or 0.42	1 b
12.6	0.27	0.21 or 0.42	0.116 or 0.475	1 c
29	0.27	0.21 or 0.42	0.17 or 0.45	1 d

Thus, large deviations can be expected with this procedure. Some calculations were also made on several hypothetical curves of $\epsilon_m = f(v_i)$, to see at what ratio ϵ_i/ϵ_o this approximative method can be used. It can be shown that this approximative method is sufficiently accurate for $BaTiO_3$ powder in p.v.c. ($\epsilon_i/\epsilon_o \approx 400$). It follows that it is not applicable in most practical cases.

Chapter V

The relation between δ_{eff} and the actual shape of the granules

In all our calculations, an effective value of δ has been used. This value of δ_{eff} was very well related to the actual shape of spherical granules. The author's technique, when used by Reynolds [27)41)], also gave good agreement for granules of extreme shapes, such as rods and lamellae. The present Chapter is an investigation of the relation between δ_{eff} and the actual form of the granules for still other shapes and for those cases in which a distribution of shapes is present in a mixture.

§ 1. *The accuracy of the determination of the eccentricity*

In order to determine the influence of a variation in the value of e upon the quantities involved in the calculations, Q, R, S', and T' were calculated as a function of the eccentricity, e, with ϵ_i/ϵ^* as a parameter. All the curves thus obtained are very flat around $e = 1$ (spherical shape). Some of the results are given in the Figures V.1 and V.2. In order to demonstrate how a variation in e manifests itself, the computations given in Table V.I will show the influence of a variation of 1% in Q, R, S', and T' on e for several discrete eccentricities.

Table V.I

Influence of a variation in p (which value is proportional to $(\epsilon_m - \epsilon_o)$) on the determination of the eccentricity e.

ϵ_i/ϵ_o	p ± 1%	$e = 1$	$e = 2$	$e = 0.5$	$e = 0.1$
→ 0	R	0.67 – 1.43	1.65 – 2.35	0.47 – 0.54	0.099 – 0.101
0.04	T'	0.67 – 1.52	1.63 – 2.65	0.47 – 0.54	0.099 – 0.101
9.75	S'	0.78 – 1.28	1.88 – 2.06	0.48 – 0.53	0.097 – 0.103
11	S'	0.78 – 1.28	1.88 – 2.08	0.48 – 0.52	0.098 – 0.102
101	S'	0.82 – 1.2	1.9 – 2.1	0.48 – 0.53	0.099 – 0.101
→ ∞	Q	0.83 – 1.2	1.96 – 2.05	0.49 – 0.52	0.099 – 0.101

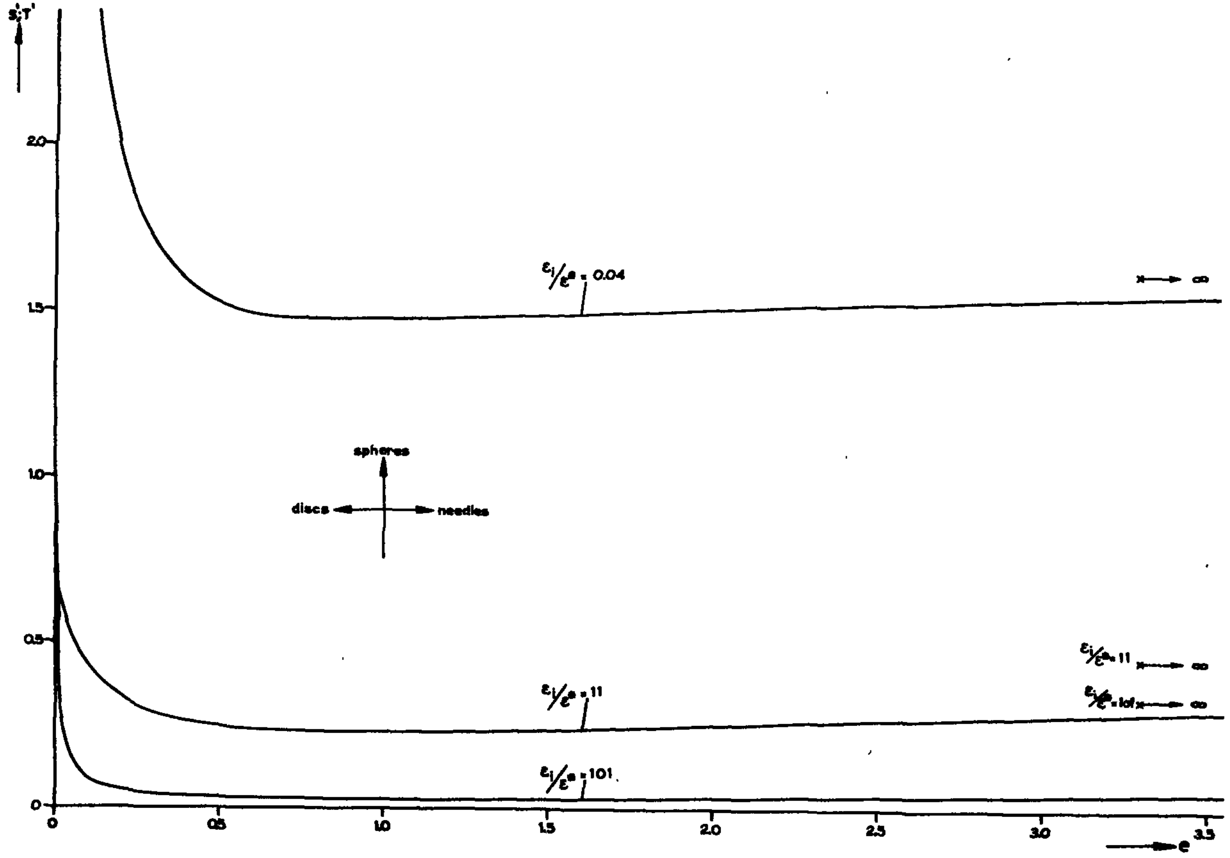

Figure V.1
S' and T' as a function of the eccentricity e
with ϵ_i/ϵ^* as a parameter.

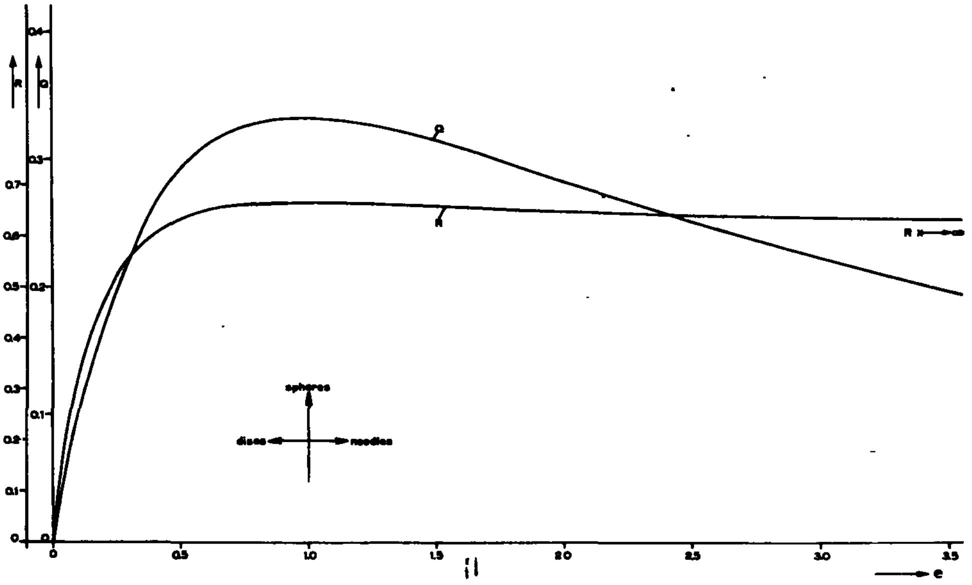

Figure V.2
Q and R as a function of the eccentricity e.

Here $\frac{\epsilon_i}{\epsilon^*} = \frac{\epsilon_i}{\epsilon_o}$ because in our method δ_{eff} is obtained for $v_i = 0$ where $\epsilon^* = \epsilon_o$. From the Table it can be seen that for a 1% accuracy in the value of $(\epsilon_m - \epsilon_o)$ a minimum deviation of ± 20% in the eccentricity e from $e = 1$ (spherical shape) can be tolerated. This explains why ϵ_m is rather insensitive to variation in e and why the determination of e (from measurements of ϵ_m) in this region is so very difficult. Only for larger eccentricities does ϵ_m become more sensitive to variations in e. For $e = 0.1$, a variation of 1% in e also causes a variation of 1% in $(\epsilon_m - \epsilon_o)$.

For the case of granules of a low d.c. in a continuum with a very large d.c., or holes or interstices in a high d.c. ceramic (thus involving $\frac{\epsilon_i}{\epsilon_o} < 1$), the influence of a variation of the eccentricity becomes very small when the interstices are needle-shaped. With a change in shape of the interstices from spheres to needles, for instance, when $\frac{\epsilon_i}{\epsilon_o} \to 0$, then T varies from 1.5 to 1.666, and when $\frac{\epsilon_i}{\epsilon_o} = 0.04$, T' varies from 1.461 to 1.615. This enables relatively accurate determinations of the bulk d.c. ϵ_0 of ceramic samples, since the holes in such a material seem to be pointed and can be assumed to be needle-shaped [48]. Originally, it seemed that such determinations would be rather difficult, because the form of the interstices varies with the range of firing temperatures and times needed to obtain variation in the porosity of the samples. However, for normal manufacturing conditions the holes are almost exclusively needle-shaped, and tend to spherical shapes [48] for higher firing temperatures and longer firing times. Therefore, the variation in T and T' appears to be limited, and a determination of the d.c. of the ceramic continuum becomes possible from measurements of $\epsilon_m = f(v_i)$. Two series of measurements are available: those of D.F. Rushman and M.A. Strivens on sintered $BaTiO_3$ and of A.R. von Hippel and co-workers on sintered TiO_2.

a. Sintered $BaTiO_3$ [49]

The averages for the different firing temperatures are given in Table V.II. In this Table, v_i is the averaged volume-filling factor of the air interstices at the different firing temperatures.

Table V.II
Sintered $BaTiO_3$, according to [49].
Average values of ϵ_m and v_i for the different firing temperatures.

v_i %	ϵ_m
41.2	447
40.0	496
32.6	903 ± 10
30.1	946 ± 35
21.2	1140 ± 40
10.0	1407 ± 18

From these values, ϵ_0 was calculated with the aid of formulae (II1.9), (II2.4), and (II3.6), with $T = 1.5$ and 1.666 respectively. Plotting the values for ϵ_0 thus obtained as a function of v_i gives $\epsilon_0 = 1650 \pm 30$. With this value the function $\epsilon_m = f(v_i)$ was recalculated. Good agreement was found for the Niesel-Bruggeman formula (II3.6) with $T = 1.5$. These results are given in Table V.III and Fig. V.3. It was first thought that T would be a func-

Table V.III
Sintered $BaTiO_3$, according to [49]. Average values for ϵ_m and calculated values.

v_i %	ϵ_m with (II3.6)	ϵ_m measured
10.0	1408	1407
21.2	1132	1140
30.1	964	946
32.6	913	903

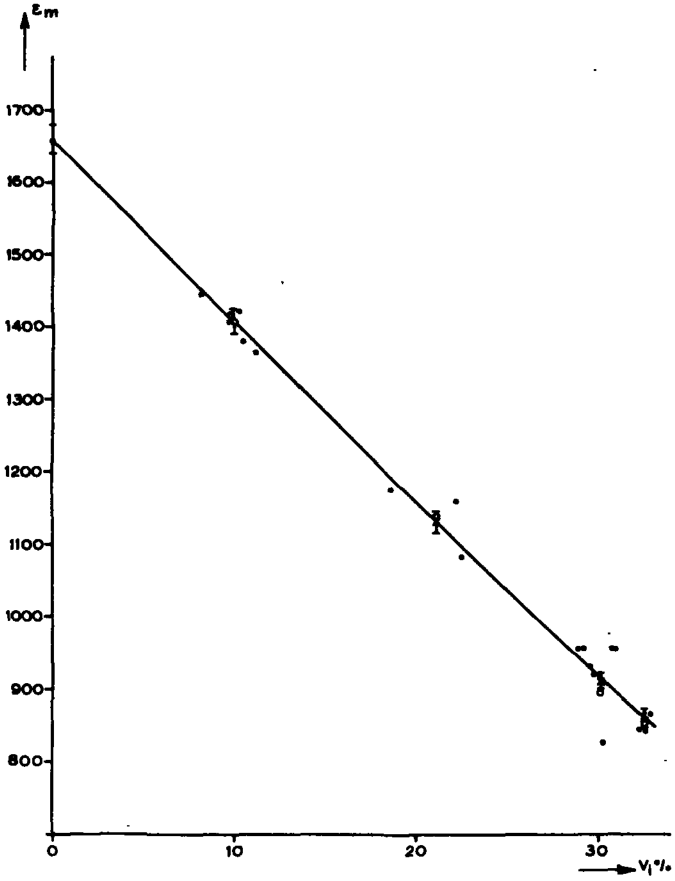

Figure V.3
Sintered $BaTiO_3$ according to [49], $\epsilon_m = f(v_i)$. × averages for one firing temperature, ○ ϵ_m as calculated.

tion of v_i, approaching 1.666 with increasing v_i. Nevertheless, good results were also obtained with a constant value (1.5). For values larger than v_i = 30%, the values of ϵ_m become rapidly smaller, and the deviations from the calculated values increase rapidly, probably because the interstices begin to merge into each other.

b. Sintered TiO$_2$ 37)

The values used were taken from a report published by the M.I.T. (ref. 37, Fig. 3 and 4) and are shown in Fig. V.4. Here a different method of calculation was followed. From the graph of $\epsilon_m = f(v_i)$, the value of ϵ_0 was extrapolated. With this value, ϵ_m was recalculated with the aid of the three formulae (II1.9), (II2.4), and (II3.6), until best agreement with the experimental results was obtained. This gave $\epsilon_0 = 104 \pm 3$ as the best value. Good agreement was obtained only by assuming T to vary from 1.5 to 1.666 as a function of v_i. This is quite reasonable as the holes are reported to become more spherical for higher TiO$_2$ content (lower v_i) (*e.g.* Jonker 48)). Best agreement was found with the equations (II2.4) and (II3.6). *Vide* Table V.IV. In this Table the values accepted finally are in italics.

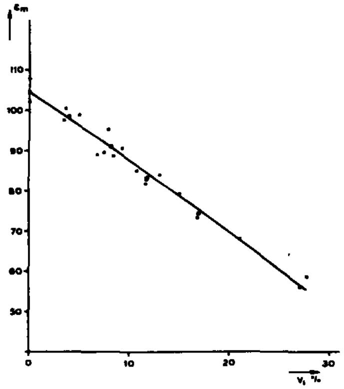

Figure V.4
Sintered TiO$_2$, according to 37),
$\epsilon_m = f(v)$, O ϵ_m as calculated.

The results are given in Fig. V.4. It is also possible that for T in this case a value larger than T = 1.666 can be used. As further discussion will show (§ 2), even a relatively small number of disc-shaped holes greatly enlarges T. The micro-photo-

Table V.IV
Sintered TiO_2, according to [37]. Averaged values for ϵ_m from experimental results, and calculated values.

v_i %	ϵ_m measured	ϵ_m with (II2.4)		ϵ_m with (II3.6)	
		T = 1.5	T = 1.667	T = 1.5	T = 1.667
4	98.4 ± 2	*97.8*	97.1	*97.8*	97.1
8.2	91.2 ± 1.6	*91.3*	89.9	*91.5*	90.3
11.8	83.2 ± 2	85.6	*83.6*	86.2	*84.4*
17	74.5 ± 1.5	77.5	*74.5*	78.6	*76.2*

The values accepted are in italics.

graphs of Jonker [48] suggest that the actual shape of the holes is a needle form which becomes more or less spherical, but that a certain amount of more or less disc-shaped holes may also be present.

§ 2. *The influence of a distribution of eccentricities on the determination of* δ_{eff}

a. In this section, the discussion is extended to the case where a single discrete eccentricity for the granules can no longer be assumed (as above in § 1), but where instead a distribution of eccentricities is present. Some calculations for this case were attempted. This required a distribution function for e which did not give negative values and had at its origin $e = 0$ with $N = 0$ (N = number of granules). Kottler [50] showed that for the analogous case of particle *sizes*, a log-normal distribution can be used, and Gaddum [51] demonstrated its more general value. This function has the required properties. It is asymmetric around the modal value. This function, $N = f(ecc)$, is determined from

$$e = A \exp. (kt)$$

$$N = \frac{1}{2\pi} \exp. (-t^2/2)$$

where A determines the mode of the curve and k its width. This distribution function was adopted because it gave sufficient indication of the influence of a distribution of eccentricities. Two different series of calculations were made: one for a wide distribution and the other for a narrow one (k = 1 and k = 0.1). In Fig. V.5 this function is given for several values of A. Now p

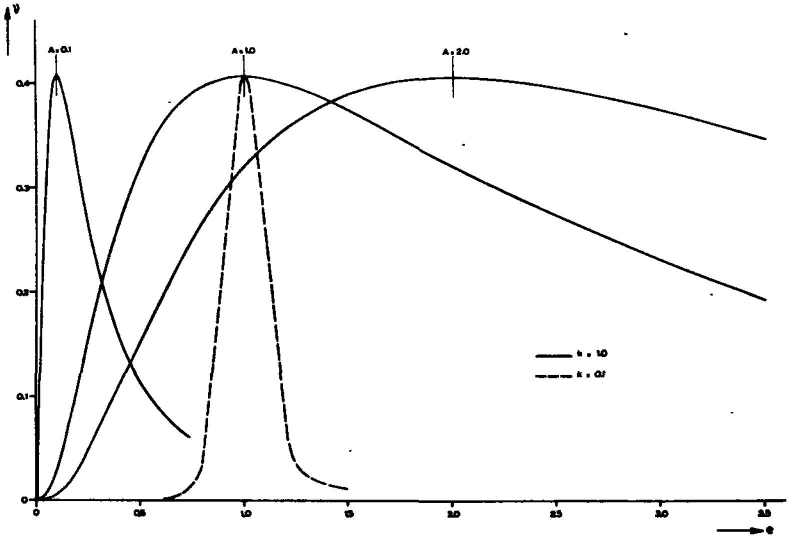

Figure V.5
Log-normal distributions. ν is proportional to $N/N_{tot.}$.

(= Q, R, S', T') was calculated using these distributions for several values of A (= e_{mode}) and ϵ_i/ϵ_0. Table V.V. gives the results. For a given e_{mode}, the value found as a result of the distribution gives a new value for $\bar{e}$. This value is calculated from p, assuming only one eccentricity to be present, as is assumed in the measurements discussed in Chapter IV. This value of $\bar{e}$ must agree with the eccentricity found from the measurements for that case.

From Table V.V it can be seen (*vide* the last determination) that we can even obtain a value for T which would normally be associated with a mixture containing disc-shaped granules (with a discrete eccentricity). This is due to the small change in T for e between $e = 1$ and $e \to \infty$. This may explain the deviations found in § 1 for the sintered TiO_2.

Some calculations for a narrow distribution were also made (*vide* Table V.VI).

For a narrow distribution function, the variation in the eccentricity will be greatest around $e = 1$, as shown in Table V.VI. However, for a narrow distribution, an accurate determination becomes possible. This explains why, in Guillien's measurements 29)

Table V.V

Influence of a given distribution of eccentricities on the determination of $\bar{e}$ when using the method described in Chapter III. Wide distribution.

$A = e_{mode}$	ϵ_i/ϵ_o	modal value of p	mean value of p	variation of p in %	this gives $\bar{e}$
0.1	11	$S'_m = 1.284$	$S' = 1.296$	+ 1.0	0.098
	$\to \infty$	$Q_m = 0.100$	$Q = 0.129$	+29	0.137
0.5	$\to 0$	$R_m = 0.637$	$R = 0.519$	-18.5	0.25
	1/25	$T'_m = 1.528$	$T' = 1.973$	+29.1	0.195
	11	$S'_m = 0.750$	$S' = 1.017$	+35.6	0.199
	$\to \infty$	$Q_m = 0.292$	$Q = 0.204$	-30.1	0.26
1	$\to 0$	$R_m = 0.667$	$R = 0.581$	+12.8	0.34
	1/25	$T'_m = 1.471$	$T' = 1.718$	+16.8	0.3
	11	$S'_m = 0.693$	$S' = 0.913$	+31.7	0.261
	$\to \infty$	$Q_m = 0.333$	$Q = 0.205$	-38.4	0.26
2	$\to 0$	$R_m = 0.650$	$R = 0.614$	+ 5.53	0.405 and ~8
	1/25	$T'_m = 1.505$	$T' = 1.684$	+11.9	0.32
	11	$S'_m = 0.755$	$S' = 0.935$	+23.8	4.1
	$\to \infty$	$Q_m = 0.283$	$Q = 0.184$	-35.0	3.75

Table V.VI

Influence of a given distribution of eccentricities on the determination of $\bar{e}$ when the method described in Chapter III is used. Narrow distribution.

$A = e_{mode}$	ϵ_i/ϵ_o	modal value of p	mean value of p	variation of p in %	$\bar{e}$	variation in e %
0.5	11	$S'_m = 0.75$	$S' = 0.752$	0.3	0.49	1.5
	101	$S'_m = 0.98$	$S' = 0.989$	0.96	0.48	4
	$\to \infty$	$Q_m = 0.292$	$Q = 0.291$	0.35	0.49	1.4
1	11	$S'_m = 0.693$	$S' = 0.695$	0,32	$\left\{\begin{matrix}0.88\\1.11\end{matrix}\right.$	13
	101	$S'_m = 0.874$	$S' = 0.878$	0.46	$\left\{\begin{matrix}0.89\\1.11\end{matrix}\right.$	11
	$\to \infty$	$Q_m = 0.333$	$Q = 0.332$	0.27	$\left\{\begin{matrix}0.9\\1.1\end{matrix}\right.$	10
2	11	$S'_m = 0.755$	$S' = 0.758$	0.39	2.03	1.5
	101	$S'_m = 0.103$	$S' = 0.105$	1.9	2.1	5
	$\to \infty$	$Q_m = 0.283$	$Q = 0.282$	0.47	2.02	1

on spheres of Hg and Wood's metal in lubricating oil, a value of $Q_o = 0.333$ is obtained accurately: no wide distribution of eccentricities is possible in this case. For Wood's metal, a slight deviation in Q_o is possible, but this is now explained by the above discussions.

A check on the reliability of the value of e, determined from the measurements of the d.c., can be obtained from actual shape measurements of the granules of the mixture. There is, however, an obstacle to a determination of e from a micro-photograph: the photographs give a two-dimensional picture of the granules, and two eccentricities can be attributed to one granule, because it can be assumed to be a needle ($e > 1$) or a disc ($e < 1$). Therefore, the Q-values given in Table V.V and obtained with the aid of the wide distributions of Fig. V.5, were recalculated, assuming that only two dimensions of the granules can be seen. Thus only eccentricities between $e = 0$ and $e = 1$ or between $e = 1$ and $e = \infty$ can be given. Because histograms must also be made from photographs, the mean values are given for $e = 0 - 0.1$; $0.1 - 0.2$; etc., and $1/e = 0 - 0.1$; $0.1 - 0.2$; etc. See Fig. V.6 and the results shown in Table V.VII.

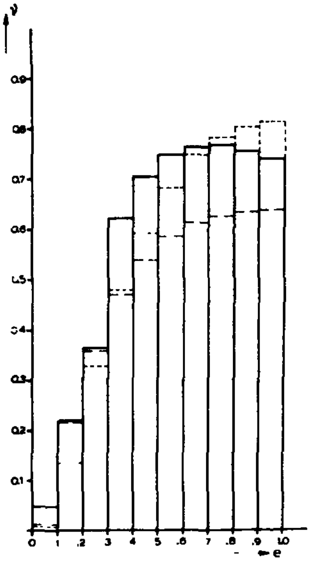

Figure V.6
Histogram $\nu = f(e)$ (ν proportional to $N/N_{tot.}$), determined from the distributions of fig. V.5, assuming that of a granule only two dimensions are known. k = 1.

———— $e_{mode} = 0.5$,
—·—·— $e_{mode} = 2$,
------ $e_{mode} = 1$.

Table V.VII
Deviations of $\bar{e}$ when e is determined from micro-photographs and only two dimensions of a granule are visible.

k = 1

e_{mode}	Q	gives $\bar{e}$	remarks
0.5	0.306	0.511	with $e < 1$
	or 0.279	2.14	assuming $e > 1$
1	0.299	0.506	assuming $e < 1$
	0.291	1.87	assuming $e > 1$
2	0.280	2.05	with $e > 1$
	or 0.291	0.5	assuming $e < 1$

Because of the two possible solutions, $e > 1$ or $e < 1$, two values for Q are obtained. Large discrepancies can thus occur for wide eccentricity distributions which extend into both the regions $e = 0 - 1$ and $e = 1 - \infty$. For a narrow distribution which is limited to only one of these two regions, the discussion of the foregoing pages remains unaltered. For wider distributions information on the third dimension is required. Another difficulty arises from the fact that on micro-photographs the granules are also seen from various angles and thus do not give an exact value for e or $1/e$. Both difficulties, however, can be handled by slightly varying the adjustment of the microscope, or, for photographs taken with an electron-microscope, by the use of shadow-casting. The author's measurements of the eccentricity as discussed in Chapter IV were checked by microscopic examination of the powders.

b. Experiments

A calculation was made on the mixtures which provided the experimental results given in Chapter IV. From two micro-photographs of the Tellurite glass powder, the eccentricity was determined (*vide* Figures V.7 and V.8). As only two dimensions were provided by the photograph, calculations were made for $e = a/b$ as well as for $e = b/a$, and S' was determined for both cases. The values obtained by this procedure are: $e = 0.57$ and $e = 1.7$. Within the accuracy of measurement, this is in agreement with the determination of e from the measurements of the d.c. as given in Chapter IV. These results suggest that $e = 1.7$.

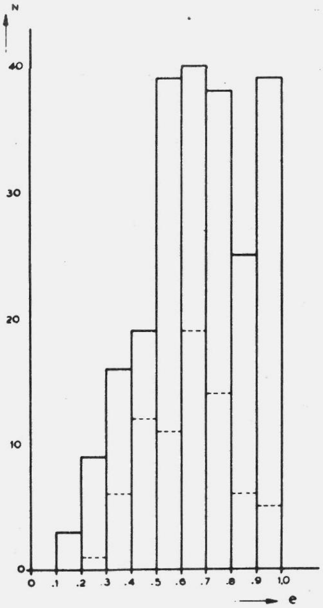

Figure V.7
Histogram $N = f(e)$ for Tellurite glass powder. Two determinations are given.

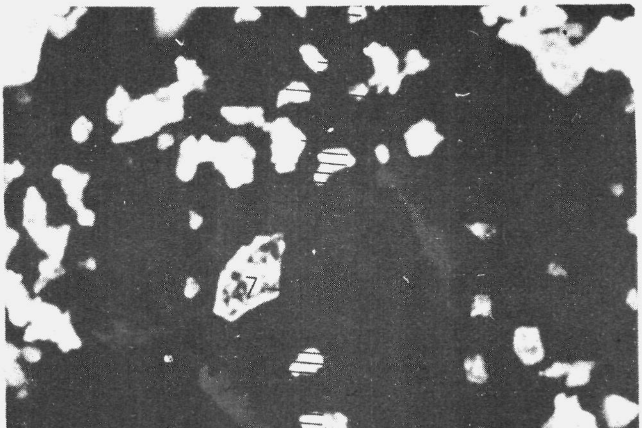

Figure V.8
Tellurite glass powder, 500 ×.

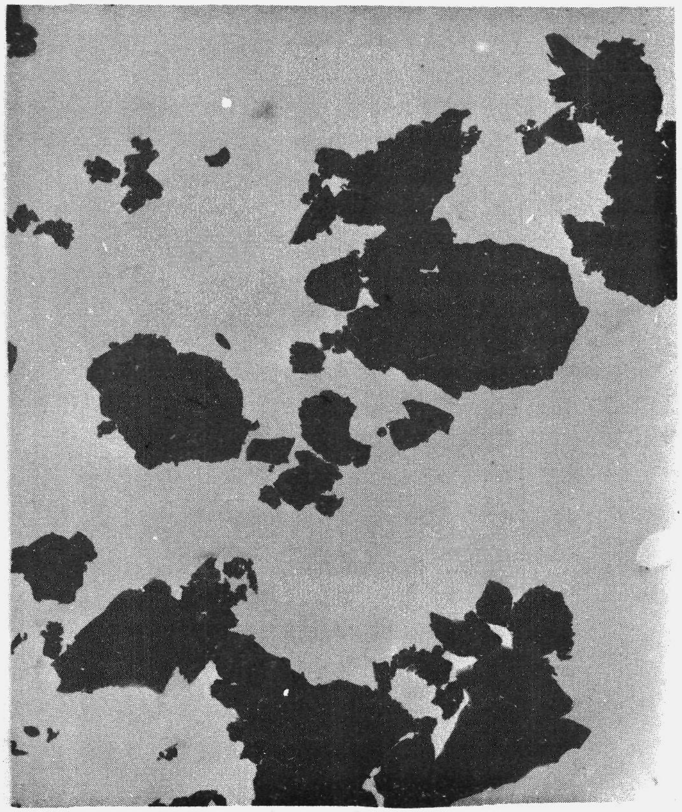

Figure V.9a *

$BaTiO_3$ powder, 10,000 ×.

The same procedure was followed for the measurements on $BaTiO_3$ powder and TiO_2 powder in p.v.c. In both these cases, the dimensions of the granules were too small for micro-photography. Therefore, two photographs of each sample were made by the Department of Electron Microscopy, T.N.O. - T.H., in Delft (*vide* Fig. V.9). For the $BaTiO_3$ powder, a distribution is found as given in Fig. V.10 resulting in the values $Q_o = 0.295$ or $e = 0.503$ and $Q_o = 0.287$ or $e = 1.96$. These values are at the limit of the boundary values obtained in Chapter IV: $e = 2.3 \pm 0.4$ and $e = 0.43 \pm 0.06$, which can be explained by one of the following considerations: 1. the distribution of eccentricities is not limited

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*) Photographs: Dpt. Electron Microscopy, Technisch Physische Dienst T.N.O. - T.H., Delft.

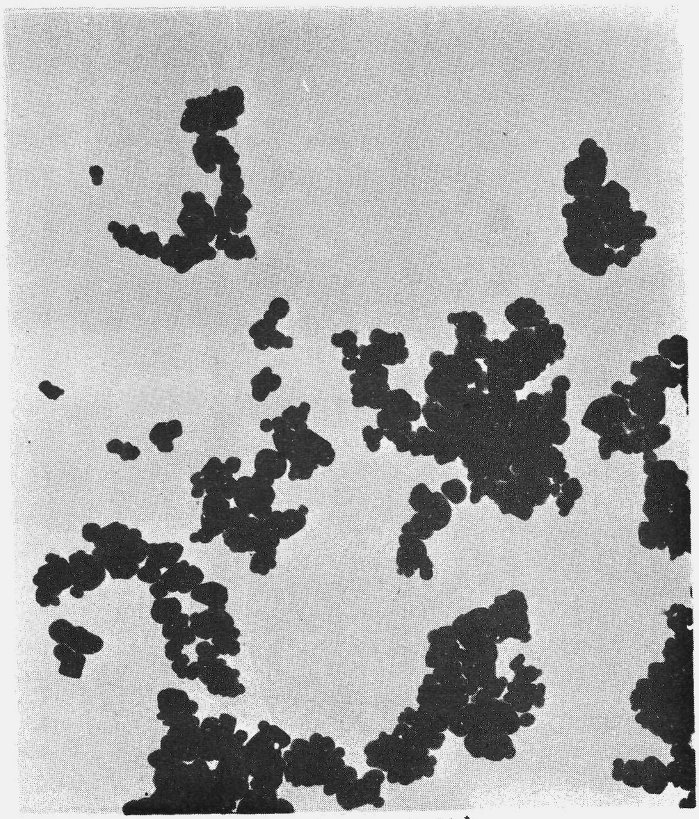

*Figure V.9b**
TiO_2 powder, 20,000 ×.

to one of the two regions, $e = 0 - 1$ or $e = 1 - \infty$, or 2.: the granules show some tendency to agglomerate, forming clusters having other eccentricities. This phenomenon of cluster formation complicated the measurements of the TiO_2 powder. The photographs also show a high degree of agglomeration for this sample, with more extreme eccentricities for the clusters than for the granules. The eccentricities of the granules found from the photographs are limited for this case to between $e = 0.6$ and 0.9, while the values given by the measurements of Chapter IV give: $e = 0.31$ or $e = 3.3$. This can now be explained by cluster formation. This clotting was also visible in the specimens used for the determination of the d.c. ϵ_m as a function of v_i.

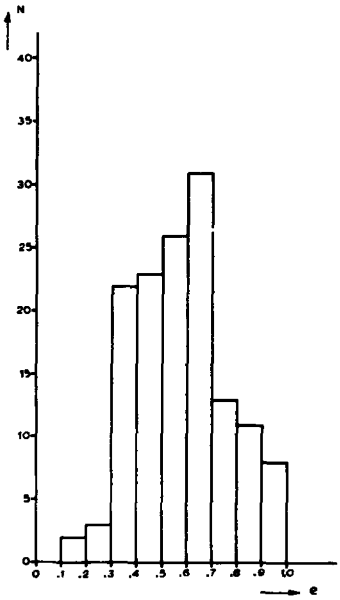

Figure V.10
Histogram $N = f(e)$ for $BaTiO_3$ powder as determined from two electron-microscope photographs.

§ 3. *Discussion*

The foregoing treatment shows that the shape factor δ_{eff}, as introduced in this work, is satisfactorily related to the actual shape of the granules. It furthermore demonstrates that δ_{eff} and Q are determined by the *form* of the granules *only*, in contradistinction to the „Formzahl”, u, as introduced by Wiener $^{16)}$.

In ϵ^*, therefore, such remaining influences as the influence of order and interaction of the granules are accounted for. ϵ^* as a function of v_i can be determined from physical measurements. In a recent article, Pearce $^{17)}$ gives the results of his measurements on a model of a mixture. He finds the Maxwell formula (III.2) to be valid for a regular arrangement of the granules; for irregular arrangements it is not applicable because higher d.c.'s are found. Pearce used spherical granules in his experiments: thus the change in d. c. cannot be ascribed to the form of the granules because the formulae used are based on spherical granules. The Maxwell formula (III.2) thus holds for the case for which it was derived. In the literature, however, this formula is often applied to irregular arrangements and non-spherical granules: it is therefore not remarkable that it does not hold for these cases. It is clear that the observed changes in d.c. tend to values predicted by the Böttcher formula (112.1). This suggests that ϵ^* is probably also a measure of the order in the arrangement of the granules. For non-spherical granules, however, the form of the granules may also have influence on ϵ^*, as, for mixtures of non-spherical conducting granules, the low values of q in the relation (114.1) suggest.

Chapter VI

Discussion and conclusions: Chapters I – V

From the material in the foregoing chapters it can be concluded that no solution has yet been found for the problem put forward. No "mixture law" proposed up to the present gives an accurate description of the dielectric behaviour of a heterogeneous mixture, and for each individual case it is still necessary to determine the particular parameters. Nevertheless, the investigation of heterogeneous mixtures is extremely useful, giving a better insight into their dielectric behaviour and the several properties governing such behaviour. This research may also be of value to a better understanding of continuous dielectric media, because the formulae used to describe their behaviour are based on a picture (*i.e.* molecules are seen as particles with a d.c. ϵ_i, *vide* Chapter I) which is better approximated by a heterogeneous mixture than by a continuous medium.

The limits between which the unknown ϵ_m lies can be determined. As already mentioned, in all the available experimental results ϵ^* lies between ϵ_o and ϵ_m. Furthermore, the form of the granules proved to be of great importance. It has been shown [7] that the highest values for the d.c. of a mixture are found (when $\frac{\epsilon_i}{\epsilon_o} > 1$) for disc-shaped granules, and that the lowest values of ϵ_m are found with mixtures containing spherical granules. Thus two general boundaries can be given for both cases, $\epsilon_i/\epsilon_o > 1$ and $\epsilon_i/\epsilon_o < 1$:

a. $\epsilon_i/\epsilon_o > 1$; as upper limit, the Polder and van Santen equation [7] (eq. (I5.11), with $\epsilon^* = \epsilon_m$) for disc-shaped granules ($A_j = 0; 0; 1$), and for the lower limit, relation (I5.11) for spherical granules with $\epsilon^* = \epsilon_o$. Since no values for ϵ_m were found smaller than those predicted by equation (II1.2), this relation can also be used as the lower boundary.

b. For the case of $\epsilon_i/\epsilon_o < 1$, the reverse is true.

When the shape of the granules is known, the boundaries can be brought still closer together by using (I5.11) with $\epsilon^* = \epsilon_m$ and $\epsilon^* = \epsilon_o$.

In the literature, formulae (II5.2) and (II5.3) are often used as boundaries. These two boundaries are much further apart than those just given, and are useful in relation to special structures where a description accorring to Fig. II.1 is possible. For the case we are investigating, *i.e.* mixtures consisting of granules homogeneously dispersed in a continuum, the boundaries just described are preferable.

Some calculations were made on this basis. For $\frac{\epsilon_i}{\epsilon_o} = 2$ for the whole volume-filling factor range, $\frac{\epsilon_m}{\epsilon_o}$ can be determined within 1.8% (± 0.9%). When the form of the granules is known, this accuracy is even better: within 1% (± 0.5%). For $\frac{\epsilon_i}{\epsilon_o} = 3$, the maximum deviation in $\frac{\epsilon_m}{\epsilon_o}$ possible up to $v_i = 30\%$ is 6% (± 3%) and for granules of known shape: 2% (± 1%). For lower values of v_i, the accuracy rapidly improves for both cases. This clearly demonstrates that for values of $\frac{\epsilon_i}{\epsilon_o}$ near one, any choice between the several relations becomes practically impossible, because here any relation lying between the two boundaries will give acceptable results. The determination of δ_{eff} also becomes very difficult for this case, because all the possible values for ϵ_m lie very near each other for all possible shapes. Moreover, the curves of S' and $T' = f(e)$ become very flat. The determination again becomes possible at $\frac{\epsilon_i}{\epsilon_o} = 3$ if highly accurate techniques are used for making the measurements. A good example is given by the measurements of van Vessem [33] on NH_4Cl powder in carbontetrachloride-benzene (Ch. IV § 1a) in which $\frac{\epsilon_i}{\epsilon_o} = 3.06$ and where δ could be determined as shown in Chapter IV. This value is the boundary provided by the precision of van Vessem's measurements (0.2%). For KCl powder in CCl_4-CBr_4 ($\frac{\epsilon_i}{\epsilon_o} = 1.97$) accurate determination of δ was no longer possible. The same applies to the measurements of W. A. Cumming [52] on snow, where, for $\frac{\epsilon_i}{\epsilon_o} = 3.15$, the experimental error was much higher. Consequently the Böttcher equation can be used satisfactorily.

The influence of the shape is especially clear in the two extreme cases of conducting granules (and $\epsilon_i/\epsilon_o \gg 1$) and $\epsilon_i/\epsilon_o \rightarrow 0$

(*vide* Fig. IV.4). The formulae for these two cases can be written, in first approximation, as

$$\epsilon_m/\epsilon_o = 1 + S\,v_i \qquad (\epsilon_i/\epsilon_o \gg 1)$$

$$\epsilon_m/\epsilon_o = 1 - T\,v_i \qquad (\epsilon_i/\epsilon_o \ll 1)$$

thus indicating that the angle of intersection of the curves $\epsilon_m/\epsilon_o = f(v_i)$ with the $\frac{\epsilon_m}{\epsilon_o}$-axis is a direct measure of the form of the granules. In this first approximation, the influence of the interaction of the granules (accounted for in ϵ^*) vanishes, thus showing it to be a second order effect here. So for $\frac{\epsilon_i}{\epsilon_o} \gg 1$, the value of ϵ_m/ϵ_o for mixtures with spherical granules can be determined within 1% up to v_i = 4%. For $\frac{\epsilon_i}{\epsilon_o} \ll 1$, this is possible up to v_i = 7%. However, when the form of the granules is not known, an accurate determination of $\frac{\epsilon_m}{\epsilon_o}$ becomes impossible even for the lowest v_i.

Because, according to the Bruggeman-Niesel relations (113.4) and (113.6), the d.c. lies between the values obtained with the equations of Polder and van Santen and of Maxwell-Fricke (*vide* Chapter II), which can be used as upper and lower boundary for the d.c. ϵ_m, these Bruggeman-Niesel equations often give a better approximation for these extreme cases than the other equations just mentioned.

Another feature stressed in Chapter IV was the observation of a change in the behaviour of a heterogeneous mixture when v_i was about 20%. One reason for this may be found in an increased mutual interaction, combined with the influence of higher order effects, which is only taken into account in the calculations of Chapter I by the introduction of ϵ^*. Another reason is that the granules begin to touch each other, so that clusters and chains are formed, thus destroying the randomness of the granular distribution [53]. This effect is also indicated by the microwave measurements made in our laboratory on mixtures containing carbon powder and carbonyl-iron powder, where a sudden increase in the losses is observed around v_i = 20%. The space around the granules can then no longer be considered as homogeneous, but begins to show a discrete structure due to the approach of the neighbouring granules.

When, with a higher volume-filling factor, v_i, the granules come closer and closer together, this contact may become still more intimate, in such a way that the granules themselves begin to form a semi-continuum and that the original continuum acquires a new constitution which is no longer continuous. This latter phenomenon probably begins to occur at a v_i around 50%. Thus, coming from low values of v_i and still considering the granules as discrete entities we have, with (15.11):

$$(\epsilon_m - \epsilon_o) = v_i \ (\epsilon_i - \epsilon_o) \ S' \ .$$

At higher values of v_i, and considering the granules now as a semi-continuum and the original continuum as becoming granular, we can write:

$$(\epsilon_m - \epsilon_i) = v_o \ (\epsilon_o - \epsilon_i) \ S''$$

where the S' refers to the granules and S'' to the interstitial medium. For this region of v_i, where both equations are valid

$$\epsilon_i + v_o \ (\epsilon_o - \epsilon_i) \ S'' = \epsilon_o + v_i \ (\epsilon_i - \epsilon_o) \ S'$$

finally resulting in

$$(1 - v_i) \ S'' + v_i \ S' = 1 \ .$$

It will be difficult, however, to find a connection between S' and S'' because they are "complementary". If the granules are ellipsoids, the case for which the formulae were derived, the now granular intersticial "continuum" cannot be. But we have introduced an effective shape factor δ_{eff} (which Chapter V demonstrated to agree well with the experimental results), and then considered the granules as if they were ellipsoidal. Therefore, for the case described here at about v_i = 50% the granules and the now granular continuum become equivalent in our description of δ_{eff}. So it is not so remarkable that, even apart from the problems encountered in describing interaction at the higher volume-filling factors, great difficulties occur.

As already remarked by Poley [54)] and confirmed by the discussions given in this thesis, mixtures of a material X in a continuum Y, and of Y in X, do not have the same dielectric behaviour. For the values of v_i discussed here, it is not always possible to distinguish in dispersions of X in Y and Y in X which is the material and which the continuum. At lower concentrations of either X or Y two regions can be distinguished: below and above v_i = 20%.

In the literature, the formulae for spheres are often used, and with reasonable success for the region around v_i = 50% [25][33]. As the curves of $\delta = f(v_i)$ needed for the determination of δ_{eff} show, for $\epsilon^* = \epsilon_m$ there is always a region of v_i where δ is about 0.33 (*vide* Fig. III.1), thus demonstrating that in that region the Böttcher formula can be used effectively. The fact that this formula apparently agrees well with the experimental results is thus purely accidental for such a case and has no real meaning.

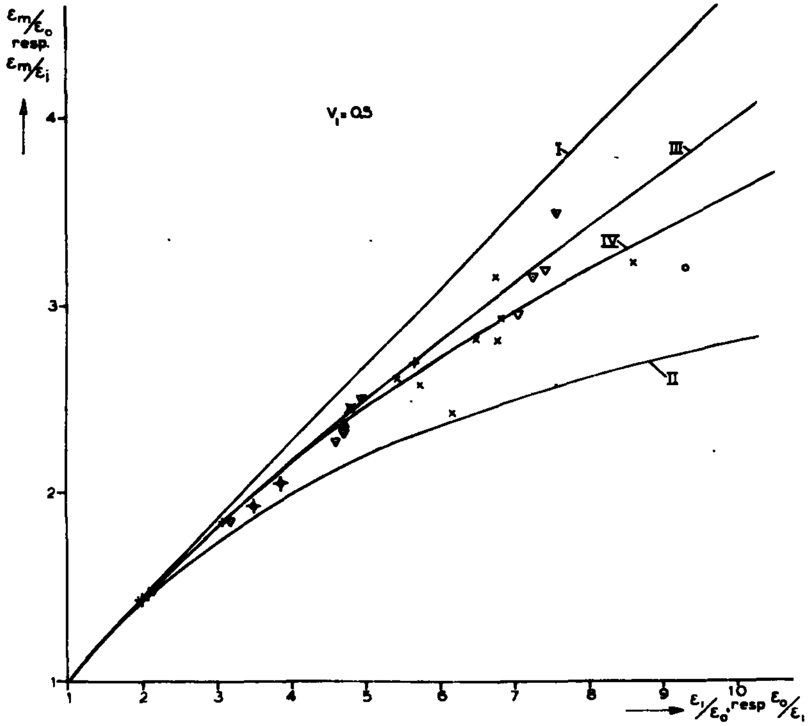

Figure VI.1

$\epsilon_m/\epsilon_o = f(\epsilon_i/\epsilon_o)$ (when $\epsilon_i/\epsilon_o > 1$), respectively $\epsilon_m/\epsilon_i = f(\epsilon_o/\epsilon_i)$ (when $\epsilon_i/\epsilon_o < 1$) for $v_i = 0.5$. I and II: boundaries, III: equation (112.1) (Böttcher), IV: equation (115.4) (Kamiyoshi). Experimental results: + van Vessem [33], × Kamiyoshi [25], ○ author, △ Guillien [29], ⊕ Scott and McPherson [71], ▽ Reynolds [27][41].

All the measurements available for this region (v_i = 50%) were compiled and plotted in Fig. VI.1. In this graph, ϵ_m/ϵ_o is given as a function of ϵ_i/ϵ_o, and for $\epsilon_i/\epsilon_o < 1$, ϵ_m/ϵ_i is given as a function of ϵ_o/ϵ_i. The limiting values are also given in Curves I and II, according to the foregoing derivations. According to the treatment just given, both cases, *i.e.* of a material X dispersed in Y and a material Y dispersed in X, have to be taken into account in determining the boundaries. It can be shown that the upper limit of ϵ_m/ϵ_o when $\epsilon_i/\epsilon_o > 1$ and the upper limit of ϵ_m/ϵ_i for the case $\epsilon_i/\epsilon_o < 1$ coincide for $v_i = 50\%$. The same applies for the lower boundary. In Fig. VI.1 material X in Y ($\epsilon_i/\epsilon_o > 1$, with $\epsilon_m/\epsilon_o = f(\epsilon_i/\epsilon_o)$) and the material Y in X ($\epsilon_i/\epsilon_o < 1$, with $\epsilon_m/\epsilon_i = f(\epsilon_o/\epsilon_i)$) are plotted. The values according to Böttcher's equation (II2.1) are inserted [19] (Curve III) as well as those according to the formula of Kamiyoshi [25] (II5.4) (Curve IV). As can be seen, the measuring results are scattered between the limiting curves, indicating no preference for a particular formula.

The value of the constant k of equation (II5.5), proposed by Pearce [26], was determined for the same measurements as those given in Fig. VI.1, and plotted in Fig. VI.2 as a function of ϵ_i/ϵ_o, giving a graph analogous to that given by Pearce (Fig. 4 of ref. 26). In Fig. VI.2, the values of k for the two boundaries mentioned above are also shown. The results are scattered between these two boundaries. It can be seen that only a part of the $(\epsilon_i/\epsilon_o; k)$-plane is of value, and the eventual good agreement with one particular relation has no real meaning, but can be ascribed to the relatively small variations in k possible. The data given in Figures VI.1 and VI.2 are summarized in Table VI.I.

Van Vessem [33] demonstrated and measured the influence of the size of the granules. He used the formulae for spherical granules almost exclusively in his thesis. In his work on the size effect, the influence of shape is not eliminated beforehand. It therefore becomes very difficult to compare the measurements he made in two measuring cells of different dimensions, and to draw definite conclusions from his measurements in general. The types of granules he used were taken from different batches, and if, as is probable, the granules in the specimens had different shapes, a variation in the measured ϵ_m could be expected. The influence of the size effect is thus not conclusively demonstrated by these measurements.

Table VI.I

$v_i = 0.5$

System (Powder in ....)	$\frac{\epsilon_i}{\epsilon_o}$	ϵ_m ϵ_o	k
A.H.Scott and A.T.McPherson 71):			
$CaCO_3$ in rubber	3.47	1.93	0.40
$CaCO_3$ in vistanex	3.82	2.05	0.40^5
Kan-Ichi Kamiyoshi 25) **):			
KI in air	5.4	2.60	0.43
NaCl in air	5.68	2.57	0.49^5
$K_2Al_2(SO_4)_4 : 24H_2O$ in air	6.1^5	2.42	0.62
CaF_2 in air	6.76	2.80	0.54^5
NH_4Cl in air	6.8	2.94	0.50
$FeSO_4.7H_2O$ in air	6.74 *)	3.15	0.40
$CuSO_4.5H_2O$ in air	6.46 *)	2.81	0.50
J.C.van Vessem 33):			
NaCl in air	5.62	2.686	0.425
NH_4Cl in CCl_4-CBr_4	3.06^2	1.849	0.300
KCl in CCl_4-CBr_4	1.97^3	1.433	0.198
J.A.Reynolds 27)41):			
glass spheres in air	4.594	2.272	0.452
glass rods in CCl_4	3.157	1.854	0.345
glass rods in air	7.034	2.944	0.525
glass lamellae in air	7.248	3.157	0.473
glass powder in CCl_4	2.102	1.489	0.202
glass powder in air	4.683	2.325	0.438
R.Guillien 29)26):			
KCl in vacuum	4.57	2.36	0.35
$PbCl_2$ in vacuum	28		0.73
	ϵ_o/ϵ_i	ϵ_m/ϵ_i	k
J.A.Reynolds 27)41):			
glass spheres in $C_6H_5NO_2$	7.551	3.481	-0.641
glass rods in $C_6H_5NO_2$	4.932	2.502	-0.617
glass powder in $C_6H_5NO_2$	7.408	3.182	-0.934

*) As determined by Cheng 55).

**) In the determination of ϵ_i from the values given by Kamiyoshi, also the measuring results of other authors are taken into account as those given by van Vessem 33) and Cheng 55).

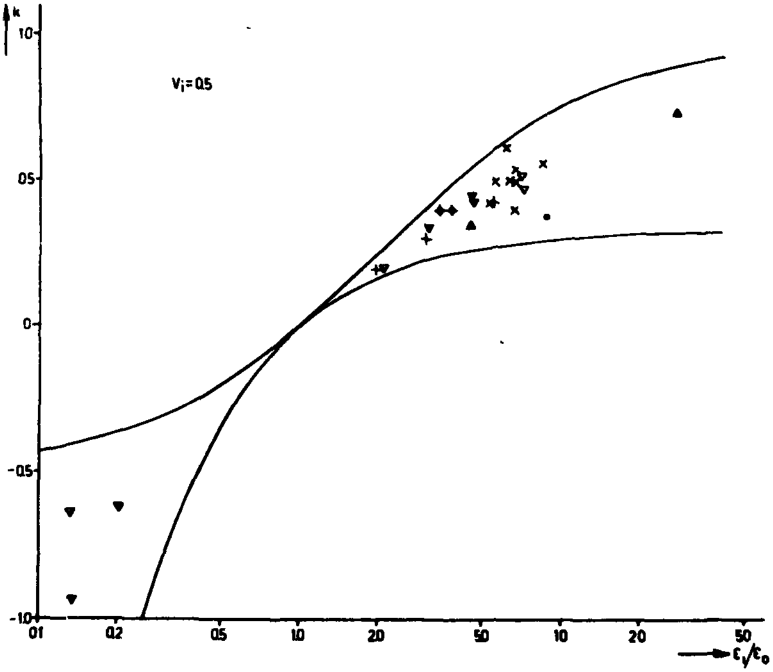

Figure VI. 2
Pearce's "empirical factor" *k* as a function of ϵ_i/ϵ_o [26]) with boundary values and the same experimental results as given in Fig. VI. 1.

Conclusions

We can now summarize the conclusions as follows:

1. No mixture relation yet proposed gives an accurate description of the dielectric behaviour of a heterogeneous mixture over a reasonable range of v_i.
2. Boundaries can only be given for the value of the d.c., ϵ_m, of such a mixture when the properties of the material of the granules and the material of the continuum are known.
3. When $\frac{1}{2} < \epsilon_i/\epsilon_o < 2$, these boundaries are so close together that a fairly accurate determination of ϵ_m becomes possible and most of the relations given in Chapter II can be used with reasonable success.
4. The shape factor δ_{eff} is satisfactorily related to the actual shape of the granules.

5. With certain restrictions, given in Chapter V, this shape factor δ_{eff} can be determined from micro-photographs.
6. The relations derived for spherical granules can only be used for non-spherical granules (contrary to general practice) when $\frac{1}{2} < \epsilon_i/\epsilon_o < 2$, and for other values of ϵ_i/ϵ_o for eccentricities of $e = 1 \pm 20\%$.
7. The d. c. ϵ^* of the immediate surroundings of an average granule lies between ϵ_o and ϵ_m.

For the extreme cases of conducting granules (with the case of $\epsilon_i/\epsilon_o >> 1$) and the case of $\epsilon_i/\epsilon_o \rightarrow 0$ the following additional conclusions apply:

1a. The d. c. of such mixtures is very sensitive to variations in the shape of the granules, their interaction, accounted for in ϵ^*, being a second order effect.
2a. For the first case ($\epsilon_i/\epsilon_o >> 1$) the approximation

$$\frac{\epsilon^*}{\epsilon_o} = \frac{1}{1 - q\ v_i}$$

gives good agreement up to $v_i = 20\%$.
3a. Because, according to the relations of Bruggeman and Niesel ((II3.4) and (II3.6)), the d. c. lies between the values obtained with the formulae of Polder and van Santen and of Maxwell, which can be used as upper and lower boundary for the d. c., these Bruggeman-Niesel equations give a better approximation for some cases than the other two.

Chapter VII

Relaxation phenomena

It is of interest to know how a heterogeneous mixture will behave when one of its constituents shows relaxation. When, for example, a polar liquid is contaminated by a granular impurety of a non-polar material, it is important to know to what extent the relaxation curve is altered and whether the relaxation time is eventually affected. Furthermore, when shifts are observed in a mixture, we want to know whether we are justified in concluding that phenomena occur other than those which can be explained by the normal behaviour of mixtures. An example of such a case is the occurrence of bound and free water in wool-water systems 56), investigated by J. J. Windle and T. M. Shaw.

When the granules of the mixture are small with respect to the wavelength of the electric field (*vide* Ch. I), quasi-static considerations can still be applied, and, for a calculation of the complex d.c. of a mixture, the respective complex d.c.'s have to be introduced in the various mixture relations 16)57). Two cases can be distinguished:

1. the material of the granules is polar ($\epsilon_i = \epsilon'_i - j\,\epsilon''_i$).
2. the material of the continuum is polar ($\epsilon_o = \epsilon'_o - j\,\epsilon''_o$).

For convenience in calculating, the curves $\epsilon'_i = f(\epsilon''_i)$, and $\epsilon'_o = f(\epsilon''_o)$, are assumed to be semicircles. This assumption is reasonable, as shown by K. S. Cole and R. H. Cole 58) and shown by later measurements 59)-66). At the same time, it was demonstrated by these authors that it is often possible to use a description of only part of a circular arc. Since we shall deal here with transformations from the $\epsilon'_i\epsilon''_i$-plane or the $\epsilon'_o\epsilon''_o$-plane to the $\epsilon'_m\epsilon''_m$-plane, when either of the two curves $\epsilon'_i = f(\epsilon''_i)$ and $\epsilon'_o = f(\epsilon''_o)$ are smaller parts of a circular arc, an equivalent part of the curve $\epsilon'_m = f(\epsilon''_m)$ can be used.

The following calculations for the several mixture relations were made using either the curve $\epsilon'_i = f(\epsilon''_i)$ or $\epsilon'_o = f(\epsilon''_o)$ each curve being a semicircle with ϵ_{is} (or ϵ_{os}) = 10, $\epsilon_{i\infty}$ (or $\epsilon_{o\infty}$) = 2 and ϵ_{is} = 100 and $\epsilon_{i\infty}$ = 5. This procedure gives a good impression of the behaviour of the various mixture relations when relaxation phenomena occur. It must be stressed here that the relaxation phenomena discussed in this chapter are typical high frequency phenomena (orientation dispersion) and must be distinguished from the low-frequency type of dispersion (moving of actual charges) such as the Maxwell-Wagner relaxation (*vide* also Ch. I). Calculations were made up to $v_i = 30\%$ for all cases, and the following results were obtained.

§ 1. $\epsilon_{is}/\epsilon_o > 1$, *the material of the granules is polar*

Thus, $\epsilon_i = \epsilon_i' - j\,\epsilon_i''$. We put $\epsilon_o = 1$. This means that the d.c. of the mixture ϵ_m ($= \epsilon_m' - j\,\epsilon_m''$) is given relative to the d.c. of the continuous phase.

a. The Maxwell-Lewin mixture relation (III.2)

Equation (III.2) can also be written as

$$\epsilon_m = 1 + 3\,v_i\,\frac{\epsilon_i - 1}{\epsilon_i\,(1 - v_i) + (2 + v_i)}\,. \qquad \text{(VIII.1)}$$

This is a conformal transformation from the $\epsilon_i'\epsilon_i''$-plane to the $\epsilon_m'\epsilon_m''$-plane. The function $\epsilon_m' = f(\epsilon_m'')$ has a semicircular locus. Thus, for ϵ_m' and ϵ_m''

$$\epsilon_m' = \epsilon_{m\infty} + \frac{\epsilon_{ms} - \epsilon_{m\infty}}{1 + \omega^2\,\tau_m^2} \qquad \text{(VIII.2)}$$

$$\epsilon_m'' = \frac{\epsilon_{ms} - \epsilon_{m\infty}}{1 + \omega^2\,\tau_m^2}\,\omega\,\tau_m \qquad \text{(VIII.3)}$$

where

$$\tau_m = \frac{\epsilon_{i\infty}(1 - v_i) + (2 + v_i)}{\epsilon_{is}(1 - v_i) + (2 + v_i)}\,\tau_i \quad {}^{*)}. \qquad \text{(VIII.4)}$$

Equation (VIII.4) shows that the relaxation time, τ_m, of the mixture is strongly shifted with regard to the relaxation time, τ_i, of the material of the granules. This shifting takes place towards lower values, thus $\tau_m < \tau_i$. In fig. VII.1 the function $\epsilon_m' = f(\epsilon_m'')$ is given for the case in which the function $\epsilon_i' = f(\epsilon_i'')$ is a semicircle with $\epsilon_{is} = 10$ and $\epsilon_{i\infty} = 2$ for four values of v_i.

b. The relation (I5.11)

A complete calculation for this case after the substitution $\epsilon^* = \epsilon_m$ or $\epsilon^* = \epsilon_o$ is very difficult. This relation was therefore studied only for several special cases:

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*) Böttcher (ref. 1), treating this case, gives an approximate formula (10.101) for low value of v_i. The exact formula is given here for mixtures containing granules. This formula is also used in the discussion of liquid data on basis of the Debye model.

I. for spherical granules ($A_j = \frac{1}{3}; \frac{1}{3}; \frac{1}{3}$)
II. for disc-shaped granules ($A_j = 0; 0; 1$) and
III. for needleshaped granules ($A_j = \frac{1}{2}; \frac{1}{2}; 0$).

I. Spherical granules

α. $\epsilon^* = \epsilon_m$. This gives Böttcher's equation (ii2.1), which can now be written as:

$$\epsilon_m = \frac{1}{4}\left[\{\epsilon_i(3\,v_i - 1) + \epsilon_o(2 - 3\,v_i)\} + \right.$$
$$\left. + \sqrt{\{\epsilon_i(3\,v_i - 1) + \epsilon_o(2 - 3\,v_i)\}^2 + 8\epsilon_i\epsilon_o}\,\right] \qquad \text{(vii1.5)}$$

This function was evaluated numerically. Curves are found depressed below a semicircular locus. In Fig. VII.2 an example is given for the case in which $\epsilon_{is} = 10$ and $\epsilon_{i\infty} = 2$ and in Fig. VII.3 for the case $\epsilon_{is} = 100$ and $\epsilon_{i\infty} = 5$. The depression becomes larger for higher values of $\epsilon_{is} - \epsilon_{i\infty}$. At ϵ_{ms} and $\epsilon_{m\infty}$, the curve intersects with the ϵ'_m-axis at 90°. Here again, the relaxation time of the mixture, τ_m, shifts to lower values, though this shift is less pronounced than for the Maxwell-Lewin relation discussed above (vii1.4).

Because of the occurrence of this depression, the relaxation behaviour of the mixture can be described macroscopically by a distribution of relaxation times, although only one relaxation time is involved in τ_i. This macroscopic description, then, requires a different distribution of relaxation times than given by Cole and Cole [67)68)]. The relaxation time connected to the material of the granules will be called the intrinsic relaxation time, in analogy with the definition given by Böttcher *) for the molecular case.

β. $\epsilon^* = \epsilon_o$. Equation (i5.11) becomes:

$$\epsilon_m = \epsilon_o + v_i(\epsilon_i - \epsilon_o)\,\frac{3\,\epsilon_o}{2\,\epsilon_o + \epsilon_i}\,. \qquad \text{(vii1.6)}$$

It can immediately be seen that for this case, also, the curve $\epsilon'_i = f(\epsilon''_i)$ transforms to a semicircular locus in the $\epsilon'_m\epsilon''_m$-plane. Therefore equations (vii1.2) and (vii1.3) apply here too, now with:

$$\tau_m = \frac{\epsilon_{i\infty} + 2}{\epsilon_{is} + 2}\,\tau_i\,. \qquad \text{(vii1.7)}$$

Again τ_m shifts to lower values.

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*) ref. 1, page 355.

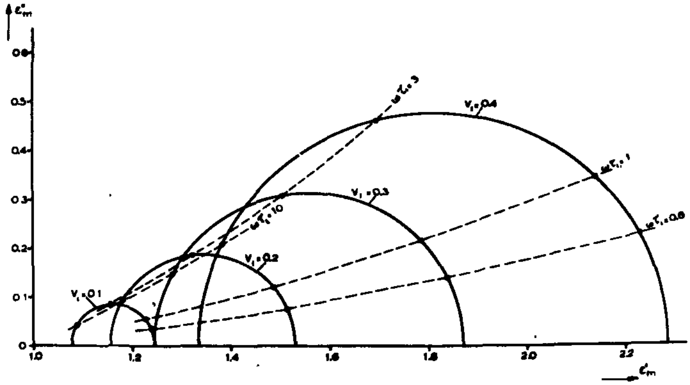

Figure VII.1
$\epsilon'_m = f(\epsilon''_m)$ according to the equation (III1.2) (Maxwell, Lewin), with $\epsilon'_i = f(\epsilon''_i)$ being a semicircular locus with $\epsilon_{is} = 10$ and $\epsilon_{i\infty} = 2$.

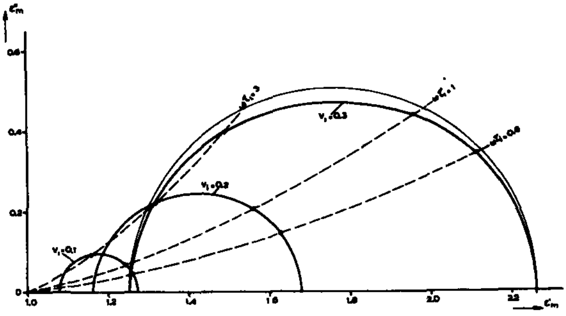

Figure VII.2
$\epsilon'_m = f(\epsilon''_m)$ according to Böttcher's equation (II2.1), with $\epsilon'_i = f(\epsilon''_i)$ being a semicircular locus with $\epsilon_{is} = 10$ and $\epsilon_{i\infty} = 2$.

II. Disc-shaped granules

Formula (I5.11) can be written

$$\epsilon_m = \epsilon_o + v_i \; (\epsilon_i - \epsilon_o) \; \frac{1}{3} \; (2 + \frac{\epsilon^*}{\epsilon_i}) \; . \qquad \text{(VII1.8)}$$

α. $\epsilon^* = \epsilon_m$

Here numerical evaluation is necessary. The curves obtained are only slightly depressed below a semicircular locus. The curves tend to the semicircle, and this tendency becomes stronger for higher values of $\epsilon_{is} - \epsilon_{i\infty}$. An example is given in Figures VII.4 and VII.5. The shifts of τ_m with regard to τ_i are small and always towards lower values.

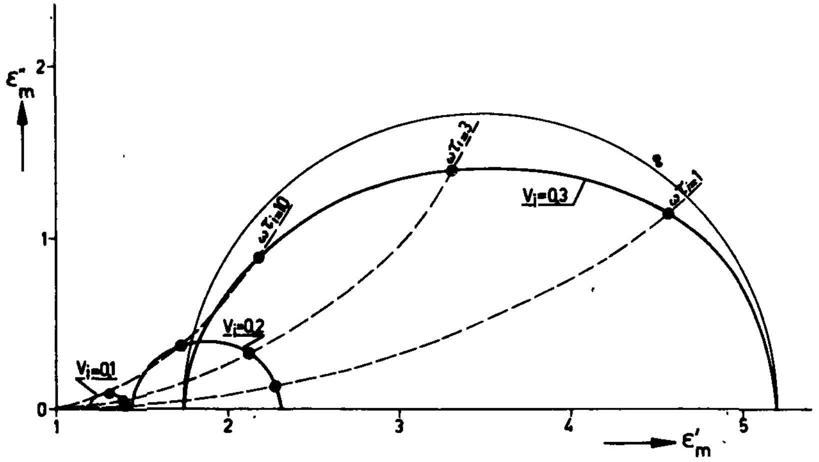

Figure VII.3
$\epsilon'_m = f(\epsilon''_m)$ according to Böttcher's equation (II2.1), with $\epsilon'_i = f(\epsilon''_i)$ being a semicircular locus with $\epsilon_{is} = 100$ and $\epsilon_{i\infty} = 5$.

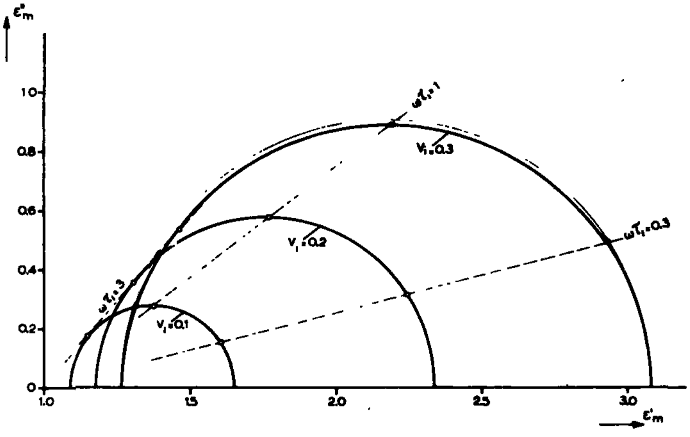

Figure VII.4
$\epsilon'_m = f(\epsilon''_m)$ for disc-shaped granules (A_j = 0;0;1), according to the equation of Polder and van Santen (eq. (I5.11) with $\epsilon^* = \epsilon_m$) with $\epsilon'_i = f(\epsilon''_i)$ being a semicircular locus with $\epsilon_{is} = 10$ and $\epsilon_{i\infty} = 2$.

β. $\epsilon^* = \epsilon_0$

The discussion given under IIα applies equally here.

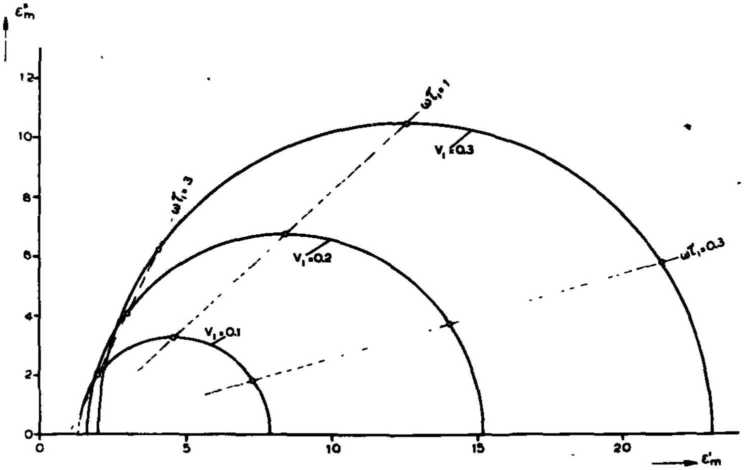

Figure VII.5
$\epsilon'_m = f(\epsilon''_m)$ for disc-shaped granules (A_j = 0;0;1), according to the equation of Polder and van Santen (eq. (I5.11) with $\epsilon^* = \epsilon_m$) with $\epsilon'_i = f(\epsilon''_i)$ being a semicircular locus with $\epsilon_{is} = 100$ and $\epsilon_{i\infty} = 5$.

III. Needle-shaped granules

Here formula (I5.11) becomes

$$\epsilon_m - \epsilon_o = v_i\ (\epsilon_i - \epsilon_o)\ \frac{1}{3}\ \frac{5\ \epsilon^* + \epsilon_i}{\epsilon^* + \epsilon_i}\ . \qquad \text{(VII1.9)}$$

α. $\epsilon^* = \epsilon_m$

Just as for the case of disc-shaped granules, the curves $\epsilon'_m = f(\epsilon''_m)$ show a tendency to approach a semicircular locus, especially for higher values of $\epsilon_{is} - \epsilon_{i\infty}$. This tendency, however, is much smaller than for disc-shaped granules. As an example, in Fig. VII.6 the curve $\epsilon'_m = f(\epsilon''_m)$ is given for v_i = 30%, the function $\epsilon'_i = f(\epsilon''_i)$ being a semicircle with $\epsilon_{is} = 10$ and $\epsilon_{i\infty} = 2$. A slight shift of τ_m is observed towards lower values.

β. $\epsilon^* = \epsilon_o$

Here the same facts apply as in the case discussed under IIIα.

§ 2. $\epsilon_i/\epsilon_{os} < 1$, *the material of the continuum is polar*

Thus, $\epsilon_o = \epsilon'_o - j\ \epsilon''_o$. To simplify calculation, ϵ_i is put equal to 1 (holes in continuous substance). So ϵ_m ($= \epsilon'_m - j\ \epsilon''_m$) is given relative to the d.c. of the granular material.

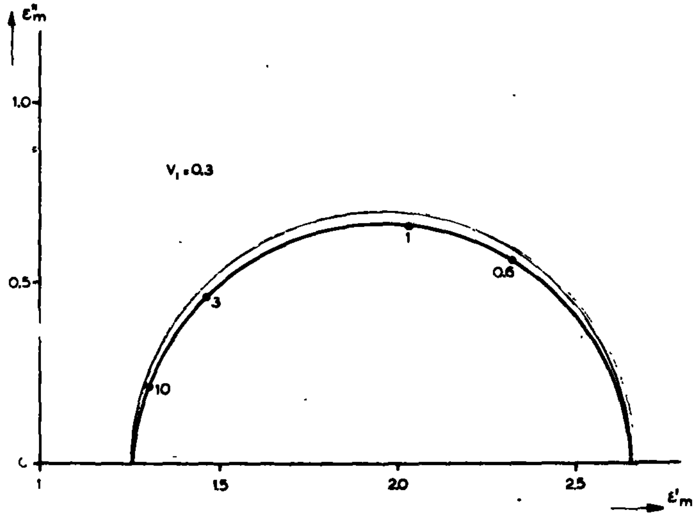

Figure VII. 6
$\epsilon'_m = f(\epsilon''_m)$ for needle-shaped granules ($A_j = ½; ½; 0$), according to the equation of Polder and van Santen (eq. (I5.11) with $\epsilon^* = \epsilon_m$) with $\epsilon'_i = f(\epsilon''_i)$ being a semicircular locus with $\epsilon_{is} = 10$ and $\epsilon_{i\infty} = 2$, for $v_i = 0.3$.

a. The Maxwell-Lewin relation (II1.2)

Equation (II1.2) can also be written:

$$\epsilon_m = \epsilon_o \frac{2\,\epsilon_o(1 - v_i) + (1 + 2v_i)}{\epsilon_o(v_i + 2) + (1 - v_i)} \;. \qquad (VII2.1)$$

For this case an approximate semicircular locus is found for the function $\epsilon'_m = f(\epsilon''_m)$. This means that here equations (VII1.2) and (VII1.3) also apply. However, for this case only a very slight shift of τ_m is observed (again towards lower values), an effect which diminishes for higher values of $\epsilon_{is} - \epsilon_{i\infty}$. *Vide* Fig. VII.7.

b. The relation (I5.11)

The same cases as those mentioned in § 1b were investigated.

I. Spherical granules

α. $\epsilon^* = \epsilon_m$ (Böttcher equation (II2.1))

Again a numerical calculation was necessary, with the aid of formula (VII1.5). A practically semicircular locus is found for $\epsilon'_m = f(\epsilon''_m)$. For lower values of $\epsilon_{is} - \epsilon_{i\infty}$, a small depression of

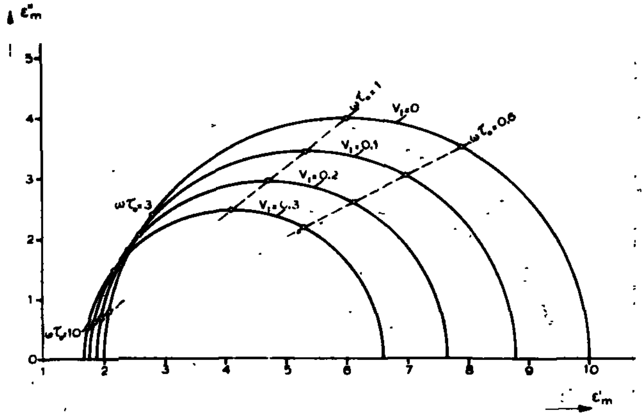

Figure VII.7
$\epsilon'_m = f(\epsilon''_m)$ according to the equation (II1.2) (Maxwell-Lewin) with $\epsilon'_o = f(\epsilon''_o)$ being a semicircular locus with $\epsilon_{os} = 10$ and $\epsilon_{o\infty} = 2$.

the top is possible (~ 1% at v_i = 30%). The relaxation time, τ_m, shifts slightly to lower values for higher v_i.

β. $\epsilon^* = \epsilon_o$

The discussion under Iα applies equally here.

II. Disc-shaped granules

α. $\epsilon^* = \epsilon_m$

Equation (I5.11) can be written as

$$\epsilon_m = \frac{\epsilon_o(3 - 2\,v_i) + 2\,v_i}{\epsilon_o\,v_i + (3 - v_i)}\,, \qquad \text{(VII2.2)}$$

giving a semicircular locus for the function $\epsilon'_m = f(\epsilon''_m)$. Thus here also equations (VII1.2) and (VII1.3) apply, now with

$$\tau_m = \frac{\epsilon_{o\infty}\,v_i + (3 - v_i)}{\epsilon_{os}\,v_i + (3 - v_i)}\,\tau_o\,. \qquad \text{(VII2.3)}$$

As an example, the curves for $\epsilon'_m = f(\epsilon''_m)$ are given for several values of v_i in Fig. VII.8, for $\epsilon'_o = f(\epsilon''_o)$ as a semicircular locus with $\epsilon_{os} = 10$ and $\epsilon_{o\infty} = 2$.

β. $\epsilon^* = \epsilon_o$

This case gives improbable values and thus can be omitted from the discussion.

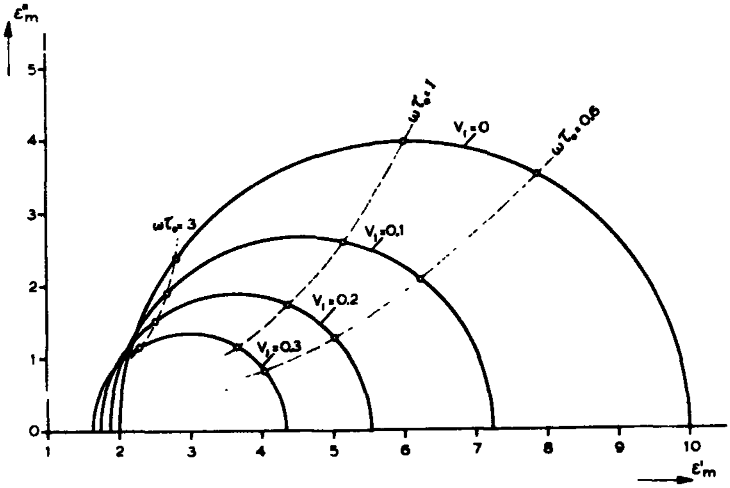

Figure VII.8
$\epsilon'_m = f(\epsilon''_m)$ for disc-shaped granules (A_j = 0; 0; 1), according to the equation of Polder and van Santen (eq. (15.11) with $\epsilon^* = \epsilon_m$) with $\epsilon'_o = f(\epsilon''_o)$ being a semicircular locus with $\epsilon_{os} = 10$ and $\epsilon_{o\infty} = 2$.

III. Needle-shaped granules

For this case, formula (VIII.9) can again be used, and for both cases, $\epsilon^* = \epsilon_m$ and $\epsilon^* = \epsilon_o$, curves are found for the function $\epsilon'_m = f(\epsilon''_m)$ slightly depressed below a semicircular locus, combined with a slight shift of the relaxation time of the mixture, τ_m, towards lower values. In Fig. VII.9 the curve $\epsilon'_m = f(\epsilon''_m)$ is given for v_i = 30% when the function $\epsilon'_o = f(\epsilon''_o)$ is a semicircular locus with $\epsilon_{os} = 10$ and $\epsilon_{o\infty} = 2$.

§ 3. *Survey*

Table VII.I (page 84) is a survey of the results.

§ 4. *Experimental evidence*

Only a few measurements are available in this field. An example will be given for each of the two cases: $\epsilon_{is}/\epsilon_o > 1$ and $\epsilon_i/\epsilon_{os} < 1$.

a. $\epsilon_{is}/\epsilon_o > 1$

To demonstrate the case of granules consisting of a material showing relaxation, microwave measurements were made on some

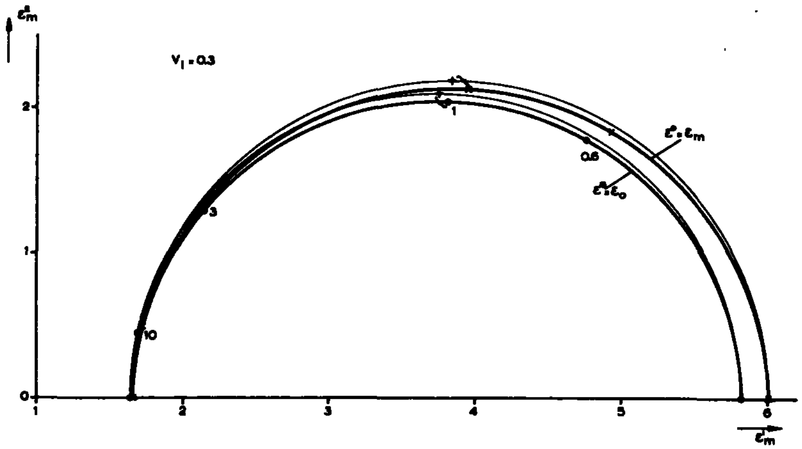

Figure VII.9
$\epsilon'_m = f(\epsilon''_m)$ for needle-shaped granules (A_j = ½;½;0), according to the equation (I5.11) with $\epsilon'_o = f(\epsilon''_o)$ being a semicircular locus with $\epsilon_{os} = 10$ and $\epsilon_{o\infty} = 2$, for $v_i = 0.3$.

specimens of $BaTiO_3$ powder in p.v.c. These specimens, however, were very difficult to handle because of their hygroscopic behaviour, and the absorption of moisture during the measurements could not be avoided. Measurements were made at 4.0, 3.2, and 1.25 cm. In spite of the technical difficulties, the data indicated that the d.c. of these mixtures does not greatly differ from the values obtained at low frequencies (*vide* Table IV.III). Measurements on samples of sintered $BaTiO_3$ of the same batch gave complex d.c.'s at microwave frequencies. The results of the measurements on the sintered material are summarised in Table VII.II.

The microwave measurements given here are not of very high accuracy, but sufficiently so for this discussion. These results are in good agreement with those made at M.I.T. *) on sintered $BaTiO_3$ and mixtures of $BaTiO_3$ powder in poly-2,5-dichlorostyrene.

All these measurements show that the sintered material is in the middle of the dispersion region, and the mixtures at the very beginning of it, thus demonstrating $\tau_m < \tau_i$ as predicted by the calculations given in § 1.

b. $\epsilon_i/\epsilon_{os} < 1$

For a mixture having a continuum consisting of a polar material, we have the measurements of S.H.M. El Sabeh and J.B. Hasted [69] on spherical granules of a polystyrene-latex, using a soap

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*) ref. 32, page 305 and 343.

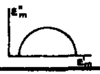
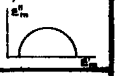
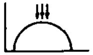
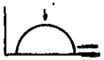
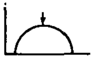
Description		$\varepsilon_{1s}/\varepsilon_0 > 1$ ε_1 polar $\varepsilon'_i = f(\varepsilon''_i)$ semi-circle $\varepsilon'_m = f(\varepsilon''_m)$		$\varepsilon_i/\varepsilon_{0s} < 1$ ε_0 polar $\varepsilon'_0 = f(\varepsilon''_0)$ semi-circle $\varepsilon'_m = f(\varepsilon''_m)$	
1 Maxwell-Lewin relation (II 1.2) spherical particles		semi-circle $\tau_m = \frac{\varepsilon_{1\infty}(1-V_i)+(2+V_i)}{\varepsilon_{1s}(1-V_i)+(2+V_i)}\tau_i$ (VII 1.4)		semi-circle (approximately) $\tau_m \approx \tau_0$	
2 Relation (I 5.11)					
I spherical particles $A_j = \frac{1}{3}:\frac{1}{3}:\frac{1}{3}$	α : $\varepsilon^* = \varepsilon_m$ Böttcher (II 2.1)	strongly depressed top $\tau_m < \tau_i$ higher shifts for higher values of $(\varepsilon_{1s} - \varepsilon_{1\infty})$		curve only slightly depressed $\tau_m \approx \tau_0$	
	β : $\varepsilon^* = \varepsilon_0$	semi-circle $\tau_m = \frac{\varepsilon_{1\infty}+2}{\varepsilon_{1s}+2}\tau_i$		ditto	
II disc-shaped particles $A_j = 0:0:1$	α : $\varepsilon^* = \varepsilon_m$	curve only slightly depressed below semi circle $\tau_m < \tau_i$		semi circle $\tau_m = \frac{\varepsilon_{0\infty}\cdot V_i+(3-V_i)}{\varepsilon_{0s}\cdot V_i+(3-V_i)}\tau_0$	
	β : $\varepsilon^* = \varepsilon_0$	ditto		improbable values	—
III needle-shaped particles $A_j = \frac{1}{2}:\frac{1}{2}:0$	α : $\varepsilon^* = \varepsilon_m$	depressed top $\tau_m < \tau_i$ lower shifts for higher values of $(\varepsilon_{1s} - \varepsilon_{1\infty})$		depressed top $\tau_m < \tau_0$	
	β : $\varepsilon^* = \varepsilon_0$	ditto		ditto	

Table VII I

Table VII.II
Dielectric properties of sintered $BaTiO_3$.
$v_i = 82\%$

freq. Mc/s	ϵ'	ϵ''	tg ∂
0.032	1060	5.4	0.005
0.13	1050	2.0	0.002
7520	340	80	0.25
9375	240	78	0.33

solution as continuum. A slight shift of τ_m is observed towards lower values [70]: $\tau_m/\tau_o = 0.99$ for a 5% latex content and $\tau_m/\tau_o = 0.93$ for a 10% latex content. This shift is in the right direction, although it is a bit larger than predicted by the calculations for this case given in § 2.

A second example is found in the measurements of N.L. Brown and R.H. Cole [72] on solid HBr. Formation of cracks and voids occurred when their specimens were cooled, and they obtained complex loci $\epsilon'_m = f(\epsilon''_m)$ of similar circular arcs, differing only in scale and frequency range with the amount of void. Here also $\tau_m < \tau_o$. The description of Brown and Cole of the phenomena observed, is best approximated in our discussion by the concept of disc-shaped holes in a polar continuum, given in equations (VII2.2) and (VII2.3) and in Fig. VII.8.

Too little is known at present about the shift of τ_m and the alteration of the locus $\epsilon'_m = f(\epsilon''_m)$ from the semicircle. Further measurements in this field will be of great value. For the latter case (polar continuum), the calculations predict only small changes which are probably too small to be observed within the accuracy permitted by current experimental techniques. The depression of the locus $\epsilon'_m = f(\epsilon''_m)$ and the shift of τ_m are larger for the former case, *i.e.* a mixture with a polar particle material. It is, however, very difficult to find good samples on which to measure such phenomena.

§ 5. *Discussion*

In the foregoing chapters, we arrived at the conclusion that ϵ^* is between ϵ_o and ϵ_m. When this holds for the case where relaxation phenomena occur, several conclusions can be drawn from the calculations given in this chapter.

For the case of a mixture with granules consisting of a polar material, curves depressed below a semicircular locus are to be expected, especially for a mixture containing spherical granules. For the granules of more extreme shapes, the semicircular locus is again approached. Strong shifts in τ_m are to be expected, which become smaller for the more extreme shapes. The relaxation time of the material of the granules, τ_i, was called the intrinsic relaxation time of the mixture.

In our calculations on mixtures containing spherical granules, the Cole and Cole diagram for the mixture was a semicircle for the relation in which the interaction of the granules was not taken into account, or could be neglected because of the regular arrangement of the granules (formula (III.2)). The Cole and Cole diagram was a curve depressed below a semicircle for that relation in which the interaction was taken into account (equation (II2.1)). In this case, one intrinsic relaxation time can still be used where, for a macroscopic description, we would usually prefer a distribution of relaxation times [68].

When the continuous medium is polar, only slight deviations from the semicircular locus for the function $\epsilon'_m = f(\epsilon''_m)$ are to be expected. The calculations predict only slight shifts, if any, of the relaxation time of the mixture towards smaller values than that of the continuum. This means that slight traces of a granular non-polar impurity in a polar dielectric (e.g. liquid) probably will not have any measurable influence on the form of the locus $\epsilon' = f(\epsilon'')$ and the value of the relaxation time. The accuracy of the measurements in this field is such that the slight variations possible will not be visible.

For all cases discussed, the relaxation time of the mixture cannot increase to values higher than that of the relaxing constituent. This means that where this phenomenon occurs it is justifiable to conclude that there is a deviation from the pure mixture behaviour as defined above in Chapter I.

Summary

Several authors have attempted to relate the permittivity of a heterogeneous mixture to the permittivities of its components. However, in the choice and application of a particular mixture relation, the special assumptions made in its derivation are often overlooked, with the result that the present situation in this field is rather chaotic. This thesis will be an attempt at clarification.

A theory of the dielectric behaviour of heterogeneous mixtures is developed, using the method for non-polar liquids given by Onsager, Böttcher, etc., who treat the influence of the immediate environment of a particle by giving it the same dielectric constant as the macroscopic liquid. This treatment is extended and generalised by giving the permittivity of the immediate environment of the granule an arbitrary value: ϵ^*. Since determination of the value of ϵ^* from the measured dielectric constant of the mixture depends upon knowing the shape of the granules, a method is developed for determining the shape factor, *A*. Measurements show a good agreement between the thus calculated shape factor and the actual geometry of the granules. Thus it is possible to calculate the effective value of ϵ^*. This effective value can be compared with the macroscopic dielectric constant of the mixture, ϵ_m, and the dielectric constant of the continuous phase, ϵ_0, in order to investigate the applicability of the assumptions made about ϵ^* in the literature.

A thorough investigation of all the available measurements leads to the conclusion that no definite choice can be made among the existing relations. Only an upper and a lower limit for the dielectric constant of a heterogeneous mixture can be defined, and for each individual case the particular parameters must be determined. When ϵ_i/ϵ_0 is approximately 1 ($2 > \epsilon_i/\epsilon_0 > \frac{1}{2}$), the Maxwell, Bruggeman or Böttcher formulae can all be used with reasonable accuracy.

In conclusion, a series of calculations are given which were made in order to study the behaviour of a heterogeneous mixture as a function of frequency when one of its constituents is polar. These calculations suggest that deviations from a semicircle are to be expected for the function $\epsilon'_m = f(\epsilon''_m)$ in case that the

material of the granules is polar and the function $\epsilon_i' = f(\epsilon_i'')$ is a semicircular locus. The relaxation time of the mixture is also different from the relaxation time of the material of the granules. No marked shifts are to be expected in the case that the granules are imbedded in a polar continuum.

Samenvatting

Om de dielectrische eigenschappen van een heterogeen mengsel te kunnen afleiden uit die van zijn componenten wordt in de literatuur vaak een willekeurige keuze gemaakt uit de mengwetten, die beschikbaar zijn. Daar bovendien in de toepassing van deze mengwetten vaak de vooronderstellingen, die gebruikt zijn om tot een bepaalde relatie te geraken, over het hoofd worden gezien, is de situatie in dit gebied nogal chaotisch. In deze dissertatie wordt een poging gedaan hierin enige verheldering te brengen.

Daartoe wordt eerst een theorie voor het dielectrisch gedrag van heterogene mengsels ontwikkeld. Deze is gebaseerd op de afleidingen voor het dielectrisch gedrag van niet-polaire vloeistoffen, zoals die gegeven zijn door Onsager, Böttcher, e.a. Deze beschrijven de invloed van de naaste omgeving van een deeltje, door aan deze omgeving de dielectrische constante van de vloeistof toe te kennen. Deze beschrijvingswijze wordt gegeneraliseerd, door aan de dielectrische constante van de onmiddellijke omgeving van een korrel in een heterogeen mengsel een nog niet nader bepaalde, gegeneraliseerde waarde ϵ^* toe te kennen.

Daar de relatie van ϵ^* met de dielectrische constante van een mengsel afhangt van de vorm van de gedispergeerde korrels, wordt vervolgens een methode ontwikkeld om de zogenaamde vormfactor A te bepalen. Metingen tonen aan, dat er een goede overeenstemming bestaat tussen de met behulp van deze vormfactor bepaalde en de werkelijke vorm der korrels. Hierdoor wordt het mogelijk de effectieve waarde van ϵ^* te bepalen. Deze waarde kan worden vergeleken met de macroscopische dielectrische constante van het mengsel ϵ_m en de dielectrische constante van de continue drager ϵ_0, teneinde de toepasbaarheid van de in de literatuur gemaakte vooronderstellingen omtrent ϵ^* te toetsen.

Een nader onderzoek van alle beschikbare metingen voert tot de conclusie, dat geen definitieve keuze uit de bestaande mengrelaties kan worden gemaakt. Slechts een boven- en een ondergrens voor de dielectrische constante van een heterogeen mengsel kunnen worden aangegeven en voor elk individueel geval moeten de verschillende parameters opnieuw worden bepaald. Alleen wanneer ϵ_i/ϵ_0 dicht bij 1 ligt ($2 > \epsilon_i/\epsilon_0 > \frac{1}{2}$) kan ϵ_m vrij nauwkeurig worden voorspeld als functie van de volumevulling. In dat geval zijn zowel de formule van Maxwell als die van Bruggeman en Böttcher toepasbaar.

Tot besluit worden een aantal berekeningen gegeven, die gemaakt zijn om het gedrag van een heterogeen mengsel te bestuderen, wanneer hetzij het materiaal van de korrels, hetzij het materiaal van de continue drager polair is. Deze berekeningen doen veronderstellen, dat afwijkingen van de halve cirkel kunnen worden verwacht voor de functie $\epsilon'_m = f(\epsilon''_m)$ in het geval dat het materiaal van de korrels polair is en de functie $\epsilon'_i = f(\epsilon''_i)$ door een halve cirkel kan worden beschreven. Ook de relaxatietijd van het mengsel zou in dat geval verschoven moeten zijn en wel naar lagere waarden dan de relaxatietijd van het materiaal der korrels. Voor het geval dat korrels gedispergeerd zijn in een polaire drager zijn geen grote verschuivingen te verwachten. De weinige beschikbare metingen zijn in overeenstemming met de berekeningen.

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Curriculum vitae

Na het behalen van mijn einddiploma gymnasium β in 1946 aan het Gereformeerd Gymnasium te Leeuwarden, liet ik mij inschrijven aan de Technische Hogeschool te Delft. Aan het einde van mijn derde studiejaar was ik gedurende twee maanden voor het Delfts Hogeschoolfonds werkzaam bij de afdeling Electronenmicroscopie. Hierna werd ik als assistent van prof. dr H. B. Dorgelo belast met de bouw van het 8 MeV bêtatron. Na het behalen van het diploma van Natuurkundig Ingenieur op 26 juni 1951 bleef ik aan deze opdracht verder werken tot ik in october 1951 werd opgeroepen in militaire dienst. In november van dat zelfde jaar werd ik als officier in dienst bij de Koninklijke Marine gedetacheerd op het Physisch Laboratorium der Rijksverdedigingsorganisatie T. N. O., Waalsdorp, 's-Gravenhage. Na het beëindigen van mijn militaire diensttijd werd ik in juli 1953 als ingenieur in vaste dienst in de wetenschappelijke staf van dit laboratorium opgenomen.

Het onderzoek beschreven in dit proefschrift is uitgevoerd in het Physisch Laboratorium R. V. O. - T. N. O. Aan de Directeur van dit laboratorium, prof. ir J. L. van Soest, en het bestuur van de Rijksverdedigingsorganisatie betuig ik mijn dank voor hun medewerking bij het tot stand komen van deze dissertatie.

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