# 2

# STATIC PERMITTIVITY OF EMULSIONS

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## 2.1  Introduction

The study on dielectric properties of emulsions is of great importance for its theoretical point of view and for its applications.

Many focuses are based on this study [1–2] and many theses too [3–8], have dealt with the static and dynamic aspects of the permittivity of emulsions. But this subject is so large that it is very difficult to analyze it thoroughly. Therefore, we have decided that it would be of more interest to deal with the static aspect only. It would allow us to analyze more precisely and completely all the existing theories elaborated to solve this problem. The study of these theories has brought us to determine the influence of the spheric symmetry on the permittivity and to elaborate a new model based on the fact that the average field depends on the state of dispersion. Finally, we have made a general comparison between all the different expressions and between these

expressions and the experimental data.

## a. Definition of the Problem

In all which follows, we will consider the study of the static permittivity of emulsions. The primary definition of emulsion is any passive and homogeneous medium made of two phases: a dispersed one and a continuous one. The dispersed phase, referred to by $D$, is made of spherical micelles of small dimension with reference to the medium, but large with reference to the molecular dimensions. This system is characterized by the volume fraction $\varphi_D$ occupied by the phase $D$ in the total volume, and by the fraction $\varphi_C$ occupied by the continuous phase $C$ in the same volume, so that:

$$\varphi_D + \varphi_C = 1 \tag{1}$$

The dielectric properties of the system are characterized by the dielectric constant $\varepsilon_D$ of the dispersed phase, by $\varepsilon_C$ of the continuous phase and by the average radius $a$ of the micelles and their average number unit volume $N_D$, so that:

$$\frac{4\pi}{3}a^3 = \frac{\varphi_D}{N_D} \tag{2}$$

The electric properties of micelles cannot be thoroughly interpreted simply by using the permittivity $\varepsilon_D$ of pure dispersed phase. Indeed some more probable orientations of molecular dipoles in a micelle and even an induced polarization can be considered. It is however possible to characterize a micelle simply by a permittivity $\varepsilon_D$, which is not necessarily equal to the purse dispersed phase one because if so, the relaxation time would be much greater than the alternating fields period in quasi-static measurements of permittivity [9].

The definition that we have used for emulsions is related to many different systems which can be characterized by the average diameter of the micelles. Therefore, in the decreasing size order, we have:

- suspensions ( $10^{-1}$ mm)
- proper emulsions ( $10^{-2}$ to $10^{-3}$ mm)
- micro emulsions ( $10^{-3}$ to $10^{-4}$ mm)
- colloidal systems ( $10^{-4}$ to $10^{-5}$ mm)

However, it is the same theory of quasistatic permittivity for all of these systems, as the theoretical results do not depend on the size of the micelles, as long as their size stays big compared to the molecules.

The dielectric behaviour of emulsions has an intermediate situation between the continuous-continuous systems (e.g., a porous material soaked by a liquid) and the dispersed-dispersed systems (e.g., a mixture of two apolar and miscible gases). There is however a fundamental difference; the permittivity of dispersed-dispersed or continuous-continuous systems is a symmetric function of the permittivities of the two phases. But, the permittivity of emulsions, continuous-dispersed systems is an asymmetric function. Therefore, by drawing the experimental curves of the permittivity of the two component systems against the volume fraction occupied by one of them, we realize that we have single curves for continuous-continuous and dispersed-dispersed systems, but a double curve for emulsions.

## b. Principal Experimental Results

The quasi-static measurements on emulsions, for frequencies between a few KHz and a few MHz, have led to the determination of two very closely related values: the dielectric permittivity and the electrical conductivity. The analysis of these measurements lead to the following conclusions on the qualitative behavior of the permittivity (and of the conductivity) of an emulsion.

The permittivity of an emulsion widely depends on:

- the value of the permittivity of each phase
- the volumic fraction occupied by each phase
- the pure phase: e.g., the curve of the permittivity vs. the concentration for the water-terpen [10] system shows a discontinuous variation of the concentration which goes with the exchange between the two phases; this is at the concentration where the dispersed water phase becomes the continuous one and the continuous one becomes the dispersed phase. In this case, as the permittivity of the dispersed phase is greater than the one of the continuous one, this curve is not at all linear. This is the so called percolation phenomenon. But, for the Nujol-Water [11] system, where the permittivity of the continuous phase is greater than that of the dispersed phase, the curve has nearly a linear behavior.

The permittivity of an emulsion slightly depends on:

- the shape of the micelles. E.g., the conductivity of an emulsion whose dispersed phases has an approximately ellipsoidal shape, as the blood [12], or an irregular one, as a suspension of sand in gelatine [13], depends on the concentration in a different way as when the micelles are spherical. Whatever concentration is chosen the permittivity increases with the deformation of the micelles, when the permittivity of the dispersed phase is greater than the one of the continuous phase, and decreases in the other case [14,15]. E.g., the permittivity of a suspension of $PbCl_2$ spheres in castor oil [9] increases with the fragmentation of these spheres.

- the intensity of the applied field. Whatever relationship between the permittivities of the two phases (if they are liquid or gas) is chosen, the permittivity of an emulsion increases with the applied field [16–17]. That is a sensible consequence of non-linear of relationships.

- the existing order of the spatial distribution of the micelles. Eg., the conductivity of a system of bakelite balls [14] or of lucite balls [18] distributed in a cubic system and put in water is a little greater than the one of identical balls but distributed at random.

- the interval of variation of the size of the micelles. E.g., the conductivity of a suspension of glass balls with a diameter between 0.049 and 6.4 mm, put in an electrolytic solution of $ZNBr_2$ [19], is different to the conductivity of a suspension where all the balls are identical. It is a second order effect, not taken account in the volume fraction.

The permittivity does not depend on:

- the size of micelles as long as they stay big compared to the molecules. Eg., the permittivity of glass balls placed next to one another in air is the same when their diameter is equal to 0.3 mm, 0.5 mm or 0.8 mm [10]. The conductivity of a suspension of glass balls put in an electrolytic solution of $ZnBr_2$ is the same for different diameters between 0.049 and 6.4 mm [19]. The permittivity of a suspension of glass balls in polystyrene does not change when the diameter of the balls doubles [20].

## c. Theoretical Approach

The theoretical problem is the determination of the apparent permittivity of an emulsion according to the permittivity of each phase

the concentration. A few satisfactory theories allow the determination of the permittivity of a homogeneous phase according to the characteristics of its components. A global theory should therefore give the value of the permittivity of a homogeneous substance according to its chemical composition and its usual intensive variables: pressure and temperature.

The oldest theories which can be used for the dielectric study of emulsions are based on apparently independent subjects such as the influence of obstacles in an electric field [21–22] and the permittivity of molecular mixtures [23–25]. Specific theories have then followed based as well as these previous models. One follows typical phenomenological deductions for example, by considering the two phases as insulators placed in parallel or in series [26–29] whereas the other deals with molecular mixtures thanks to cavity models [30].

Finally, a third direction consists in the study of the dielectric behavior of systems of two components without taking into account their composition [31–33].

The hypotheses and the results of these theories will be given in Section 2.2, 2.3a, and 2.4a. A comparison between the models will be given in Section 2.5b.

## 2.2   Theories Based on Phenomenological Models

The phenomenological models try to determine the permittivity of a global system made of two phases and not the polarizations of each phase as in the molecular treatments. Therefore we can consider that usually the micelles of the dispersed phases are surrounded by the continuous phase, by a medium of permittivity $\varepsilon_C$ and not of apparent permittivity $\varepsilon_E$. Consequently, the local composition is usually identical to the average composition.

In all models which are quoted, except in the first, the dispersed phase is considered as being composed of spheres put in a continuous system. Thus, the expressions of the permittivity are asymmetric with reference to an exchange between the phases.

### a.  Wiener Theory [22]

This model considers an emulsion as being made of parallel layers of dispersed and continuous pure phases (Fig. 2.1).
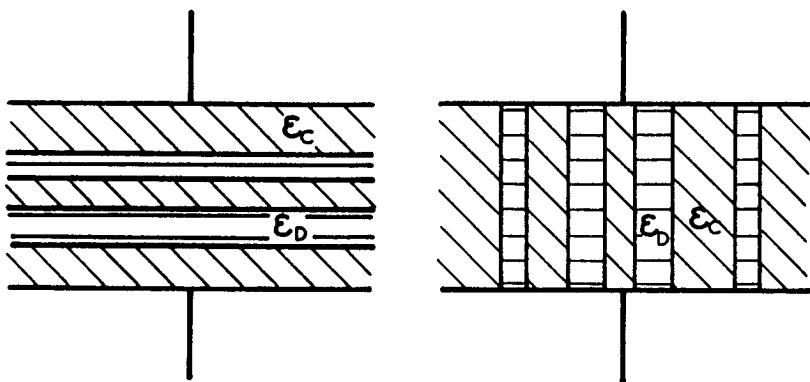
**Figure 2.1  Wiener model. Model made of flat layers of dispersed and continuous phases, parallel or perpendicular to the field.**

A system of this kind is anisotropic and therefore its apparent permittivity depends on the field direction with reference to the stratification axis.

If the layers are parallel to the armatures of the measuring condenser, the system is equivalent to two condensers in series and the permittivity is given by:

$$\frac{1}{\varepsilon_E} = \frac{\varphi_D}{\varepsilon_D} + \frac{1 - \varphi_D}{\varepsilon_C} \tag{3}$$

But if the layers are perpendicular to the armatures of the condenser, the system is equivalent to two condensers in parallel and the permittivity is given by the relationship:

$$\varepsilon_E = \varphi_D \varepsilon_D + (1 - \varphi_D)\varepsilon_C \tag{4}$$

These two expressions can be put into one:

$$\frac{\varepsilon_E - \varepsilon_C}{\varepsilon_E + u\varepsilon_C} = \varphi_D \frac{\varepsilon_D - \varepsilon_C}{\varepsilon_D + u\varepsilon_C} \tag{5}$$

which is equivalent to (3) for $u = 0$ and to (4) for $u = \infty$. Wiener considers that the permittivity of an emulsion made of spherical micelles

can be obtained by (5) with $u$ in the range of 0 to $\infty$. It is important to point out that the expression (5) is asymmetric for a phase inversion whereas (3) and (4) are totally symmetric.

## b. Rayleigh Theory [21]

The great difference between the Wiener model and what we describe as an emulsion has brought Rayleigh to do an initial theory where the dispersed phase is made of spherical micelles. Strictly speaking, Rayleigh's goal was to verify and to specify the approximations which lead to the expression of Lorenz-Lorentz [34,35]. The apparent permittivity calculation has been made on the grounds that the micelles are layed in a regular way on a cubic chain. Originally, the permittivity of the continuous system was considered equal to unity but the extension to the general case is immediately done. This particular distribution allows the calculation of the solution of the Laplace equation to take the form of an infinite series. The approximate expression without neglecting the interactions between micelles, is:

$$\varepsilon_E = \varepsilon_C \left[ \frac{\varepsilon_D + 2\varepsilon_C + 2\varphi_D(\varepsilon_D - \varepsilon_C) - \varphi_D^{10/3} \frac{\pi^2(\varepsilon_D - \varepsilon_C)^2}{6(\varepsilon_D + 4\varepsilon_C/3)} + \cdots}{\varepsilon_D + 2\varepsilon_C - \varphi_D(\varepsilon_D - \varepsilon_C)\varphi_D^{10/3}\frac{\pi^2(\varepsilon_D - \varepsilon_C)^2}{6(\varepsilon_D + 4\varepsilon_C/3)} + \cdots} \right] \quad (6)$$

As we have used an ordinate model, the apparent dielectric constant $\varepsilon_E$ is not equal to the one of the dispersed phase $\varepsilon_D$ if the dispersed phase is pure. However, Rayleigh concluded that (6) could also be used for an irregular or an isotropic distribution.

In the opposite case, when the concentration of the dispersed phase is very low, the factor $\varphi_D^{10/3}$, which corresponds to the interactions between micelles, can be neglected; this leads to the result limit:

$$\varepsilon_E = \varepsilon_C \left[ \frac{\varepsilon_D + 2\varepsilon_C + 2\varphi_D(\varepsilon_D - \varepsilon_C)}{\varepsilon_D + 2\varepsilon_C - \varphi_D(\varepsilon_D - \varepsilon_C)} \right] \quad (7)$$

This expression is still disymmetric even after neglecting the interactions between micelles. On the other hand, if $u = 2$ in (5), this equation is equal to the result of Clausius-Mosotti or, in optics, to the result of Lorenz-Lorentz.
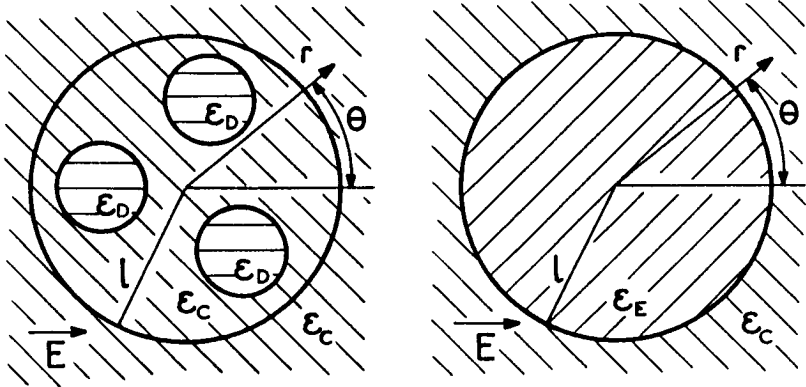
**Figure 2.2  Wagner model. Identification of the apparent moment of a large heterogeneous or homogeneous sphere.**

## c. Wagner Theory

This theory [26] has originally been associated with the behavior of dielectrics in alternating fields. This model considers a hypothetic structure of a dielectric made of spheres put in a continuous system, and identifies, for a low concentration of the dispersed phase, the apparent moment of a big sphere of the emulsion to the one of an identical sphere of the dielectric of permittivity $\varepsilon_E$. Thus, the spheres are considered put in a dielectric $\varepsilon_C$ with a macroscopic field $\overline{E}$ (Fig. 2.2).

If 1 is the radius of the sphere, the potential for $r \geq 1$ is the addition of two terms: the potential of an uniform field $\overline{E}$ and the one of the $\frac{4\pi}{3} l^3 N_D$ polarized micelles.

By considering low concentrations, we can neglect the interactions between the micelles, which allows us to write the apparent or external moment of each of them as:

$$m^* = \frac{\varepsilon_D - \varepsilon_C}{\varepsilon_D + 2\varepsilon_C} 4\pi\varepsilon_0\varepsilon_C a^3 E \tag{8}$$

Moreover, by taking into account the symmetry of our problem, we can replace the potential of all the micelles by the potential of a

pin-point dipole placed at the origin. The potential outside the big sphere is therefore:

$$U = -E_r \cos\theta + \frac{1}{4\pi\varepsilon_0\varepsilon_C} \frac{4\pi}{3} N_D l^3 m^* \frac{\cos\theta}{r^2} \qquad (9)$$

Whereas the one of the sphere of average permittivity $\varepsilon_E$ is, in the same conditions:

$$U = -E_r \cos\theta + \frac{E(\varepsilon_E - \varepsilon_C)}{4\pi\varepsilon_0\varepsilon_C(\varepsilon_E + 2\varepsilon_C)} 4\pi\varepsilon_0\varepsilon_C l^3 \frac{\cos\theta}{r^2} \qquad (10)$$

By comparing of both expressions, we come up with the result:

$$\varepsilon_E = \varepsilon_C \left[ \frac{\varepsilon_D + 2\varepsilon_C + 2\varphi_D(\varepsilon_D - \varepsilon_C)}{\varepsilon_D + 2\varepsilon_C - \varphi_D(\varepsilon_D - \varepsilon_C)} \right] \qquad (11)$$

As predicted, this expression is the same as the limiting expression of Rayleigh, (7), because each of them was made by neglecting the interactions between micelles.

### d. Higuchi Theory

This theory [36] is a Wagner extension (2.2c) for higher concentrations because it allows one to take into account the interactions between micelles, at least at the first order. Therefore the average field acting on the micelles is put into two terms:

$$\overline{E}'_C = \overline{E}_C + \Delta\overline{E}_C \qquad (12)$$

Where $\overline{E}_C$ is the average field existing in the continuous phase and is the only field considered in the Wagner theory. $\Delta\overline{E}_C$ is the average reaction field caused by all the other micelles.

This field has been evaluated at the center of one micelle, all the others considered as polarizable pin-point dipoles.

The expression of the reaction field is

$$\Delta\overline{E}_C = \frac{1}{(4\pi\varepsilon_0)^2} \sum_{i=1}^{N} \frac{\alpha_D^{*2}}{r_i^6}(3\cos^2\theta_i + 1)\overline{E}'_C \qquad (13)$$

where:

$$\alpha_D^* = \frac{\varepsilon_D - \varepsilon_C}{\varepsilon_D + 2\varepsilon_C} 4\pi\varepsilon_0\varepsilon_C a^3 \qquad (14)$$

is the apparent polarizability of a micelle with a radius " $a$ " in a continuous system $\varepsilon_C$; $r_i$ is the distance between the micelle considered and the micelle $i$; $\theta_i$ is the angle between $r_i$ and the direction of the applied field. The calculation of the sum in (13), by neglecting terms of $\alpha_D^*/r_i^3$ of order greater than two and by supposing that all the micelles have the same radius " $a$ ," leads to:

$$\Delta \overline{E}_C = \frac{\alpha_D^{*^2} \overline{E}_C'}{a^6} K \tag{15}$$

where $K/a^6$ is a function of $\varphi_D$ whose precise expression is unknown, as it depends on the radial distribution of the micelles in the emulsion. The result (15) leads to this expression of the permittivity of an emulsion:

$$\varepsilon_E = \varepsilon_C \left[ \frac{\varepsilon_D + 2\varepsilon_C + 2\varphi_D(\varepsilon_D - \varepsilon_C) - K\frac{(\varepsilon_D - \varepsilon_C)^2}{\varepsilon_D + 2\varepsilon_C}(1 - \varphi_D)}{\varepsilon_D + 2\varepsilon_C - \varphi_D(\varepsilon_D - \varepsilon_C) - K\frac{(\varepsilon_D - \varepsilon_C)^2}{\varepsilon_D + 2\varepsilon_C}(1 - \varphi_D)} \right] \tag{16}$$

This expression is very similar to Rayleigh's, and both are equivalent to the Wagner's when neglecting the interactions which means $K = 0$. However, the corrective terms are very different; for Rayleigh, they are proportional to $\varphi_D^{10/3}$ and for Higuchi, $K$ slightly depends on $\varphi_D$ and therefore the corrective terms are proportional to $1 - \varphi_D$. This has the advantage of coming to an expression of $\varepsilon_E$ which is equal to $\varepsilon_D$ when $\varphi_D = 1$. For Higuchi, $K = 0.78$ is the best value for explaining the experimental results for a wide range of systems.

### e. Bruggeman and Hanai Theories

Bruggeman has taken a totally new approach to elaborate an expression of the permittivity of emulsions at any concentration. He began with the limiting expression of Rayleigh's equation (7). He considered that if this equation was correct for $\varphi_D$ small, it could be interpreted as an expression, for any concentration, of the incrementation of the permittivity, due to a small quantity of dispersed phase added to the system. Therefore, we consider the emulsion as a volume $V_C$ of continuous phase to which is added progressively the dispersed phase. The volume of this phase lies between 0 and a maximum value $V_D$ so that:

$$\frac{V_D}{V_C + V_D} = \varphi_D \tag{17}$$

At an intermediate moment corresponding to a volume $V_D'$, the permittivity of the emulsion is $\varepsilon_E'$. The variation $d\varepsilon_E$ of this permittivity when a small volume $dV_D'$ of dispersed phase is added, can be obtained by making in (17) these substitutions:

$$
\begin{aligned}
\varepsilon_C &\to \varepsilon_E' \\
\varepsilon_E &\to \varepsilon_E' + d\varepsilon_E' \\
\varphi_D &\to \frac{dV_D'}{V_C + V_D'}
\end{aligned}
\tag{18}
$$

This substitution can be transformed by a differentiation of (17) where $V_D$ has been replaced by $\varphi_D$ and $V_D'$ by $\varphi_D'$.
This leads to:

$$
d\varphi_D' = \frac{V_C}{(V_C + V_D')^2}dV_D' = \frac{1 - \varphi_D'}{V_C + V_D'}dV_D'
\tag{19}
$$

Another substitution can be made for the concentration:

$$
\varphi_D \to \frac{\varphi_D'}{1 - \varphi_D'}
\tag{20}
$$

The limiting expression of Rayleigh becomes:

$$
\frac{(\varepsilon_D + 2\varepsilon_E')d\varepsilon_E'}{(\varepsilon_D - \varepsilon_E')3\varepsilon_E'} = \frac{d\varphi_D'}{1 - \varphi_D'}
\tag{21}
$$

which can be integrated between the limits $\varepsilon_C$ and $\varepsilon_E$ and between the limits 0 and $\varphi_D$. This gives us the expression:

$$
\frac{\varepsilon_D - \varepsilon_E}{\varepsilon_D - \varepsilon_C} \cdot \left(\frac{\varepsilon_C}{\varepsilon_E}\right)^{1/3} = 1 - \varphi_D
\tag{22}
$$

The same result, but for complex permittivity, has been found by Hanai [28] by starting from (11) of Wagner and using a similar method.

## f. Kubo-Nakamura Theory

This theory [29], as the previous one, allows the determination of the permittivity of emulsions by considering a succession of intermediate states due to progressive additions of dispersed phase, but does not start from the limiting expression of Rayleigh.
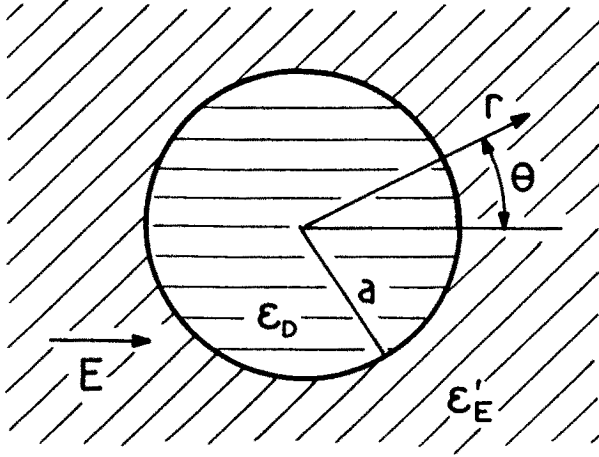
**Figure 2.3** **Kubo-Nakamura model. The medium is an intermediate status of its formation.**

Let's consider a system in an intermediate state of its formation with a permittivity $\varepsilon'_E$, in a uniform field $E$, and let's study the variation of the total moment when a micelle of the dispersed phase is added (Fig. 2.3).

The dielectric moment, in the occupied volume of a micelle, varies on:

$$\Delta m_{y\,\text{int}} = \frac{4\pi}{3}a^3\varepsilon_0 E\left[(\varepsilon_D - 1)\frac{3\varepsilon'_E}{\varepsilon_D + 2\varepsilon'_E} - (\varepsilon'_E - 1)\right] \qquad (23)$$

whereas the variation of the external moment can be determined by the variation of the potential:

$$\Delta U_{\text{ext}} = Ea^3 \cdot \frac{\varepsilon_D - \varepsilon'_E}{\varepsilon_D + 2\varepsilon'_E}\frac{\cos\theta}{r^2} \qquad (24)$$

so:

$$\Delta m_{v\,\text{ext}} = \varepsilon_0(\varepsilon'_E - 1)Ea^3 \cdot \frac{\varepsilon_D - \varepsilon'_E}{\varepsilon_D + 2\varepsilon'_E}\int_r\int_\theta(3\cos^2\theta + 1)^{1/2}2\pi\sin\theta d\theta\frac{dr}{r}$$
$$(25)$$

To evaluate this integral, it is necessary to fix integration boundaries other than $a$ and $\infty$ for $r$, and other than 0 and $\pi$ for $\theta$. If not

it would diverge. But if the integration takes place on the inside of a surface where the modulus of the field stays constant, we come to the expression of the variation of the total moment:

$$\Delta m_v = \Delta m_{v\,\text{int}} + \Delta m_{v\,\text{ext}} = \frac{4\pi}{3} a^3 \varepsilon_0 E \frac{(\varepsilon_D - \varepsilon'_E)[(2+C)\varepsilon'_E + 1 - C]}{\varepsilon_D + 2\varepsilon'_E}$$

(26)

where:

$$C = 1 - \frac{4\pi}{9\sqrt{3}}$$

(27)

The variation of the total moment can linked to the variation of $\varepsilon'_E$ by the relationship:

$$\Delta\varepsilon'_E = \frac{\Delta m_v}{\varepsilon_0 EV}$$

(28)

And, as in the Bruggeman theory (2.2e), the variation of the composition is determined by:

$$\frac{d\varphi'_D}{1 - \varphi'_D} = \frac{4\pi}{3} a^3 \frac{1}{V}$$

(29)

Thanks to these substitutions, the permittivity $\varepsilon'_E$ can be integrated between $\varepsilon_C$ and $\varepsilon_D$ and the volume fraction $\varphi'_D$ between 0 and $\varphi_D$, which leads to this implicit expression:

$$\frac{3\varepsilon_D}{(2+C)\varepsilon_D + 1 - C} \cdot \ln\left[\frac{\varepsilon_D - \varepsilon_E}{\varepsilon_D - \varepsilon_C}\right]$$
$$- \frac{(2+C)\varepsilon_D - 2(1-C)}{[(2+C)\varepsilon_D + 1 - C](2+C)} \cdot \ln\left[\frac{(2+C)\varepsilon_E + 1 - C}{(2+C)\varepsilon_C + 1 - C}\right] = \ln(1 - \varphi_D)$$

(30)

This result can be put in a similar form to (22):

$$\frac{\varepsilon_D - \varepsilon_E}{\varepsilon_D - \varepsilon_C} \left[\frac{\varepsilon_C + Q}{\varepsilon_E + Q}\right]^{\frac{1}{3}(1 - \frac{2Q}{\varepsilon_D})} = (1 - \varphi_D)^{(\frac{1 + Q \varepsilon_D}{1 - Q})}$$

(31)

with:

$$Q = \frac{1 - C}{1 + C} = 0.37$$

(32)

We can point out that this expression is more asymmetric than the one of Bruggeman, this means that it leads to lower values of the permittivity if $\varepsilon_D > \varepsilon_C$, and higher ones if $\varepsilon_D < \varepsilon_C$.

This equation, as well as the one of Bruggeman, does not have a simple physical interpretation because they are both based on models that do not represent a polarized dielectric but a stage of its formation. Therefore it is very difficult to estimate how to approximate the evaluation of interactions between micelles is.

### g. Landau-Lifshitz Theory for Low Concentrations

These last theories we have quoted offer approximate methods to evaluate the permittivity for any concentration. On the contrary, the theory of Landau-Lifshitz [32] leads to a rigorous expression, suitable for any low concentration.

This very general theory starts from the fundamental expression:

$$\frac{1}{V} \int_V (D - \varepsilon_C E) dV = \overline{D} - \varepsilon_C \overline{E} \tag{33}$$

where $V$ is the volume of the emulsion and were $\overline{D}$ and $\overline{E}$ are two averages taken over the volume.

This function which needs to be integrated is equal to zero except in the micelles. Therefore, it must be proportional to the volume fraction $\varphi_D$. For every low concentrations, the field in the micelles must be calculated while considering the micelles in a field of value $\overline{E}$, which leads to

$$\overline{E}_D = \frac{3\varepsilon_C}{2\varepsilon_C + \varepsilon_D} \overline{E} \tag{34}$$

for spherical micelles. This allows one to integrate the function so that:

$$\varphi_D \frac{3\varepsilon_C}{2\varepsilon_C + \varepsilon_D} (\varepsilon_D \overline{E} - \varepsilon_C \overline{E}) = \overline{D} - \varepsilon_C \overline{E} \tag{35}$$

And if we consider the definition $\overline{D} = \varepsilon_E \overline{E}$

$$\varepsilon_E = \varepsilon_C + \frac{3\varepsilon_C}{2\varepsilon_C + \varepsilon_D} (\varepsilon_D - \varepsilon_C) \varphi_D \tag{36}$$

This is a rigorous expression only for very low concentrations. It is linear in $\varphi_D$, but can not give $\varepsilon_E = \varepsilon_D$ for $\varphi_D = 1$. Its principal

advantage is to test the other formula which must be equal to this expression when $\varphi_D$ tends toward zero.

## 2.3   Theories Based on Molecular Models

The classical molecular theories on the dielectric behavior of mixtures always sum up to the calculation of average dipole moments of each molecular species to determine the relative permittivity in vacuum $\varepsilon_M$ by using the definition of the polarization:

$$\varepsilon_0(\varepsilon_M - 1)E = \sum_j N_{Mj}\langle m_j \rangle \tag{37}$$

In this expression, $\varepsilon_0$ is the permittivity in vacuum, E the macroscopic field in the dielectric (Maxwell Field), $N_{Mj}$ the number of molecules of the $j$ species by volume unit and $\langle m_j \rangle$ their average dipole moment.

The calculation of average molecular moments always takes these successive stages:
- The molecules of each species are given a permanent dipole moment $\mu_j$ and a polarizability $\alpha_j$ generally isotropic.
- The local field $\overline{F}_j$ is calculated, it is the field where the molecule of the $j$ species is, when the entire dielectric is in the macroscopic field $\overline{E}$.
- The average moment $\langle m_j \rangle$ of the molecule of the $j$ species is then determined, taking into consideration that this molecule is in vacuum and in the field $\overline{F}_j$.

This calculation can be extended to an emulsion as the treatment of the dispersed phase presents no difficulty. Indeed, a sphere of radius " $a$ " and of permittivity $\varepsilon_D$ acts just like a molecule, on an electrostatic point of view, and has an isotropic polarizability:

$$\alpha_D = 4\pi\varepsilon_0 a^3 \frac{\varepsilon_D - 1}{\varepsilon_D + 2} \tag{38}$$

But the treatment of the continuous phase with $N_C$ "molecules" by volume unit with a microscopic radius $a_C$ and a polarizability $\alpha_C$ so that:

$$\alpha_C = 4\pi\varepsilon_0 a_C^3 \frac{\varepsilon_C - 1}{\varepsilon_C + 2} \tag{39}$$
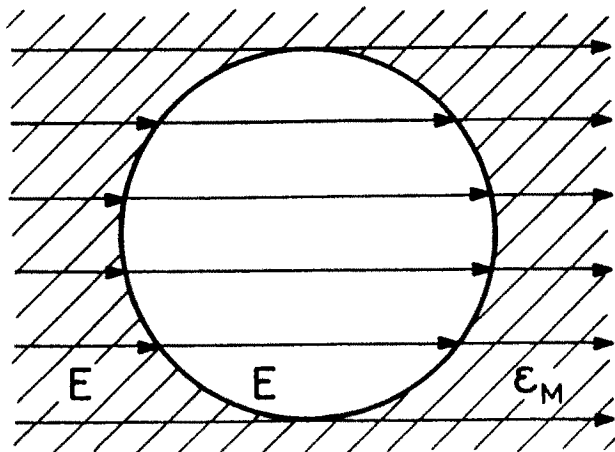
Figure 2.4  Clausius-Mossotti model. $\dot{E}$: Maxwell field.

is much less justified.

The radius $a_C$ must represent a macroscopic variable and there-
fore can not be equal to the radius of the molecules of the continuous
phase, because this would lead to an expression of the permittivity
of emulsions which depends on $\varepsilon_D$, on the molecular parameters $\alpha_j$
and may even depend on the moments $\mu_j$ but not on the microscopic
parameter $\varepsilon_C$.

Even though the volume $a_C^3$ does not appear in the final expres-
sions of the permittivity, as it is associated to $N_C$, this calculation
leads to a symmetric dependence of the resulting permittivity $\varepsilon_E$ with
reference to the D and C phases. This means that an exchange between
the two phases does not affect the permittivity; this disagrees with the
experimental results.

### a. Clausius-Mosotti Theory

The local field of a molecule can be written as a sum of three terms:

$$\overline{F} = \overline{E} + \overline{E}_2 + \overline{E}_3 \tag{40}$$

where $\overline{E}$ is the field in the dielectric due to the external field (Maxwell
field, Fig. 2.4) $\overline{E}_2$ is the field due to the external molecules of the

dielectric on a sphere centered on the molecule and $\overline{E}_3$ is the field due to the internal molecules of this sphere. If its radius is sufficiently long so that the internal molecules can be considered as forming a uniformly polarized dielectric, then the external molecules as well, so that:

$$\overline{E}_2 = \frac{1}{3\varepsilon_0}\overline{P} \tag{41}$$

where $\overline{P}$ is the polarization.

If the internal molecules are uniformly distributed around a central molecule, their contribution to the local field of this molecule is equal to zero on average:

$$\overline{E}_3 = 0 \tag{42}$$

so:

$$\overline{F} = \frac{\varepsilon + 2}{3}\overline{E} \tag{43}$$

It is the same local field (Lorentz field [35]) for all the molecules of all the species in the mixture, so that:

$$m_j = \langle m_j \rangle = \alpha_j F \tag{44}$$

For an emulsion, this result leads to the following expression of the permittivity:

$$\varepsilon_0(\varepsilon_E - 1) = \frac{\varepsilon_E + 2}{3}(N_D\alpha_D + N_C\alpha_C) \tag{45}$$

And as:
where $N_D$ is the average number unit volume of the micelles in the disperse phase and $N_C$ the same in the continuous phase.

$$N_D\frac{4\pi}{3}a_D^3 + N_C\frac{4\pi}{3}a_C^3 = \varphi_D + (1 - \varphi_D) = 1 \tag{46}$$

Finally:

$$\varepsilon_E = \frac{\varepsilon_C(\varepsilon_D + 2) + 2\varphi_D(\varepsilon_D - \varepsilon_C)}{\varepsilon_C + 2 - \varphi_D(\varepsilon_D - \varepsilon_C)} \tag{47}$$

The Clausius-Mosotti theory is quite satisfactory for apolar-apolar mixtures. Therefore, its application to emulsions is quite limited, this is essentially due to the symmetric treatment of the disperse and continuous field.
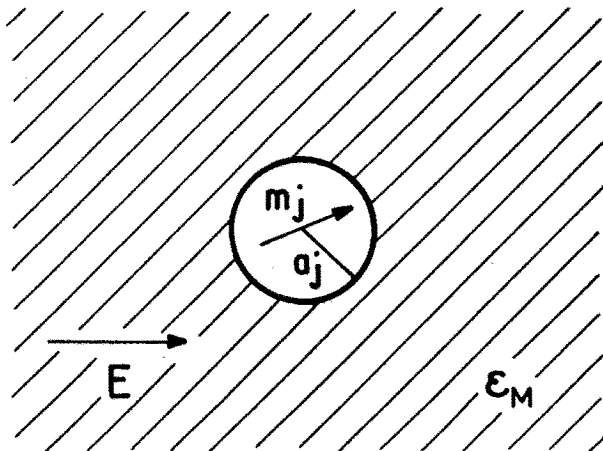
**Figure 2.5  Onsager-Bottcher cavity.**

### b. Onsager-Bottcher Theory

The local field is calculated while considering the molecule of a $j$ species in a spherical cavity of radius $a_j$ in the dielectric; the dielectric is considered as a continuous system with a permittivity $\varepsilon_M$ (Fig. 2.5).

This is a uniform field and results from two contributions:

$$\overline{F}_j = \overline{C} + \overline{R}_j \tag{48}$$

where $\overline{C}$ is the cavity field and does not depend on the internal molecule:

$$\overline{C} = \frac{3\varepsilon_M}{2\varepsilon_M + 1}\overline{E} \tag{49}$$

where $\overline{R}_j$ is the reaction field and does not depend on the external field:

$$\overline{R}_j = \frac{2(\varepsilon_M - 1)}{2\varepsilon_M + 1} \cdot \frac{\overline{m}_j}{4\pi\varepsilon_0 a_j^3} \tag{50}$$

As the reaction field depends on the total dipole moment of the considered molecule, the local field, even in average, is different for each molecular species in the mixture. For polar molecules, the local field of Onsager is much more efficient than the one of Lorentz; for apolar pure

substances, there is no difference between the two fields. Bottcher has used the Onsager theory for emulsions and has the following expression for the permittivity:

$$\varepsilon_0(\varepsilon_E - 1) = \frac{3\varepsilon_E}{2\varepsilon_E + 1}\left[\frac{N_D\alpha_D}{1 - \frac{2(\varepsilon_E-1)}{2\varepsilon_E+1}\cdot\frac{\alpha_D}{4\pi\varepsilon_0 a_D^3}} + \frac{N_C\alpha_C}{1 - \frac{2(\varepsilon_E-1)}{2\varepsilon_E+1}\cdot\frac{\alpha_C}{4\pi\varepsilon_0 a_C^3}}\right]$$
(51)

Or more simply:

$$\frac{(\varepsilon_E - \varepsilon_C)(2\varepsilon_E + \varepsilon_D)}{3\varepsilon_E} = \varphi_D(\varepsilon_D - \varepsilon_C) \qquad (52)$$

This expression is symmetric and leads to values of permittivity always greater than the ones calculated from (57) of Clausius-Mosotti. The greater the difference between the permittivities of two phases is, the greater the difference between the results of the two theories will be.

On another hand, like the previous model, the symmetric way the dispersed and continuous phase were treated limits the application of Onsager's results for the emulsions.

### c. Clausius-Mosotti Theory of a Pure Substance Adapted to the Emulsions

The asymmetry of the emulsion can be taken into account by the theory of Clausius-Mosotti if the emulsion is considered as a pure material made of "molecules" with a permittivity $\varepsilon_D$ but put in a continuous system of permittivity $\varepsilon_C$ and not in vacuum (Fig. 2.6).

The equation (41) becomes:

$$\overline{E}_2 = \frac{1}{3\varepsilon_0\varepsilon_C}(\overline{P}_{exp} - \overline{P}_{int}) = \frac{1}{3\varepsilon_0\varepsilon_C}$$
$$[\varepsilon_o(\varepsilon_E - 1) - \varepsilon_o(\varepsilon_C - 1)]\overline{E} = \frac{\varepsilon_E - \varepsilon_C}{3\varepsilon_C}\cdot\overline{E} \qquad (53)$$

which is the field of the full cavity of the continuous system $\varepsilon_C$ due to the distributions of the external and internal charges on its surface.

The local field is then:

$$\overline{F} = \overline{E} + \overline{E}_2 = \frac{\varepsilon_E + 2\varepsilon_C}{3\varepsilon_C}\overline{E} \qquad (54)$$
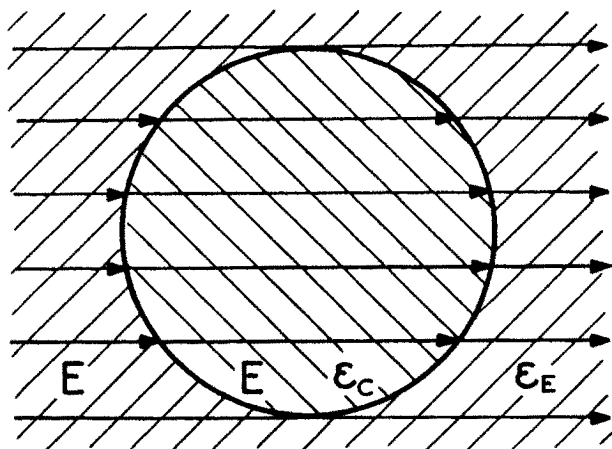
**Figure 2.6  Clausius-Mossotti asymmetrical model.**

and the apparent moment of the micelle:

$$m^* = \alpha^* F \tag{55}$$

where:

$$\alpha^* = \frac{\varepsilon_D - \varepsilon_C}{\varepsilon_D + 2\varepsilon_C} 4\pi\varepsilon_0\varepsilon_C a^3 \tag{56}$$

is the apparent polarizability of a sphere of radius " $a$ " and permittivity $\varepsilon_D$, put in a continuous system of permittivity $\varepsilon_C$. The equation (37) becomes:

$$\varepsilon_0(\varepsilon_E - 1)E - \varepsilon_0(\varepsilon_C - 1)E = N_D m^* \tag{57}$$

because the existence of micelles determines the variation of permittivity of the continuous system $\varepsilon_C$. The condition:

$$\frac{4\pi}{3}a^3 = \frac{\varphi_D}{N_D} \tag{58}$$

finally leads to the result:

$$\varepsilon_0(\varepsilon_E - \varepsilon_C)E = \varphi_D \frac{3}{4\pi a^3} 4\pi\varepsilon_0\varepsilon_C a^3 \frac{\varepsilon_D - \varepsilon_C}{\varepsilon_D + 2\varepsilon_C} \cdot \frac{\varepsilon_E + 2\varepsilon_C}{3\varepsilon_C} E \tag{59}$$
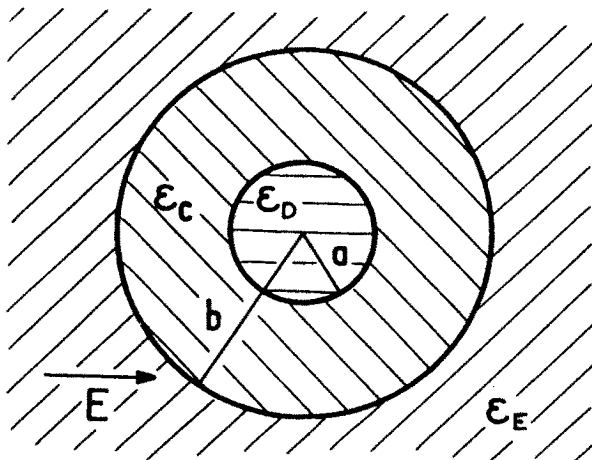
**Figure 2.7  Model with spherical shell.**

or

$$\varepsilon_E = \varepsilon_C \left[ \frac{\varepsilon_D 2\varepsilon + 2\varepsilon_C + 2\varphi_D(\varepsilon_D - \varepsilon_C)}{\varepsilon_D + 2\varepsilon_C - \varphi_D(\varepsilon_D - \varepsilon_C)} \right] \tag{60}$$

which is the result of Wagner (2.2c).

## d. Onsager Theory of a Pure Substance Adapted to the Emulsions

As the previous theory the emulsion is considered as a pure material of "molecules" with a permittivity $\varepsilon_D$ and a radius $a$, put in a continuous system with a permittivity $\varepsilon_C$ (Fig. 2.7).

The local field (48), (49), (50), is

$$\overline{F} = \overline{C} + \overline{R} \tag{61}$$

$$\overline{C} = \frac{3\varepsilon_E}{2\varepsilon_E + \varepsilon_C} \overline{E} \tag{62}$$

$$\overline{R} = \frac{2(\varepsilon_E - \varepsilon_C)}{2\varepsilon_E + \varepsilon_C} \frac{m^*}{4\pi\varepsilon_0\varepsilon_C b^3} \tag{63}$$

Where $b$ can be determined by:

$$\frac{4\pi}{3} b^3 = \frac{1}{N_D} = \frac{4\pi}{3} \frac{a^3}{\varphi_D} \tag{64}$$

The apparent moment of the micelles $m^* = \alpha^* F$, where $\alpha^*$ can be obtained by (38), is:

$$m^* = \frac{\alpha^* C}{1 - \frac{\alpha^* R}{m^*}} = \frac{4\pi\varepsilon_0\varepsilon_C a^3 \cdot \frac{\varepsilon_D - \varepsilon_C}{\varepsilon_D + 2\varepsilon_C} \cdot \frac{3\varepsilon_E}{2\varepsilon_E + \varepsilon_C} \cdot E}{1 - 4\pi\varepsilon_0\varepsilon_c a^3 \cdot \frac{\varepsilon_D - \varepsilon_C}{\varepsilon_D + 2\varepsilon_C} \cdot \frac{2(\varepsilon_E - \varepsilon_C)}{2\varepsilon_E + \varepsilon_C} \cdot \frac{\varphi_D}{4\pi\varepsilon_0\varepsilon_C a^3}} \quad (65)$$

The permittivity is finally determined by the expression of the variation of the polarization due to the presence of micelles:

$$\varepsilon_0(\varepsilon_E - 1)E - \varepsilon_0(\varepsilon_C - 1)E = \frac{3\varphi_D}{4\pi a^3} m^* \quad (66)$$

which leads again to the result of Wagner (2.2c):

$$\varepsilon_E = \varepsilon_C \left[ \frac{\varepsilon_D + 2\varepsilon_C + 2\varphi_D(\varepsilon_D - \varepsilon_C)}{\varepsilon_D + 2\varepsilon_C - \varphi_D(\varepsilon_D - \varepsilon_C)} \right] \quad (67)$$

The fact that the results (60) and (67) are identical, and that (47) and (52) are different, is well known; indeed, it comes from the fact that the theories of Clausius-Mosotti and of Onsager lead to the same result for pure apolar substances and to different results for apolar mixtures.

The equality of the results of these two theories, (60) or (67), and of the result of Wagner, seems to confirm the validity of (11) for low concentrations, as the expression does not seem to depend on the model chosen.

## 2.4 General Theories

The theories [31] quoted in this chapter have been established to obtain expressions of the permittivity for general systems with two components. This means that these theories can be applied to continuous-continuous systems, to continuous-dispersed systems or to dispersed-dispersed systems. The generality of these theories is their weakest characteristic because for any permittivity of the two components and for their concentration, for each system considered there are different permittivities.

## a. Lichtenecker-Rother Theory [31]

By this theory, we can obtain an expression of the permittivity of a system with two components with mathematical hypotheses on the function $\varepsilon_E = \varepsilon_E(\varepsilon_D, \varepsilon_C, \varphi_D)$. These hypotheses are:

 i) the function $\varepsilon_E$ is continuous, monotonic and derivable with reference to 3 variables $\varepsilon_D, \varepsilon_C, \varphi_D$.

 ii) the function $\varepsilon_E$ is homogeneous and is of order one with reference to the variables: $\varepsilon_D$ and $\varepsilon_C$, this means:

$$\varepsilon_E(h\varepsilon_D, h\varepsilon_C, \varphi_D) = h\varepsilon_E(\varepsilon_D, \varepsilon_C, \varphi_D) \tag{68}$$

where $h$ is a constant.

 iii) the mixture formula is applicable to a mixture of mixtures. So, if two emulsions are mixed together with a permittivity:

$$\varepsilon_{E1} = \varepsilon_E(\varepsilon_D, \varepsilon_C, \varphi_{D1})$$

and

$$\varepsilon_{E2} = \varepsilon_E(\varepsilon_D, \varepsilon_C, \varphi_{D2}) \tag{69}$$

this leads to a new emulsion whose apparent permittivity is:

$$\varepsilon_E = \varepsilon_E(\varepsilon_{E1}, \varepsilon_{E2}, \varphi_1) = \varepsilon_E(\varepsilon_D, \varepsilon_C, \varphi_D) \tag{70}$$

In this expression, $\varphi_1$ is the volumic fraction occupied by the emulsion 1 in the final emulsion and is related to $\varphi_D$ by:

$$\varphi_D = \varphi_1\varphi_{D1} + (1 - \varphi_1)\varphi_{D_2} \tag{71}$$

The two first hypotheses seem obvious and they are verified by all the expressions of the permittivity of the emulsions, except the one of Kubo-Nakamura (2.2f). But, the third hypothesis may be criticized because of the emulsion of permittivity $\varepsilon_E$, does not form micelles in the continuous system made of the emulsion of permittivity $\varepsilon_{E2}$. Naturally, this objection does not make any meaning if we do not take into account the action of the fine structure of the dielectric on the permittivity. The only expressions that follow the three previous hypotheses are:

$$\varepsilon_E^k = \varphi_D \varepsilon_D^k + (1 - \varphi_D)\varepsilon_C^k \tag{72}$$

where $k$ is a constant, not equal to zero, and:

$$\ln \varepsilon_E = \varphi_D \ln \varepsilon_D + (1 - \varphi_D) \ln \varepsilon_C \qquad (73)$$

It is the second formula that seems the best adapted to the experimental data on the mixtures and had previously been proposed empirically before being established. The equation (72) is interesting because it allows us to find the limit formulas of Wiener (2.2a) respectively when $k = -1$ (3) and $k = 1$ (4); and when $k = 1/3$, we can find the formulas of Landau-Lifshitz and of Looyenga that we are about to see.

## b. Landau and Lifshitz Theory

This theory [32] allows one to obtain an expression of the permittivity of a very general system with two components. However, this theory is correct only if the permittivities of two components are quite close. In this case, we can write:

$$\begin{aligned} \varepsilon_D &= \bar{\varepsilon} + \delta\varepsilon_D \\ \varepsilon_C &= \bar{\varepsilon} + \delta\varepsilon_C \end{aligned} \qquad (74)$$

were $\bar{\varepsilon}$ is the average value of the permittivity:

$$\bar{\varepsilon} = \varphi_D \varepsilon_D + (1 - \varphi_D)\varepsilon_C \qquad (75)$$

Whereas $\delta\varepsilon_D$ and $\delta\varepsilon_C$ are respectively the difference between the permittivities of the two phases and its average. The permittivity of the emulsion is then calculated from the definition of the displacement vector:

$$\overline{D} = \varepsilon_E \overline{E} \qquad (76)$$

where the cross-bar represents an average taken over the whole of the volume. This definition can be written, like:

$$\overline{D} = \overline{(\bar{\varepsilon} + \delta\varepsilon)(\overline{E} + \delta E)} \qquad (77)$$

where $\varepsilon$ is the permittivity in a point of the emulsion, this means that $\varepsilon$ is either equal to $\varepsilon_C$ or $\varepsilon_D$; The fundamental condition is that:

$$\mathrm{div} D = 0 \qquad (78)$$

extended to all the emulsion volume. This leads to the following result, correct at the second order in $\delta_\varepsilon$ :

$$\varepsilon_E = \bar{\varepsilon} - \frac{\varphi_D(\delta\varepsilon_D)^2 + (1 - \varphi_D)(\delta\varepsilon_C)^2}{3\varepsilon} \qquad (79)$$

At the same order of approximation, we can also write the result under the following expression:

$$\varepsilon_E^{1/3} = \varphi_D\varepsilon_D^{1/3} + (1 - \varphi_D)\varepsilon_C^{1/3} \qquad (80)$$

because (79) and (80) at the second order in $\varepsilon_D - \varepsilon_C$, lead to:

$$\varepsilon_E = \varepsilon_C + \varphi_D(\varepsilon_D - \varepsilon_C) - \frac{\varphi_D(1 - \varphi_D)(\varepsilon_D - \varepsilon_C)^2}{3[\varepsilon_C + \varphi_D(\varepsilon_D - \varepsilon_C)]} \qquad (81)$$

The denominator of the last term has been put equal to $\bar{\varepsilon}$ to show the symmetry of the expression, but it could have been put equal to $\varepsilon_C$ or $\varepsilon_D$, because this would have only brought changes at the third order in $\delta\varepsilon$. The applicability of these expressions to the emulsions is limited by the condition on the permittivities of the two phases which need to be very close.

However, (81) is a test to verify all the other expressions which must be equal to this equation when $\varepsilon_D \approx \varepsilon_C$. In this case, it points out that the asymmetry of the emulsion has hardly no effect on the permittivity.

A similar treatment has been done by W. F. Brown, Jr. [38], who obtains the same expression (81) but with a term of order 3 of $\delta\varepsilon$. But this term, which depends of geometrical factors, can't be calculated in practice.

## c. Looyenga Theory

This theory [33] considers an homogeneous emulsion as the succession of regions whose concentrations are slightly different. The permittivities of these regions are: $\varepsilon_E + \Delta\varepsilon_E$, and: $\varepsilon_E - \Delta\varepsilon_E$, whereas the volumic fractions are respectively: $\varphi^+$, and $1 - \varphi^+$. The concentrations in the dispersed phase in the whole of the emulsion $(\varphi_D)$, and each of the regions $(\varphi_D^+$ and $\varphi_D^-)$ are all connected by the condition of conservation for the dispersed phase:

$$\varphi_D = \varphi^+\varphi_D^+ + (1 - \varphi^+)\varphi_D^- \qquad (82)$$

The value of $\varphi^+$ originates from the fact that the permittivity of a system of regions must be equal to $\varepsilon_E$. Therefore, in our case, we can use (81) of Landau-Lifshitz (2.4b). This bring us:

$$\varepsilon_E = \varepsilon_E - \Delta\varepsilon_E + \varphi^+ 2\Delta\varepsilon_E - \frac{4(\Delta\varepsilon_E)^2\varphi^+(1-\varphi^+)}{3\varepsilon_E} \tag{83}$$

and at the first order in $\Delta\varepsilon_E$:

$$\varphi^+ = \frac{1}{2} + \frac{\Delta\varepsilon_E}{6\varepsilon_E} \tag{84}$$

By using (82), we come to:

$$\frac{\varphi_D - \varphi_D^-}{\varphi_D^+ - \varphi_D^-} = \frac{1}{2} + \frac{\Delta\varepsilon_E}{6\varepsilon_E} \tag{85}$$

We must give an expression of $\varphi_D^+$ and $\varphi_D^-$ with reference to $\Delta\varepsilon_E$. Let's consider the following expressions at the second order:

$$\varphi_D^+ = \varphi_D + \frac{d\varphi_D}{d\varepsilon_E}\Delta\varepsilon_E + \frac{1}{2}\frac{d^2\varphi_D}{d\varepsilon_E^2}(\Delta\varepsilon_E)^2$$

$$\varphi_D^- = \varphi_D - \frac{d\varphi_D}{d\varepsilon_E}\Delta\varepsilon_E + \frac{1}{2}\frac{d^2\varphi_D}{d\varepsilon_E^2}(\Delta\varepsilon_E)^2 \tag{86}$$

By combining these expressions with (85), we come to the differential equation for $\varphi_D$:

$$3\varepsilon_E\frac{d^2\varphi_D}{d\varepsilon_E^2} + 2\frac{d\varphi_D}{d\varepsilon_E} = 0 \tag{87}$$

whose solution is:

$$\varphi_D = C_1\varepsilon_E^{1/3} + C_2 \tag{88}$$

where the integration constants are calculated from the values give again $\varepsilon_E$ respectively for $\varphi_D = 0$ and $\varphi_D = 1$. This gives us:

$$\varepsilon_E^{1/3} = \varphi_D\varepsilon_D^{1/3} + (1 - \varepsilon_D)\varepsilon_C^{1/3} \tag{89}$$

This result is the same as the one of Landau-Lifshitz's, (80), and the one of Lichtenecker-Rother, (72), with $k = 1/3$. This is not surprising because Looyenga starts by representing an emulsion as regions of different concentrations and then determines the permittivity of this system by the equation of Landau-Lifshitz. This leads us again to the equation of Landau-Lifshitz, but for the components of the emulsion. Therefore, Looyenga's treatment follows the third theory of Lichtenecker-Rother. It is interesting to point out the fact that (84) of Landau-Lifshitz can be calculated from the expressions of Onsager-Bottcher (52), of Bruggeman (22) or of Wiener-Wagner (5; 11), because they are all equal to (81) when $\varepsilon_D \approx \varepsilon_C$.

## 2.5 Comparison Between Different Theories

A comparison between different theories that have been previously quoted, is difficult because of the very different formulations used. Therefore, it seems worthwhile to find a method which allows us to deduce the different results from a single model. This is possible with the theories we are about to see.

### a. General Theory of Reynolds-Hugh

This theory [37] does not lead to a new expression of the permittivity of an emulsion. But it leads to a general expression from which many existing equations can be deduced. This is very interesting because it allows us to compare the different hypothesis or approximations made in the different theories. It is very simple to obtain the general formula.

The electric field, related to the tension applied to the measuring cell by geometrical factors, is in fact an average over the volume:

$$\overline{E} = \varphi_D \overline{E}_D + (1 - \varphi_D)\overline{E}_C \tag{90}$$

where $\overline{E}_C$ is the average field over the volume occupied by the continuous phase and $\overline{E}_D$ over the volume of the dispersed phase.

The average electric displacement is:

$$\varepsilon_0 \varepsilon_E \overline{E} = \varphi_D \varepsilon_0 \varepsilon_D \overline{E}_D + (1 - \varphi_D)\varepsilon_0 \varepsilon_C \overline{E}_C \tag{91}$$

Combined these two equations can be written as:

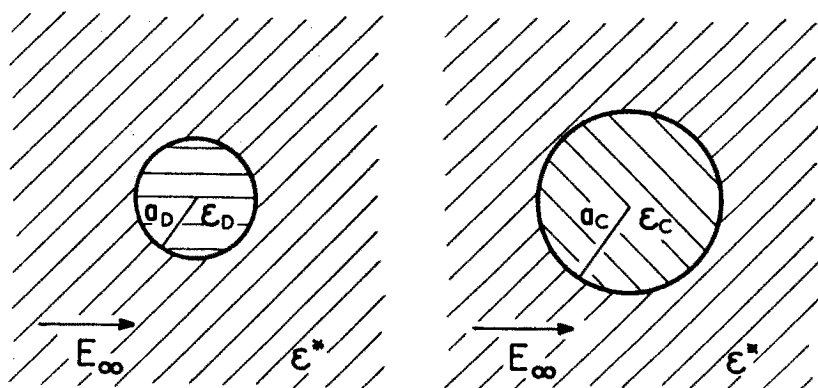$$\varepsilon_E = \varepsilon_C + \frac{\overline{E}_D}{E}(\varepsilon_D - \varepsilon_C)\varphi_D \tag{92}$$

**Figure 2.8 Reynolds-Hugh model. Separate treatment of spheres of permittivity $\varepsilon_D$ and $\varepsilon_C$ in a continuous system of permittivity $\varepsilon^*$.**

$$\varepsilon_E = \varepsilon_D + \frac{\overline{E}_C}{E}(\varepsilon_D - \varepsilon_C)(1 - \varphi_D) \tag{93}$$

and

$$\frac{\overline{E}_D}{E}(\varepsilon_E - \varepsilon_D)\varphi_D + \frac{\overline{E}_C}{E}(\varepsilon_E - \varepsilon_C)(1 - \varphi_D) = 0 \tag{94}$$

which are the general expressions of Reynolds-Hugh. These three equations should be identical but, the first two are asymmetric and third one is symmetric. Therefore, when approximations are used to determine the ratio between the average fields, the first equation leads to more adapted relationships for emulsions, and the third one for apolar-apolar mixtures. The general model for the determination of the ratio $\overline{E}_D/\overline{E}$ or $\overline{E}_C/\overline{E}$ considers a sphere of permittivity $\varepsilon_D$ or $\varepsilon_C$ in a continuous system of permittivity $\varepsilon^*$ in a long distance uniform field $E_\infty$ (Fig. 2.8).

Then, (92) and (93) become:

$$\varepsilon_E = \varepsilon_C + \frac{3\varepsilon^*}{2\varepsilon^* + \varepsilon_D}\frac{E_\infty}{E}(\varepsilon_D - \varepsilon_C)\varphi_D \tag{95}$$

$$\varepsilon_E = \varepsilon_D + \frac{3\varepsilon^*}{2\varepsilon^* + \varepsilon_C}\frac{E_\infty}{E}(\varepsilon_D - \varepsilon_C)(1 - \varphi_D) \tag{96}$$

And (94):

$$\frac{3\varepsilon^*}{2\varepsilon^* + \varepsilon_C} \frac{E_\infty}{E}(\varepsilon_E - \varepsilon_C)(1 - \varphi_D) + \frac{3\varepsilon^*}{2\varepsilon^* + \varepsilon_D} \frac{E_\infty}{E}(\varepsilon_E - \varepsilon_D)\varphi_D = 0 \quad (97)$$

or:

$$\frac{\varepsilon_E - \varepsilon_C}{2\varepsilon^* + \varepsilon_E} = \frac{\varepsilon_D - \varepsilon_C}{2\varepsilon^* + \varepsilon_D}\varphi_D \qquad (98)$$

As we will see, the choice of the values of $\varepsilon^*$ and $E_\infty$ makes the difference between the models. The following theory gives a physical interpretation of the continuous system of permittivity $\varepsilon^*$.

## b. de Loor Theory

This theory [39] is similar to the one of Onsager-Bottcher because the emulsion's permittivity is calculated with the local field of Onsager, but the permittivity of the continuous system which surrounds the micelles, is not considered equal to $\varepsilon_E$ but equal to an unknown value $\varepsilon'$.

The equation of the permittivity is:

$$\varepsilon_E = \varepsilon_C + \frac{3\varepsilon'}{2\varepsilon' + \varepsilon_D}(\varepsilon_D - \varepsilon_C)\varphi_D \qquad (99)$$

For $\varepsilon' = \varepsilon_E$, this expression is equal to the equation of Onsager-Bottcher, whereas for $\varepsilon' = \varepsilon_C$, it is equal to the limiting equation of Landau-Lifshitz (36). Generally, $\varepsilon'$ is a function of the concentration and, for de Loor it measures the interactions between the micelles: for $\varepsilon' = \varepsilon_C$, the interactions do not exist; for $\varepsilon' = \varepsilon_E$, they are maximum. But this interpretation is not rigorous because, without any interaction, the emulsion's permittivity is given by Wagner's formula (11) and not by Landau-Lifshitz's formula (36). These two expressions are identical only for very low values of $\varphi_D$ as we will see in (2.8).

De Loor's model is very close to the one of Reynolds-Hugh as (99) and (95) are very similar. The only difference is the term $E_\infty/\overline{E}$ which allows us to explain the interaction between micelles using $\varepsilon^*$ instead of $\varepsilon'$. The principal advantage of de Loor's theory is the calculation, for spherical micelles, of the permittivity $\varepsilon'$ thanks to (99) with the experimental measures of $\varepsilon_E$, $\varepsilon_D$, $\varepsilon_C$ and $\varphi_D$. This gives the value of $\varepsilon'$, which are always between $\varepsilon_C$ and $\varepsilon_E$. The permittivity

$\varepsilon'$ is equal to $\varepsilon_C$ when $\varphi_D$ tends toward zero and becomes different when $\varphi_D$ increases as long as the ratio $\varepsilon_D/\varepsilon_C$ gets higher. This shows that Wagner's theory underestimates the interactions, and Onsager-Bottcher's theory overestimates them. Therefore, a treatment as the one of Bruggeman where the permittivity of the continuous system surrounding the micelles varies during the integration between the limits $\varepsilon_C$ and $\varepsilon_D$, must lead to a better harmony with the experimental data.

## c. Comparison Between the Different Models

For very low concentrations in the dispersed phase, a good representation of the emulsion is naturally obtained for $\varepsilon^* = \varepsilon_C$ and $E_\infty = \overline{E}$. In this case, (95) leads to the limit formula (36) of Landau-Lifshitz, whereas (98) becomes (11) of Wagner. The choice of $\varepsilon^* = \varepsilon_C$ for the calculation of $\overline{E}_D$ and $\overline{E}_C$ leads to these two asymmetric results.

For increasing values of $\varphi_D$, the hypothesis $\varepsilon^* = \varepsilon_C$ can be maintained but this means neglecting, the interactions between micelles. But, the approximation of saying that the field $E_\infty$ in the continuous system is equal to the field $E$ can not be kept. Let's consider $\varepsilon^* = \varepsilon_C$ and $E_\infty = \overline{E}_C$ so that;

$$\overline{E}_D = \frac{3\varepsilon_C}{2\varepsilon_C + \varepsilon_D}\overline{E}_C \tag{100}$$

and from (34)

$$\frac{\overline{E}_C}{E} = \frac{2\varepsilon_C + \varepsilon_D}{2\varepsilon_C + \varepsilon_D - \varphi_D(\varepsilon_D - \varepsilon_C)} \tag{101}$$

From this point (95) and (98) lead to the same expression (11) of Wagner.

For high $\varphi_D$, it is not possible to neglect the interactions between the micelles. In this cases, (95) and (98) lead to the same expressions (18) of Onsager-Bottcher. These two results are symmetric because the choices $\varepsilon^* = \varepsilon_E$ and $E_\infty = \overline{E}$ for the calculation of $\overline{E}_D$ and $\overline{E}_C$ give the same importance to the two phases.

The results of Clausius-Mosotti cannot be obtained from (95) or (98). It can be deduced from Reynolds-Hugh's theory only if the value of $\varepsilon^*$ used in the calculation of $\overline{E}_D$ is different the one used for $\overline{E}_C$. Equation (94) leads to the expression of Clausius-Mosotti when considering the calculation of $\overline{E}_D$ that:

$$\varepsilon^* = \frac{\varepsilon_D(\varepsilon_E + 2)}{3(\varepsilon_D - \varepsilon_E) + \varepsilon_E + 2} \tag{102}$$

in the calculation of $\overline{E}_C$ where:

$$\varepsilon^* = \frac{\varepsilon_C(\varepsilon_E + 2)}{3(\varepsilon_C - \varepsilon_E) + \varepsilon_E + 2} \tag{103}$$

Finally in the two cases: $E_\infty = \overline{E}$.

The theory of Reynolds-Hugh does not allow us to deduce the results of Bruggeman (2.2e), of Kubo-Nakamura (2.2f), the logarithmic formula of Lichtenecker-Rother (73), nor the result of Landau-Lifshitz-Looyenga (2.4c).

This shows that by comparison, the fundamental equations, those that correspond to the most reasonable approximations, are the equations of Wagner and of Onsager. But, the necessary hypothesis on the values of $\varepsilon^*$ for the calculation of the equation of Clausius-Mosotti seems totally arbitrary.

In the Wagner model, the hypotheses $\varepsilon^* = \varepsilon_C$ shows clearly that the interactions between micelles are not taken into account. But, the hypothesis $\varepsilon^* = \varepsilon_E$ in the Onsager model shows that the interactions between micelles are overestimated.

Consequently the models of Bruggeman and Kubo-Nakamura are the most accurate because the interpretation method used corresponds to a continuous variation of $\varepsilon^*$ between the extreme values $\varepsilon_C$ and $\varepsilon_E$. Two other approaches, with the same goal, are given in the next section.

## 2.6 Importance of the Spherical Symmetry in the Calculation of the Dielectric Permittivity

Between all the theories we have examined, Wagner's theory (2.2c) seems to be the closest to reality. However, it can only be used for low concentrations. An extension to the higher concentrations needs to take into account the interactions between micelles. They are clearly considered in the Rayleigh models (2.2b), but with the hypothesis of a cubic distribution, and in the one of Higuchi (2.2d) with an unknown parameter. They are tacitly considered in the theories of Bruggeman (2.2e) and of Kubo-Nakamura (2.2f) but the integration methods used

do not give a satisfactory physical interpretation. The method of Reynolds-Hugh (2.5a), combined with the conclusion of the one of De Loor (2.5b) on the value of $\varepsilon'$ —which means that it is always between $\varepsilon_C$ and $\varepsilon_E^-$ —suggests another emulsion model which leads to the calculation of $\overline{E}_D/\overline{E}$ and: $\overline{E}_C/\overline{E}$. Let's consider Fig. 2.7 when the micelle is surrounded by a layer of dispersed phase and when there is a field $E_\infty = \overline{E}$ after the continuous system. This model seems intermediate between the one of Wagner and the one of Onsager-Bottcher (2.3b); however, when the expression of the permittivity is calculated with the symmetric expression (94) or with any other asymmetric equations (92) or (93), we always obtain the equation of Wagner. This has a very simple explanation. Indeed the Wagner model is based on the comparison between the dielectric behavior of a large sphere of emulsion and an identical sphere of a continuous system of permittivity $\varepsilon_E$ (Fig. 2.4).

However, in this model, the interactions between micelles are neglected and therefore, we come to the same results if the large micelle contains just one micelle. This is true only if the radius is determined by the equation so that the internal composition is equal to the average composition of the emulsion and if the micelle is in its center so that the external potential is equal to a pin-point dipole at the origin (Fig. 2.8).

To compare the dielectric behavior of the two spheres of Fig. 2.2 in a field, Wagner considers that they are in a continuous system of permittivity $\varepsilon_C$. This choice is of no importance on the final result which can be obtained when considering the spheres of Fig. 2.9 in a vacuum or in a continuous system of permittivity $\varepsilon_E$. This last possibility is, however, quite interesting: the model can now be interpreted as a representation of the whole emulsion and, in this expression, the interactions between micelles exist and are given in a field due to the external dielectric of permittivity $\varepsilon_E$.

These interactions do not affect the result because, on the average the fields of the other micelles compensate themselves exactly in the center. The interactions between micelles can be approximately taken into account if we do not consider the spherical symmetry.

### a. Chosen Model

Let's consider an emulsion as a homogeneous continuous system of permittivity $\varepsilon_E$, surrounding a spherical fraction where the dispersed
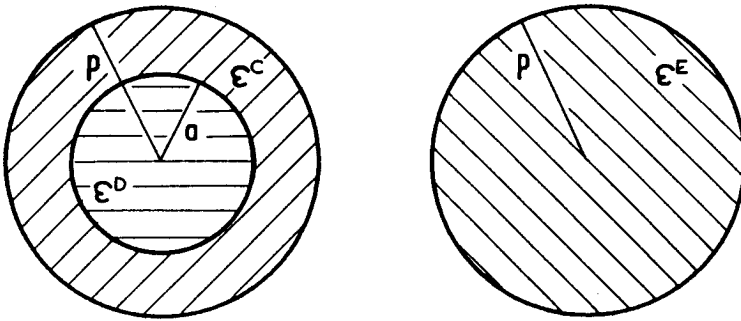
**Figure 2.9 Wagner model. Identification between a model with spherical shell and the equivalent large sphere.**
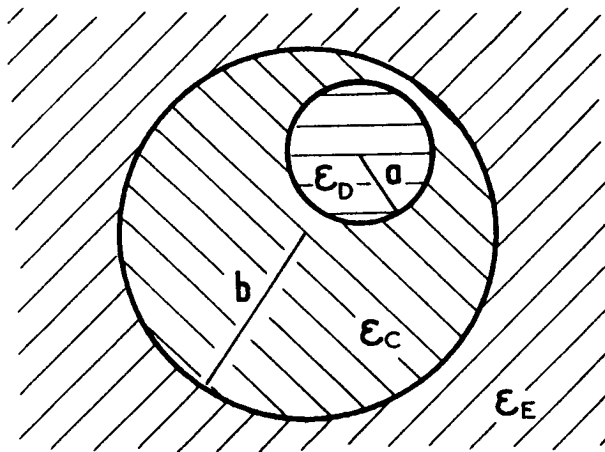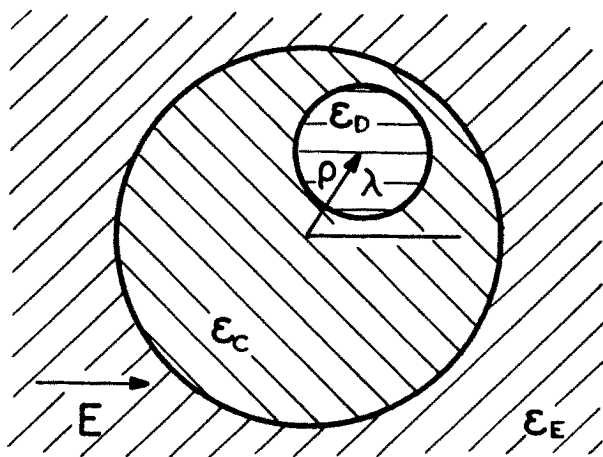


**Figure 2.10 New proposed model.**

**Figure 2.11** Statistics for all the distance $\rho$ from 0 to $b - a$ and $\lambda$ all angles from 0 to $\pi$.

and continuous phases are separated (Fig. 2.10).

$$\frac{4\pi}{3}a^3 \Big/ \frac{4\pi}{3}b^3 = \varphi_D \tag{104}$$

This condition insures that the local composition is equal to the average composition. This allows the determination of the expression of the dielectric constant while comparing the behavior of this model when the whole of the dielectric is in a macroscopic field $\overline{E}$, with the behavior of a sphere of radius $b$ full of a continuous system of permittivity $\varepsilon_E$. In this last case, the external field of the sphere of radius $b$ is naturally uniform. But, in this model, the field is not and depends on the position of the micelle. Therefore, the fact that the average external field is equal to the uniform field $\overline{E}$, is the condition to draw to calculate the apparent permittivity: the average must consider all the possible positions of the micelle in the sphere of radius $b$.

The expression of the permittivity of an emulsion is obtained by the following method.

Let's consider a specific configuration of the micelle in the sphere of radius $b$, with a distance to the center $\rho$ and angle $\lambda$ between the direction of this distance and the direction of the applied field

(Fig. 2.11). Then, the external dipole moment $M^*(\rho, \lambda)$ of the sphere of radius $b$ is determined. The average value of this moment in the direction of the applied field is calculated. This average for all the possible positions, equally probable of the micelle, is given by the average scalar product:

$$\langle \overline{M}^* \cdot \overline{E} \rangle = \frac{1}{(4\pi/3)(b-a)^3} \int_0^\pi \int_0^{b-a} (M^*(\rho, \lambda) \cdot \overline{E}) 2\pi \rho^2 \cdot \sin \lambda \cdot d\lambda d\rho$$

(105)

The bounds of the integration have been chosen so that the entire volume of the micelle is in the sphere of radius $b$.

We can deduce the expression of the apparent permittivity $\varepsilon_E$ from the condition that, on average, the external field must be uniform. Therefore:

$$\langle \overline{M}^* \cdot \overline{E} \rangle = 0$$

(106)

because the average moment $\overline{M}^*$ over all the other components and the average over all the multipolar terms at the higher order are equal to zero, due to the axial and unidirectional symmetry of this problem. In fact, the difficulty is the calculation of $\overline{M}^*(\rho, \lambda)$. Therefore, we must first determine the external moment of the micelle $m^*(\rho, \lambda)$. It can be approximated to:

$$\overline{m}^*(\rho, \lambda) = (\overline{C} + \overline{R})_{\alpha^*}$$

(107)

where $\overline{(C + R)}$ is the average local field over the micelle and $\alpha^*$ is the external polarizability of the sphere of permittivity $\varepsilon_D$ in a continuous system of permittivity $\varepsilon_C$ and given by (109):

$$\alpha^* = \frac{\varepsilon_D - \varepsilon_C}{\varepsilon_D + 2\varepsilon_C} 4\pi\varepsilon_0\varepsilon_C a^3$$

(108)

As the local field $\overline{C} + \overline{R}$ depends on the moment $\overline{m}^*(\rho, \lambda)$, it can be determined from the general configuration of the model by replacing the micelle by a pinpoint dipole $\overline{m}^*$ considered known (Fig. 2.12).

The cavity field $\overline{C}$, which is uniform and does not depend on $\overline{m}^*$, is:

$$\overline{C} = \frac{3\varepsilon_E}{2\varepsilon_E + \varepsilon_C} \overline{E}$$

(109)

whereas the field $\overline{R}$, which is non uniform and does not depend on $\overline{E}$, can be calculated if the dipole $\overline{m}^*$ is replaced by a multipolar series
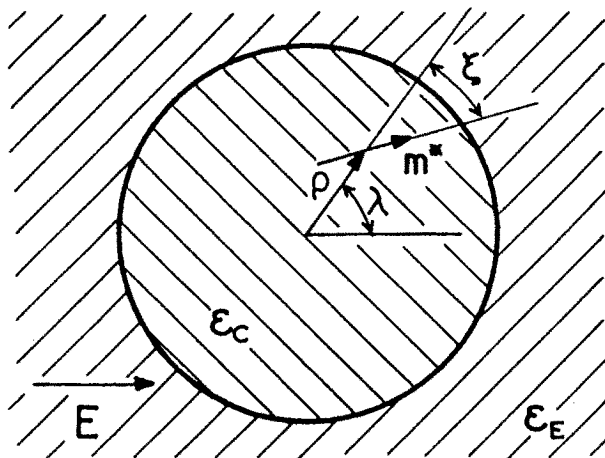
**Figure 2.12  The micelle is replaced by an equivalent micelle $m^*$.**

at the center, chosen so that the field produced outside the sphere of radius $b$ is equal to the dipole, which has been decentered.

Once the local field has been determined as a function of $\overline{m}^*$, we can calculate its average over the volume of the micelle and obtain the value of the dipole moment when accepting the validity of (107).

Finally, $\overline{M}^*(\rho, \lambda)$ is obtained from $\overline{m}^*(\rho, \lambda)$ by this expression:

$$\overline{M}^*(\rho, \lambda) = \frac{\varepsilon_C - \varepsilon_E}{\varepsilon_C + 2\varepsilon_E} 4\pi\varepsilon_0 b^3 \overline{E} + \frac{3\varepsilon_E}{\varepsilon_C + 2\varepsilon_E} \overline{m}^*(\rho, \lambda) \qquad (110)$$

where the first term corresponds to the external moment of the large sphere polarized by the applied field, and the second to the external field of the dipole $\overline{m}^*(\rho, \lambda)$ in the center. As we will see, the difference between the decentered dipole field and the one of a dipole in the center corresponds to the multipolar terms at an order greater than two that do not contribute any more to the value of $\overline{M}^*$.

### b. Reaction Field in the Center of the Micelle

The multipolar series necessary to the calculation of the reaction field $\overline{R}(\overline{m}^*)$ is deduced from the consideration that only one charge $q_i$ exists in the sphere of radius $b$ (Fig. 2.13). The solution to the Laplace
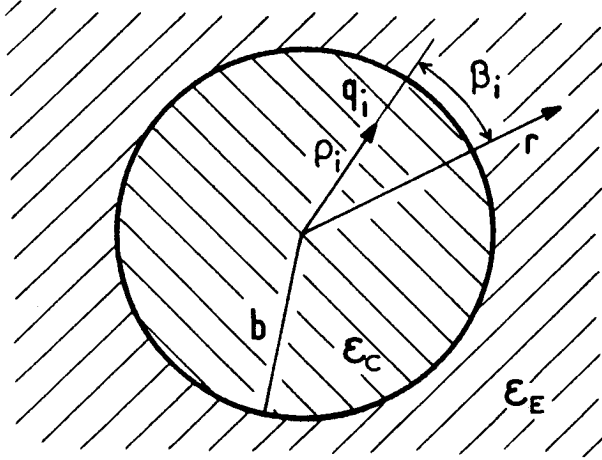
**Figure 2.13 Resolution of Laplace equation $U(r,\beta)$ with multipolar series functions of $b, q, \rho, \varepsilon_E$ and $\varepsilon_C$.**

equation leads to the potentials [40,41]:

$$U_{i\,\text{int}}(r,\beta_i) = \frac{q_i}{4\pi\varepsilon_0\varepsilon_C}\sum_{n=0}^{\infty}\left[\frac{1}{r^{n+1}} - \frac{(n+1)(\varepsilon_E - \varepsilon_C)}{(n+1)\varepsilon_E + n\varepsilon_C}\frac{r^n}{b^{2n+1}}\right]\rho_i^n P_n(\cos\beta_i)$$

$$U_{i\,\text{ext}}(r,\beta_i) = \frac{q_i}{4\pi\varepsilon_0}\sum_{n=0}^{\infty}\frac{2n+1}{(n+1)\varepsilon_E + n\varepsilon_C}\rho_i^n\frac{P_n(\cos\beta_i)}{r^{n+1}} \qquad (111)$$

This result is equal to the expression of Kirkwood [40] for the potential of an thrown off center charge in a double layer cavity.

The equation (111) of the potentials of the multipoles series in the center are different to the expression of the potential of the charge placed at the point determined by $\bar{\rho}_i$, because the terms of negative power of $r$ in $U_{i\,\text{int}}$ are not the same, as these terms were obtained with the condition that $r > \rho_i$. But the field $\bar{R}_i(r,\beta_i)$ is calculated from the terms of positive power of $r$ in $U_{i\,\text{int}}$ and this give us:

$$\bar{R}_i(r,\beta_i) = \frac{q_i}{4\pi\varepsilon_0\varepsilon_C}\sum_{n=1}^{\infty}\frac{(n+1)(\varepsilon_E - \varepsilon_C)}{(n+1)\varepsilon_E + n\varepsilon_C}\frac{r^{n-1}\rho_i^n}{b^{2n+1}}$$

$$\cdot\,[nP_n(\cos\beta_i)\bar{u}_r - \sin\beta_i P_n'(\cos\beta_i)\bar{u}_{\beta i}] \quad (112)$$

where $\bar{u}_r, \bar{u}_{\beta i}$ are the unit vectors in the directions $r$ and $\beta_i$ and the apostrophe refers to the derivation with reference to $\cos \beta_i$. Thanks to this equation, we can deduce the field $(\overline{R}_{12})_{\rho,\lambda}$ due to the charges $-q$ and $q$ are placed like on (107) at the coordinates $\rho$ and $\lambda$ :

$$(\overline{R}_{12})_{\rho,\lambda} = \frac{q_i}{4\pi\varepsilon_0\varepsilon_C} \sum_{n=1}^{\infty} \frac{(n+1)(\varepsilon_E - \varepsilon_C)}{(n+1)\varepsilon_E + n\varepsilon_C} \frac{\rho_{n-1}}{b^{2n+1}}$$
$$\cdot \left[ -\rho^n n P_n(1)u_\rho + \rho_2^n n P_n(\cos\delta)\bar{u}_\rho - \rho_2^n \sin\delta P'_n(\cos\delta)\bar{u}_\lambda \right] \quad (113)$$

The equation:

$$P_n(1) = 1$$
$$P'_n(1) = n(n+1)/2 \qquad\qquad (114)$$
$$\rho_2 = (\rho^2 + h + 2\rho\cos\xi)^{1/2} = h\sin\xi/\sin\delta$$

allows the following expression of the field:

$$(\overline{R}_{12})_{\lambda,\rho} = \frac{q}{4\pi\varepsilon_0\varepsilon_C} \sum_{n=1}^{\infty} \frac{(n+1)(\varepsilon_E - \varepsilon_C)}{(n+1)\varepsilon_E + n\varepsilon_C} \frac{\rho^{n-1}}{b^{2n+1}}$$
$$\cdot \left\{ \left[ (\rho^2 + h^2 + 2\rho h\cos\xi)^{n/2} P_n(\cos\delta) - \rho^n \right] n \right.$$
$$\left. - (\rho^2 + h^2 + 2\rho h\cos\xi P'n(\cos\delta)\bar{u}\lambda \right\} \quad (115)$$

Finally, the limit expression of this field when $h$ tends toward zero, $h.q.$ staying constant and equal to $m^*$, leads to the field $(\overline{R})_{\rho,\lambda}$ corresponding to the dipole $m^*$ and placed at the decentered point given by $\rho$ and the circulation $\xi$ (109)

$$\overline{R}(\overline{m}^*)_{\rho,\lambda} = \frac{m^*}{4\pi\varepsilon_0\varepsilon_C b^3} \sum_{n=1}^{\infty} \frac{(n+1)(\varepsilon_E - \varepsilon_C)}{(n+1)\varepsilon_E + n\varepsilon_C} \frac{\rho^{2(n-1)}}{b^{2(n-1)}}$$
$$\cdot \left[ n^2 \cos\xi\bar{u}_\rho - \frac{n(n+1)}{2} \sin\xi\bar{u}_\lambda \right] \quad (116)$$

When the dipole $\overline{m}^*$ is in the center, this means $\rho = 0$, the sum is equal to its first term and the classical expression of the reaction field is:

$$\overline{R} = \frac{m^*}{4\pi\varepsilon_0\varepsilon_C b^3} \frac{2(\varepsilon_E - \varepsilon_C)}{2\varepsilon_E + \varepsilon_C} [\cos\xi\bar{u}_\rho - \sin\xi\bar{u}_\lambda] \quad (117)$$

In a general case, this field, uniform and parallel to $\overline{m}^*$, is modified by the terms at a greater order, their relative importance given by coefficients more or less equal to $n^2(\rho/b)^{2(u-1)}$

The expression of the reaction field at the center of the micelle, (80), allows the exact calculation, with (71) and (73), of the value of the dipole moment of a pinpoint entity of polarizability $\alpha^*$ at the coordinates $\rho$ and in a sphere of radius $b$.

However, when $\alpha^*$ is determined by (108), it gives an approximate value of the apparent moment of the micelle because the field $[\overline{R}(\overline{m}^*)]\rho, \lambda$ has only been calculated at its center. Nevertheless, this field varies with $\overline{r}$ and this variation increases as rapidly as the multipolar order $n$ increases. Therefore, it would be more rigorous to calculate $m^*$ with (116) only for very low concentrations. For higher concentrations, it is better to calculate $\overline{m}^*$ with the average value of the reaction field taken over all the micelle's volume. However, this field has an expression expanded in the form of a series, whose principal term is equal to the one at the center of the micelle. Therefore, the correction brought by the more rigorous calculation is very small.

### c. Expression of the Permittivity

The expression of the local field at the center of the micelle when combining (109) and (116) allows the determination of the value of the apparent dipole moment $m^*$ thanks to the expression (Fig. 2.14):

The two components of this moment are (109):

$$m_\rho^* = \alpha^*(R_\rho + C\cos\lambda)$$

$$-m_\lambda^* = \alpha^*(-R_\lambda + C\sin\lambda) \tag{118}$$

which allow the determination of the value of the dipole moment in the direction of the field $E$.

$$\frac{\overline{m}^* \cdot \overline{E}}{E} = \alpha^* C \left[ \frac{\cos^2\lambda}{1 - \frac{\alpha^* R_\rho}{m^* \cos\xi}} + \frac{\sin^2\lambda}{1 + \frac{\alpha^* R_\lambda}{m^* \sin\xi}} \right] \tag{119}$$

or:

$$\frac{\overline{m}^* \cdot \overline{E}}{E} = \alpha^* C \left[ \frac{\cos^2\lambda}{1 - \frac{\alpha^*}{4\pi\epsilon_0\epsilon_C b^3} \sum_n \frac{n^2(n+1)(\epsilon_B - \epsilon_C)}{(n+1)\epsilon_B + n\epsilon_C} \cdot (\frac{\rho}{b})^{2(n-1)}} \right.$$

$$\left. + \frac{\sin^2\lambda}{1 - \frac{\alpha^*}{4\pi\epsilon_0\epsilon_C b^3} \sum_n \frac{(n/2)(n+1)^2(\epsilon_B - \epsilon_C)}{(n+1)\epsilon_B + n\epsilon_C} \cdot (\frac{\rho}{b})^{2(n-1)}} \right] \tag{120}$$

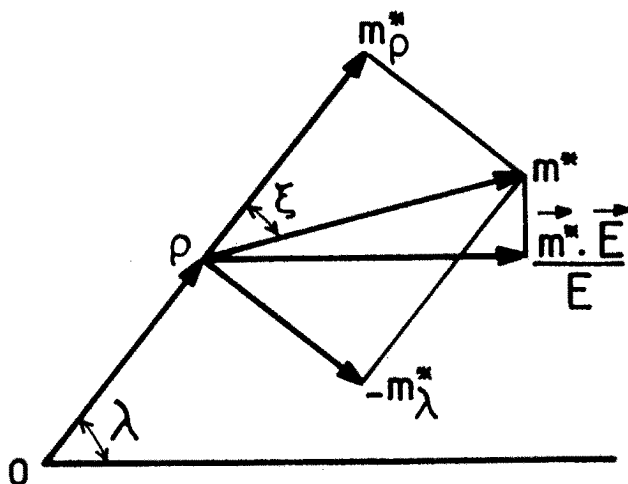**Figure 2.14  Apparent dipole $m^*$ and its components $m_\phi^*$ and $m_\lambda^*$.**

By combining this expression and (110), we can calculate $\overline{m}^*(\rho, \lambda)^* E$. The permittivity is finally determined by the condition (106) which can be written as the following expression while taking into account (110):

$$\varepsilon_E - \varepsilon_C = \frac{3}{4\pi\varepsilon_0 b^3} \frac{\overline{m}^* \cdot \overline{E}}{E^2} \tag{121}$$

This expression combined with (105), (108) and (116) gives us the final result:

$$\varepsilon_E - \varepsilon_C = \frac{(\varepsilon_D - \varepsilon_C) 9 \varepsilon_E \varepsilon_C}{(\varepsilon_D + 2\varepsilon_C)(2\varepsilon_E + \varepsilon_C)} \frac{\varphi}{(1 - \varphi^{1/3})^3}$$

$$\cdot \left[ \int_0^{1-\varphi^{1/3}} \frac{u^2 du}{1 - \frac{\varepsilon_D - \varepsilon_C}{\varepsilon_D + 2\varepsilon_C} \varphi_D \sum_n \frac{n^2(n+1)(\varepsilon_E - \varepsilon_C)}{(n+1)\varepsilon_E + n\varepsilon_C} \cdot u^{2(n-1)}} \right.$$

$$\left. +2 \int_0^{1-\varphi^{1/3}} \frac{u^2 du}{1 - \frac{\varepsilon_D - \varepsilon_C}{\varepsilon_D + 2\varepsilon_C} \varphi_D \sum_n \frac{(n/2)(n+1)^2(\varepsilon_E - \varepsilon_C)}{(n+1)\varepsilon_E + n\varepsilon_C} \cdot u^{2(n-1)}} \right] \tag{122}$$

where  $u = \rho/b$.

In a general case, this equation can only be numerically integrated. Its convergence is however quite rapid as we will see, so this allows us to choose the precision of the result.

The number of terms to take in the sums is ruled by the expansion of the scale of integration $(1 - \varphi_D^{1/3})$ whereas the relative importance is ruled by the factor $\varphi_D$.

At the limit of high concentrations of the dispersed phase, the interval of integration is very small and we must only keep the first term, which does not depend on $u$ as all the other terms cancel themselves with $u$. For decreasing concentrations, the number of terms to be kept increases but always stays definite as for any value of $u$, (as long as $u < 1$), we have $n^2(u)^{2(n-1)} = 0$

In spite of their increasing number, the relative importance of the whole of these terms goes by a maximum for medium concentrations and finally decreases for low concentrations because of the coefficient $\varphi_D$.

As a first approximation (122) leads to the result:

$$\varepsilon_E - \varepsilon_C = \frac{(\varepsilon_D - \varepsilon_C)9\varepsilon_E\varepsilon_C}{(\varepsilon_D + 2\varepsilon_C)(2\varepsilon_E + \varepsilon_C)}$$
$$\times \frac{\varphi_D}{1 - \frac{2(\varepsilon_E - \varepsilon_C)(\varepsilon_D - \varepsilon_C)}{(2\varepsilon_E + \varepsilon_C)(\varepsilon_D + 2\varepsilon_C)}\varphi_D} \quad (123)$$

or:

$$\varepsilon_E = \varepsilon_C \left[\frac{\varepsilon_D + 2\varepsilon_C + 2\varphi_D(\varepsilon_D - \varepsilon_C)}{\varepsilon_D + 2\varepsilon_C - \varphi_D(\varepsilon_D - \varepsilon_C)}\right] \quad (124)$$

The result is equal to the one of Wagner (11). As a second approximation, the integrations of (122) can be solved and gives us:

$$\varepsilon_E - \varepsilon_C = \frac{(\varepsilon_D - \varepsilon_C)9\varepsilon_E\varepsilon_C}{(\varepsilon_D + 2\varepsilon_C)(2\varepsilon_E + \varepsilon_C)} \frac{\varphi_D}{1 - \frac{2(\varepsilon_E - \varepsilon_C)(\varepsilon_D - \varepsilon_C)}{(2\varepsilon_E + \varepsilon_C)(\varepsilon_D + 2\varepsilon_C)}\varphi_D}$$
$$\times \left[\frac{1}{4\Delta}\left[\frac{1}{\sqrt{4\Delta}}\frac{1}{2}\ln\frac{1 + \sqrt{4\Delta}}{1 - \sqrt{4\Delta}} - 1\right]\right. \quad (125)$$
$$\left. + \frac{2}{3\Delta}\left[\frac{1}{\sqrt{3\Delta}}\frac{1}{2}\ln\frac{1 + \sqrt{3\Delta}}{1 - \sqrt{3\Delta}} - 1\right]\right]$$

or:

$$\Delta = (1 - \varphi_D^{1/3})^2 \frac{\frac{3(\varepsilon_B - \varepsilon_C)(\varepsilon_D - \varepsilon_C)}{(3\varepsilon_B + 2\varepsilon_C)(\varepsilon_D + 2\varepsilon_C)}\varphi_D}{1 - \frac{2(\varepsilon_B - \varepsilon_C)(\varepsilon_D - \varepsilon_C)}{(2\varepsilon_B + \varepsilon_C)(\varepsilon_D + 2\varepsilon_C)}\varphi_D} \tag{126}$$

When the permittivities of the two phases are equal or the concentrations are very high or very low, the values of $\Delta$ become much smaller than unity. This allows us to expand the logarithms in form of series, which leads to the approximate result:

$$\varepsilon_E - \varepsilon_C = \frac{(\varepsilon_D - \varepsilon_C)9\varepsilon_E\varepsilon_C}{(\varepsilon_D + 2\varepsilon_C)(2\varepsilon_E + \varepsilon_C)} \frac{\varphi_D}{1 - \frac{2(\varepsilon_B - \varepsilon_C)(\varepsilon_D - \varepsilon_C)}{(2\varepsilon_B + \varepsilon_C)(\varepsilon_D + 2\varepsilon_C)}\varphi_D}(1 + 2\Delta) \tag{127}$$

Compared to the result when only the first term in the sums is kept, (123) shows that for $\varepsilon_D = \varepsilon_C, \varphi_D = 0$ and $\varphi_D = 1$, the convergence is rapid. Compared to the expression of Wagner (2.2c), (134) always brings a correction greater than unity. So this allows us to conclude that when the permittivity of the dispersed phase is greater than the one of the continuous phase, the apparent permittivity given by (122) is greater than the one by the expression of Wagner.

This means that if $\varepsilon_D > \varepsilon_C$, then:

$$(\varepsilon_E)_{(122)} > (\varepsilon_E)_W \tag{128}$$

especially at medium concentrations. But, when the permittivity of the dispersed phase is smaller than the one of the continuous phase, the relationship between the apparent permittivities for these theories is inverted, this means that for $\varepsilon_D < \varepsilon_C$, we have:

$$(\varepsilon_E)_{(122)} < (\varepsilon_E)_W \tag{129}$$

This shows that the qualitative behavior of (122) is equal to the one of the expression of Bruggeman., with a moderate asymmetring played by the permittivities of the dispersed and the continuous phases. Even though the correction, brought by neglecting the spherical symmetry, goes in the right way, it is far too insufficient.

The more complete treatment, which takes into account the average reaction field on the micelle, increases the value of the correction, but this value stays equal to about 5%.
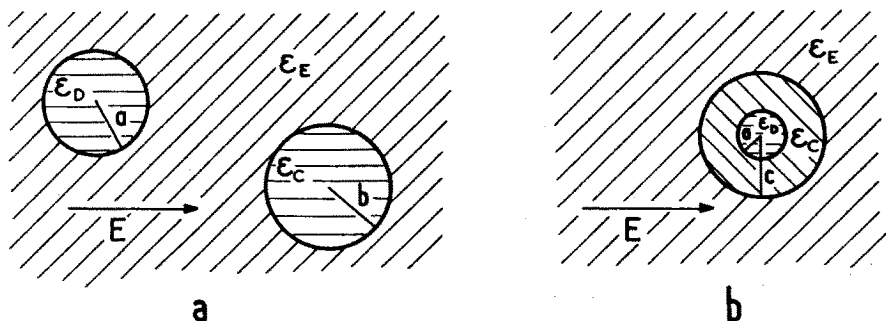
**Figure 2.15** Two extreme situations of the model of continuous and dispersed systems.

## 2.7 New Proposed Expression

We have seen that the expressions of Wagner (11) and of Onsager-Bottcher (52) correspond to an upper and lower limit amount of cases and that, therefore, the real behavior of an emulsion must be between these two behaviours. To deduce a better expression of the permittivity, which has this intermediate behavior, we have to unify the model from which the expression of Wagner and Onsager-Bottcher are determined. This means that we have to consider a model which has in both cases the same values of $\varepsilon^*$ and $E_\infty$ and in which the average fields can be obtained simultaneously.

The statistical treatments of the permittivity of pure substances lead to the result that, without any interactions between the molecules next to one and another, the value of $\varepsilon^*$ is equal to $\varepsilon_E$. This choice needs that $E_\infty = E$.

In these conditions, to determine the expression of Onsager (67), the average fields must be calculated with the model represented by Fig. 2.15a where the spheres of permittivity $\varepsilon_D$ and $\varepsilon_C$ have the radius $a$ and $b$ so that:

$$\frac{a^3}{b^3} = \frac{\varphi_D}{1 - \varphi_D} \tag{130}$$

and they are sufficiently far from each other so that we can neglect any direct interactions between them. The expression of Wagner can be obtained by calculating the average fields of the model represented in Fig. 2.15b; the sphere of permittivity $\varepsilon_D$ is considered to be surrounded of by a spherical layer of continuous system of permittivity $\varepsilon_C$, the radii $a$ and $c$ being so that:

$$\frac{a^3}{b^3} = \varphi_D \tag{131}$$

From the configuration of the Fig. 2.15a, we have:

$$\left(\frac{\overline{E}_D}{\overline{E}}\right)_0 = \frac{3\varepsilon_E}{2\varepsilon_E + \varepsilon_D} \tag{132}$$

and:

$$\left(\frac{\overline{E}_C}{\overline{E}}\right)_0 = \frac{3\varepsilon_E}{2\varepsilon_E + \varepsilon_C} \tag{133}$$

Whereas the configuration of the Fig. 2.15b leads to:

$$\left(\frac{\overline{E}_D}{E}\right)_W = \frac{9\varepsilon_E \varepsilon_C}{(2\varepsilon_E + \varepsilon_C)(\varepsilon_D + 2\varepsilon_C) - 2\varphi_D(\varepsilon_D - \varepsilon_C)(\varepsilon_E - \varepsilon_C)} \tag{134}$$

$$\left(\frac{\overline{E}_C}{E}\right)_W = \frac{3\varepsilon_E(2\varepsilon_C + \varepsilon_D)}{(2\varepsilon_E + \varepsilon_C)(\varepsilon_D + 2\varepsilon_C) - 2\varphi_D(\varepsilon_D - \varepsilon_C)(\varepsilon_E - \varepsilon_C)} \tag{135}$$

Combined with any asymmetric equations (92) and (93) or with the symmetric equation (94), the expressions (132) and (133) lead to the result of Onsager, whereas (134) and (135) lead to the expression of Wagner. These equations can as well be established while considering, after [33], that the long distance field mustn't be disturbed if proportional volumes to $\varphi_D$ and to $(1 - \varphi_D)$ of respectively dispersed and continuous phases are added to the emulsion. The condition, which says that the sum of apparent dipole moments of spheres without any interaction of the Fig. 2.15a is equal to zero, leads to the expression of Onsager. The expression of Wagner is obtained by saying that the apparent moment of the system of the Fig. 2.15b is equal to zero too.

The configuration of the Fig. 2.15a neglects any direct interactions between the dispersed and continuous phases. This seems reasonable according to the average interaction of each of these two phases with the continuous system of permittivity $\varepsilon_E$. In this model, the dispersed and continuous phase geometry is the same; for the continuous phase, this can not be correct because a continuous system can not be correct because a continuous system can not be polarized like a sphere.

The configuration of the Fig. 2.15b sets a definite local field, this leads to an excessive direct interaction between the dispersed and continuous phases. In this model the geometries of these two phases are not identical; the continuous phase being represented by a spherical layer, which is a good representation of a continuous system.

If we compare the two configurations of the Figs. 2.15a and b, we can see that the first one necessarily leads to a best result of $\overline{E}_D/\overline{E}$. Indeed, in the second configuration, the continuous phase forms an excessive screen around the dispersed phase; this neglects any interaction between the micelles, because of the symmetry of this configuration. The quantitative difference between the results of these configurations is very important. For instance, for an emulsion of water ($\varepsilon_D = 81$) in terpen ($\varepsilon_C = 2.6$); at the concentration $\varphi_D = 0.6$, the permittivity of the emulsion is $\varepsilon_E = 20.0$; and this gives us;

$$(\overline{E}_D/\overline{E})_0 = 0.496$$
$$(\overline{E}_D/\overline{E})_W = 0.238 \tag{136}$$

The experimental value of the quotient of these average fields due to the asymmetric equation (94), in this case:

$$(\overline{E}_D/\overline{E})_{exp} = 0.370 \tag{137}$$

It seems sure that the configuration of the Fig. 2.15 leads to the best value of the ratio $\overline{E}_C/\overline{E}$. This is due to the more realistic geometry of the continuous phase in this model. The difference between the results of these two models is again very important.

In the example we had chosen, we come to:

$$(\overline{E}_C/\overline{E})_0 = 1.41$$
$$(\overline{E}_C/\overline{E})_W = 2.63 \tag{138}$$

whereas the experimental value deduced from the asymmetric equation (93) is:

$$(\overline{E}_C/\overline{E})_{exp} = 1.95 \tag{139}$$

The difference between the values of the average fields in the continuous phase to the models of Onsager and Wagner is due to two factors. The first one is the difference between the geometries given to the continuous phases, the second is the interaction of this phase only with the continuous system of permittivity $\varepsilon_E$ in the model of Onsager, and with the same continuous system and the dispersed phase with the model of Wagner. The geometrical factor is the most important as we can see if we substitute $\varepsilon_D$ by $\varepsilon_E$ in the configuration of the Fig. 2.15b.

In this case, the continuous phase interacts only with the continuous system of permittivity $\varepsilon_E$, just as in the configuration of the Fig. 2.15. However, the difference of geometry leads, in our case, to the value:

$$\overline{E}_C/\overline{E} = 2.14 \tag{140}$$

closer to $(\overline{E}_C/\overline{E})_W$ than to $(\overline{E}_C/\overline{E})_0$.

This discussion shows us that in the model of Onsager, $(\overline{E}_D/\overline{E})_0$. is greater and $(\overline{E}_C/\overline{E})_0$ is much smaller than the experimental values. But, in the Wagner model, we have the reverse situation $(\overline{E}_D/\overline{E})_W$ is much smaller and $(\overline{E}_C/\overline{E})_W$ is greater than the experimental results. If the symmetric equation (94) is used to determine the expressions of the permittivity, we notice that the absolute value of the average fields in each phase isn't the most important parameter. The most important in the determination of $\varepsilon_E$ is the ratio between the average fields of the two phases. The value of this ratio changes a lot when we go from one model to another. For instance, in the chosen example, we have:

$$(\overline{E}_C/\overline{E}_D)_0 = 2.84$$
$$(\overline{E}_C/\overline{E}_D)_W = 11.0 \tag{141}$$

whereas the experimental value is:

$$(\overline{E}_C/\overline{E}_D)_{exp} = 5.25$$

If we consider the ratio between the average field in the continuous phase, determined by the Wagner model and the average field in the dispersed phase, determined by the Onsager model, we come to:

$$(\overline{E}_C)_W/(\overline{E}_D)_0 = 5.3 \tag{142}$$

This shows that, for the simple treatments based on the calculation of the average fields on the two phases, the best model must consider

$(\overline{E}_D/\overline{E})$ with the configuration of the Fig. 2.15a, and $(\overline{E}_C/\overline{E})$ with the one of the Fig. 2.15b.

When combining the expression of Onsager for the average field of the dispersed phase (132), with the one of Wagner for the average field of the continuous phase (135), and with the symmetric expression (94), we come to a new result that we are presenting:

$$\frac{(\varepsilon_E-\varepsilon_C)(2\varepsilon_E+\varepsilon_D)}{3\varepsilon_E} = (\varepsilon_D - \varepsilon_C)\varphi_D - \frac{2(\varepsilon_D-\varepsilon_C)(\varepsilon_E-\varepsilon_C)(\varepsilon_D-\varepsilon_E)}{3\varepsilon_E(2\varepsilon_C+\varepsilon_D)}\varphi_D^2 \quad (143)$$

This expression has the same form as the one of Onsager, but has an additional term. For very low concentrations, this terms tends to zero and this equation behaves like the one of Onsager. This additional term becomes important for medium concentrations and then tends again to zero for very high concentrations, because in this case, $\varepsilon_E$ tends to $\varepsilon_D$. However, when $\varphi_D$ tends toward unity, (143) behaves like the one of Wagner and not like the one of Onsager, as it will be confirmed in the next section.

## 2.8   Comparison Between the Results of the Different Theories and the Result and the Experimental Data

### a. Limit Expressions for Low Concentrations

The different expressions of the permittivity of emulsions are very hard to compare because of their different mathematical formulations. It is therefore interesting to determine their limited expressions for very low concentrations; these expressions are linear functions of the volumic fraction $\varphi_D$ of the dispersed phase and become even more correct as $\varphi_D$ gets smaller.

Indeed, each equation $\varepsilon_E = \varepsilon_E(\varepsilon_D, \varepsilon_C, \varphi_D)$ can be expanded in the form of a series of Taylor around $\varphi_D = 0$, which leads to:

$$\varepsilon_E = \varepsilon_C + \left(\frac{\delta\varepsilon_E}{\delta\varphi_D}\right)_{\varphi_D=0} \varphi_D \quad (144)$$

The details of the calculation of the series of the different expressions offer no particular interest. For the different cases, (144) leads to the following expressions:

Wiener

$$\varepsilon_E = \varepsilon_C + \frac{(u+1)\varepsilon_C}{\varepsilon_D + u\varepsilon_C}(\varepsilon_D - \varepsilon_C)\varphi_D, \quad u \geq 0 \tag{145}$$

Rayleigh

$$\varepsilon_E = \varepsilon_C + \frac{3\varepsilon_C}{\varepsilon_D + 2\varepsilon_C}(\varepsilon_D - \varepsilon_C)\varphi_D \tag{146}$$

Wagner

$$\varepsilon_E = \varepsilon_C + \frac{3\varepsilon_C}{\varepsilon_D + 2\varepsilon_C}(\varepsilon_D - \varepsilon_C)\varphi_D \tag{147}$$

Higuchi

$$\varepsilon_E = \varepsilon_C + \frac{3\varepsilon_C}{\varepsilon_D + 2\varepsilon_C - K\frac{(\varepsilon_D - \varepsilon_C)^2}{\varepsilon_D + 2\varepsilon_C}}(\varepsilon_D - \varepsilon_C)\varphi_D \tag{148}$$

Bruggeman

$$\varepsilon_E = \varepsilon_C + \frac{3\varepsilon_C}{\varepsilon_D + 2\varepsilon_C}(\varepsilon_D - \varepsilon_C)\varphi_D \tag{149}$$

Kubo-Nakamura

$$\varepsilon_E = \varepsilon_C + \frac{(2+C)\varepsilon_C + 1 - C}{\varepsilon_D + 2\varepsilon_C}(\varepsilon_D - \varepsilon_C)\varphi_D, \quad C = 1 - \frac{4\pi}{9\sqrt{3}} \tag{150}$$

Clausius-Mossoti

$$\varepsilon_E = \varepsilon_C + \frac{\varepsilon_C + 2}{\varepsilon_D + 2}(\varepsilon_D - \varepsilon_C)\varphi_D \tag{151}$$

Onsager-Böttcher

$$\varepsilon_E = \varepsilon_C + \frac{3\varepsilon_C}{\varepsilon_D + 2\varepsilon_C}(\varepsilon_D - \varepsilon_C)\varphi_D \tag{152}$$

Lichtenecker-Rother

$$\varepsilon_E = \varepsilon_C(\ln\frac{\varepsilon_D}{\varepsilon_C})\varphi_D \tag{153}$$

Looyenga

$$\varepsilon_E = \varepsilon_C + 3\varepsilon_C\left[(\frac{\varepsilon_D}{\varepsilon_C})^{1/3} - 1\right]\varphi_D \tag{154}$$

Equation (143)

$$\varepsilon_E = \varepsilon_C + \frac{3\varepsilon_C}{\varepsilon_D + 2\varepsilon_C}(\varepsilon_D - \varepsilon_C)\varphi_D \tag{155}$$

When comparing these expressions, for low concentrations of the disperse phase the formulas of Rayleigh, Wagner, Bruggeman, Onsager and the equation that we are presenting, all have the same limiting behavior. This behavior is equal to the one given by the expression of Landau-Lifshitz for low global concentration. This gives an advantage to these theories rather to the others.

### b. Limit Expressions for High Concentrations

The qualitative difference of these theories can be obtained by calculating the limit expressions for high concentrations of the dispersed phase. The permittivity $\varepsilon_E$ can be expanded in the form of a series of Taylor around $\varphi_D = 1$ :

$$\varepsilon_E = \varepsilon_D + (\frac{\delta\varepsilon_E}{\delta\varphi_D})_{\varphi_D=1}(1 - \varphi_D) \tag{156}$$

This expression has more of a mathematical than a physical interest because it is hard to imagine a pure dispersed phase.

However, as all the expressions of $\varepsilon_E = \varepsilon_E(\varepsilon_D, \varepsilon_C, \varphi_D)$ are monotonous functions of $\varphi_D$, (156) connected to (144), allows us to forsee the qualitative expressions that we are seeking. The limiting expressions for high concentrations given by the different theories will follow.

The expression of Rayleigh has not been quoted because is does not give $\varepsilon_D$ when $\varphi_D$ tends towards unity:

Weiner

$$\varepsilon_E = \varepsilon_D - \frac{\varepsilon_D + u\varepsilon_C}{\varepsilon_D + u\varepsilon_C - (\varepsilon_D - \varepsilon_C)}(\varepsilon_D - \varepsilon_C)(1 - \varphi_D), \quad u \geq 0 \tag{157}$$

Wagner

$$\varepsilon_E = \varepsilon_D - \frac{\varepsilon_D + 2\varepsilon_C}{3\varepsilon_C}(\varepsilon_D - \varepsilon_C)(1 - \varphi_D) \tag{158}$$

Higuchi

$$\varepsilon_E = \varepsilon_D - \left[\varepsilon_D + 2\varepsilon_C - K\frac{(\varepsilon_D - \varepsilon_C)^2}{\varepsilon_D + 2\varepsilon_C}\right]\frac{(\varepsilon_D - \varepsilon_C)}{3\varepsilon_C}(1 - \varphi_D) \tag{159}$$

Bruggeman

$$\varepsilon_E = \varepsilon_D - (\frac{\varepsilon_D}{\varepsilon_C})^{1/3}(\varepsilon_D - \varepsilon_C)(1 - \varphi_D) \tag{160}$$

Kubo-Nakamura

$$\varepsilon_E = \varepsilon_D - \infty(\varepsilon_D - \varepsilon_C)(1 - \varphi_D)(1 - \varphi_D) \tag{161}$$

Clausius-Mossoti

$$\varepsilon_E = \varepsilon_D - \frac{\varepsilon_D + 2}{2 + \varepsilon_C}(\varepsilon_D - \varepsilon_C)(1 - \varphi_D) \tag{162}$$

Onsager

$$\varepsilon_E = \varepsilon_D - \frac{3\varepsilon_D}{2\varepsilon_D + \varepsilon_C}(\varepsilon_D - \varepsilon_C)(1 - \varphi_D) \tag{163}$$

Lichtenecker-Rother

$$\varepsilon_E = \varepsilon_D - \varepsilon_D \left(\ln \frac{\varepsilon_D}{\varepsilon_C}\right)(1 - \varphi_D) \tag{164}$$

Looyenga

$$\varepsilon_E = \varepsilon_D - 3\varepsilon_D \left[1 - (\frac{\varepsilon_C}{\varepsilon_D})^{1/3}\right](1 - \varphi_D) \tag{165}$$

Equation (143)

$$\varepsilon_E = \varepsilon_D - \frac{\varepsilon_D + 2\varepsilon_C}{3\varepsilon_C}(\varepsilon_D - \varepsilon_C)(1 - \varphi_D) \tag{166}$$

As opposed to the results for $\varphi_D$ tending towards zero, the limit expressions for high concentrations are quite different, except for the model of Wagner and the one that we are presenting because they both have the same limited behavior for low and high concentrations of the dispersed phase.

## c. Qualitative Relationship Between the Results of the Different Theories

A comparison between the limited expressions leads to the following conclusions. To begin with, a few expressions can not be be used for the study of emulsions; because they are symmetric, and because their behavior for low concentrations is not correct. This is the case of the expression (4) of Wiener for $u = \infty$, of the equation (89) of Looyenga, of the equation (63) of Lichtenecker-Rother, of the equation (47) of Clausius-Mosotti and of the equation (3) of Wiener for $u = 0$; which lead to the decreasing values of $\varepsilon_E$ in the same order that they are quoted; this means that, without taking into account the existing relationship between the permittivities of the two phases, we have:

$$(\varepsilon_E)_{\text{Wi0}} \leq (\varepsilon_E)_{\text{CM}} \leq (\varepsilon_E)_{\text{LR}} \leq (\varepsilon_E)_{\text{L}} \leq (\varepsilon_E)_{\text{Wi}\infty} \tag{167}$$

These differences become greater as the difference between the permittivities of the two phases becomes important. They are displayed
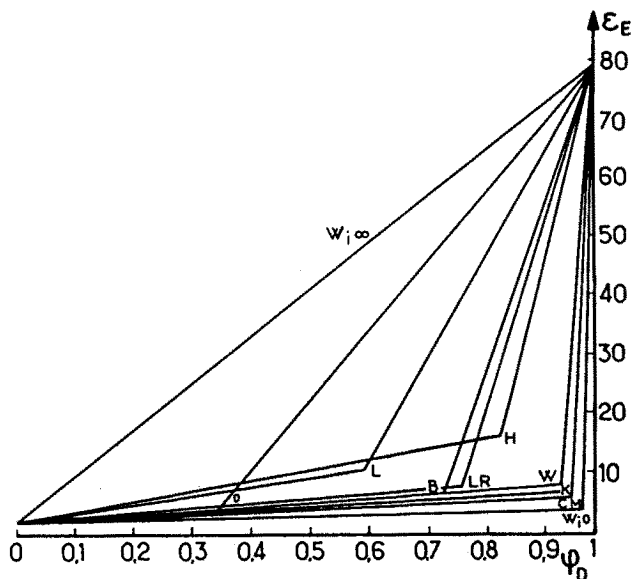
**Figure 2.16  Junction of the limiting expressions at $\varepsilon_D = 80, \varepsilon_B = 2$.**

on the Fig. 2.16 and 2.17, where the limiting expressions are plotted up to their intersection for $\varepsilon_D = 80$, $\varepsilon_D = 2$ and for $\varepsilon_D = 2$, $\varepsilon_C = 80$ respectively. These permittivities are approximately the ones of the emulsions of water in oil and of oil in water. The only symmetric expression which remains is the equation of Onsager-Bottcher. This expression can be used for the study of emulsions due to its positive results at low concentrations. This is why we are going to compare it to all the asymmetric expressions.

The most asymmetric expression we have encountered, this means the one which gives the most important difference of permittivity with an exchange of phases, is the equation (30) of Kubo-Nakamura. But it keeps an incorrect behavior for extreme concentrations. Then comes (11) of Wagner whatever excessively asymmetric, but which has a good behaviour at low concentrations. The behavior of equation (22) of Bruggeman is intermediate between the equations of Onsager and
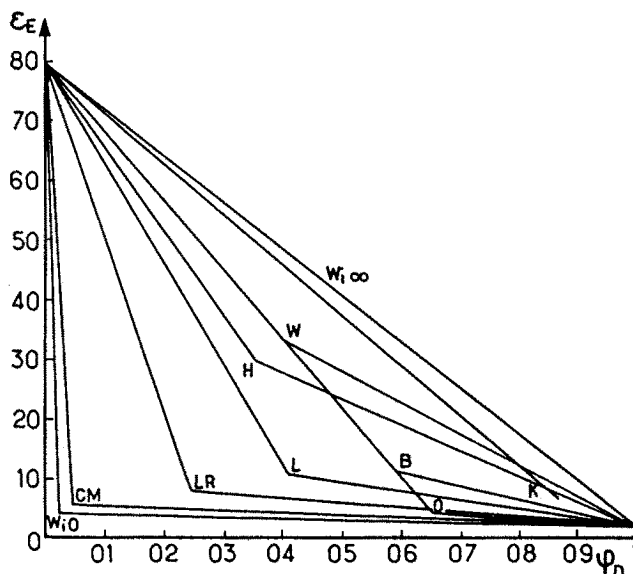
**Figure 2.17  Junction of the limiting expressions at $\varepsilon_D = 2, \varepsilon_B = 80$.**

of Wagner: it is moderately asymmetric and its limit at low concentrations is correct. For these three fundamental equations, there is a simple qualitative relationship: for $\varepsilon_C < \varepsilon_D$, we always have:

$$(\varepsilon_E)_W \leq (\varepsilon_E)_B \leq (\varepsilon_E)_0 \tag{168}$$

whereas for $\varepsilon_C > \varepsilon_D$

$$(\varepsilon_E)_{W_0} \leq (\varepsilon_E)_B \leq (\varepsilon_E)_W \tag{169}$$

The expression (16) of Higuchi's is asymmetric but its behaviour at low concentrations is incorrect. The only simple relationship from this equation, is for $\varepsilon_C < \varepsilon_D$ :

$$(\varepsilon_E)_W \leq (\varepsilon_E)_H \tag{170}$$

whereas for $\varepsilon_D < \varepsilon_C$ :

$$(\varepsilon_E)_H \leq (\varepsilon_E)_W \tag{171}$$

Although the correction brought about by the expression of Wagner goes in the right way, this correction is overestimated, at least for low concentrations this leads to the fact that the expression of Higuchi becomes equal to the one of Onsager for medium concentrations. Finally, the expression (143) that we are presenting is asymmetric and has the correct behavior for low concentrations. Qualitatively, this behavior is: for $\varepsilon_C < \varepsilon_D$ :

$$(\varepsilon_E)_W \leq (\varepsilon_E)_{143} \leq (\varepsilon_E)_0 \tag{172}$$

and for $\varepsilon_D < \varepsilon_C$ :

$$(\varepsilon_E)_0 \leq (\varepsilon_E)_{143} \leq (\varepsilon_E)_W \tag{173}$$

This qualitative behavior can only be compared to the one of the equation of Bruggeman.

### d. Experimental Verification

There aren't many experiments on the permittivity of emulsions, except for the system of water in oil, which offers a technological point of view very interesting.

We have chosen two systems to verify the validity of the different theories. First the measurements made by Naiki, Fugita and Matsumura [10] on the system water-terpen which presents a high difference between the permittivities of the two phases and which allows us to notice the effect of the exchange between the phases on the apparent permittivity. Secondly, we have chosen to take the measurements made by Guillen [9] on a system of spheres of potassium chloride in vacuum of the two phases.

The results for the system water-terpen are given on the Fig. 2.18 where the squares represent the experimental data.

The values of the abscissa are the volume fraction of water. These are equal to the one of the dispersed phase $\varphi_D$ for equation that curves of Wagner $W_1$, of Bruggeman $B_1$, and of the equation we are presenting (143) and to $(1 - \varphi_D)$ for the superior curves $W_2$, $B_2$ and $(143)_2$. The curves of Onsager (0) and of Clausius-Mosotti (C.M.) are single because the substitution of $\varphi_D$ into $1 - \varphi_D$ and of $\varepsilon_C$ into $\varepsilon_D$ and vice-versa has no effect on these curves. The exchange between the phases takes place for the volume fraction of water of 0.85.

The theoretical curves have been calculated for the permittivity of water equal to 81 and for the permittivity of terpen equal to 2.60. We must point out that the last value is not the one of pure terpen
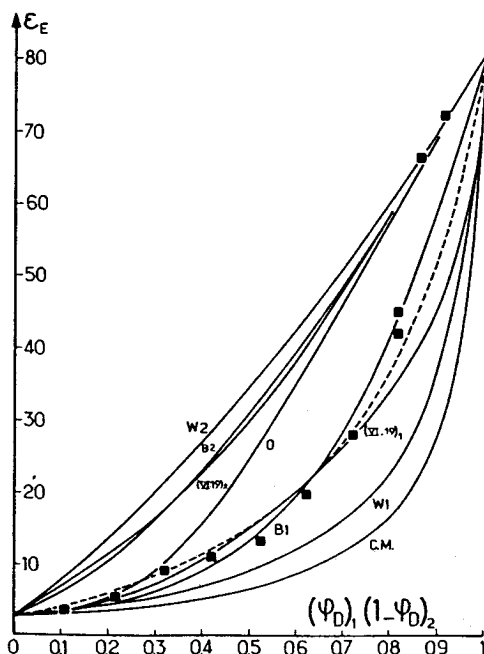
**Figure 2.18 Water terpen system. Permittivity of the emulsion $\phi_D$. Comparison of different theories with experimental results.**

which is equal to 2.20, because we must add to the terpen an emulsifier which has a permittivity equal to 7.48. Its proportion is of 10%, but it slightly varies with $\varphi_D$. This variation has not been included in the calculation of the theoretical curves.

The results for the system of spheres of potassium chloride in vacuum are now given:

| $\varepsilon_{exp}$ | $\varepsilon_{CM}$ | $\varepsilon_0$ | $\varepsilon_B$ | $(\varepsilon_E)_{143}$ | $\varepsilon_W$ |
|---------------------|--------------------|-----------------|------------------|-------------------------|------------------|
| 2.34                | 2.23               | 2.51            | 2.36             | 2.36                    | 2.23             |

The spheres of potassium chloride have radii between $10^{-2}$ and $10^{-1}$ mm and their permittivity is equal to 4.65. The measuring condenser is completely full, which leads to a single concentration: $\varphi_D = 0.53$.

## 2.9   Discussion

The comparison between the theoretical results and the experimental data shows that the expressions deduced from molecular or general models are not well adapted to give an expression for the permittivity of emulsions, essentially because they are symmetric with reference to the permittivities of the two phases. However, among these expressions, Onsager's is the most correct because its values of permittivity are always between the experimental values when one or the other phase is dispersed. Moreover, this expression has a correct limited behavior for low concentrations. Among the phenomenological expressions, the result of Wagner has an opposite behavior because the values of permittivity deduced from this result are not between the experimental values due to its exaggerated asymmetric behavior. The expression of Bruggeman is the closest to the experimental data. This agreement is extremely positive for $\varepsilon_D > \varepsilon_C$ (Fig. 2.18) and for $\varepsilon_C > \varepsilon_D$ [11]. For low differences between the permittivities of the two phases this agreement remains positive, although the differences between the different expressions become low so that it is difficult to say which one is the best.

It is quite difficult to explain theoretically why the formula of Bruggeman is so practical. As we have previously seen, it isn't deduced from a physical model of the emulsion but on a mathematical basis from the limited equation of Rayleigh or of Wagner. It is important to point out that the asymmetric behaviour of the equation of Bruggeman only comes from its mathematical basis and from the fact that the initial equation of Wagner is extremely asymmetric. This conclusion is drawn by the fact that we can arrive at the equation of Bruggeman by the same integration method either from the result of Onsager which is symmetric, or from the limit expression of Landau-Lifshitz.

One of the reasons of the success of this equation can be given by the theory of De Loor [39]. As we have seen in Section 2.5b, the expression of the permittivity, given by this author, is determined when considering the micelle in a continuous system of permittivity $\varepsilon'$, whose value has been calculated by setting the condition that the theoretical permittivity must be equal to the experimental one. These value $\varepsilon'$ are always between the ones of the continuous phase $\varepsilon_C$ and theories of the emulsion $\varepsilon_E$. These extremes correspond to the models of Wagner and of Onsager respectively. This observation allows us to conclude that the model of Bruggeman, where the equivalent of $\varepsilon'$ comes

from the integration over $\varepsilon'_E$ between $\varepsilon_C$ and $\varepsilon_E$, is more adapted to explain the dielectric behavior of emulsions.

The expression that we are presenting seems to agree with the experimental data as well as the equation of Bruggeman. These two expressions lead to very close values of the permittivity. Significant differences only appear for very high concentration: $\varphi > 0.8$, but at these concentrations, many systems do not remain emulsions. It is interesting to note that this equation has total different basis to the theories of Bruggeman. Indeed, it takes into account the differences of geometry of the two phases and not the interactions between micelles. As these two expressions lead to similar results, it is difficult to choose which one is best just by comparing them to the experimental data. But, a comparison is possible with the empirical expression of Pearce [49] which, as this author says, represents the behaviour of seventeen different systems with an lower error to the experimental one.

The expression of Pearce is:

$$\varepsilon_E = \varepsilon_C + (\varepsilon_D - \varepsilon_C)\frac{(1-v)\varphi_D}{1-v\varphi_D} \tag{174}$$

where $v$ is an empirical coefficient, which depends on the system but not on the concentration. It is interesting to note that this expression has a good limiting behavior for low concentrations only if $v$ has the following expression;

$$v = \frac{\varepsilon_D - \varepsilon_C}{\varepsilon_D + 2\varepsilon_C} \tag{175}$$

In this case, the equation of Pearce is equal to the one of Wagner. Generally, the experimental values of this empirical factor $v$ is inferior to the ones given by (175).

On the Fig. 2.18, we have represented in a line of points the expression of Pearce with a factor $v$, which has been calculated from the intersection of the curves of Bruggeman and of the curve given by (143), this is not to give any preference to any of the two expressions This shows that the curve of Pearce is even closer than the one that we are presenting

# Acknowledgment

The origin of this work is the first part of the speciality doctorat thesis C. Grosse [8], made at the laboratory of theoretical chemistry

# References

[1] Van Beek, L. K. H. "Dielectric behavior of heterogeneous systems," *Prog. Dielectrics,* **7**, 69, 1967.

[2] Hanai, T. *Emulsion Science,* Electrical Properties of Emulsions, Ph. Sherman Ed., Acad. Press, London, New York, Ch. 5, 353–478, 1968.

[3] de Loor, G. P., "Dielectric properties of heterogeneous mixtures," Thesis, Univ. de Leiden, 1956.

[4] Prost, C., "Etude de la constante diéléctrique des mélanges héterogènes," Thése, Univ. de Nancy, 1965.

[5] Tinga, W. R., *Thesis,* Univ. de Alberta, Canada, 1969.

[6] Clausse, M., "Contribution à l'étude des propriétés diéléctriques des émulsions," Thése, Univ. de Pau, 1971.

[7] Paletto, J., "Etude de la permittivité diélectrique des matériaux composites," *Thése,* Univ. de Lyon, 1972.

[8] Grosse, C., "Permittivité statique des émulsions. Application à l'étude diélectrique des mélanges critiques," *Thèse,* Univ. de Nancy I, 1976.

[9] Guillien, R., "Variation de la polarisation diélectrique avec la densité," *Ann. de Phys.,* **16**, 205–252, 1941.

[10] Naiki, T., F. Kujita, and S. Matsumura, "Dielectric behavior of two phase mixtures," *Mem. Fac. Ind. Arts., Kyoto Techn. Univ.,* **8**, 1–19, 1959.

[11] Hanai, T., N. Koizuma, and R. Goto, "Dieletric properties of emulsions, I. Dielectric constant of O/W emulsions," *Kolloid-Zeischrift,*

167, 41–43, 1959.

[12] Fricke, H., "A mathematical treatment of the electrical conductivity and capacity of disperse sytems. I. The electric conductivity of a suspension of homogeneous spheroids," *Phys. Rev.*, 24, 575–587, 1924.

[13] Oker-Blom, M., "Thierische Safte und Gewebe in physikalish-chemishcer Beziechusz," *Arch. Ges. Phys.*, 79, 510, 1900.

[14] Pearce, C. A. R., "The electrical conductivity and permittivity of mixtures with special reference to emulsion of water in fuel oil," *Br. J. Appl. Phys.*, 6, 113–120, 1955.

[15] Grosse, C., and J. L. Greffe, "Influence de la forme des micelles sur la permittivité d'une émulsion," *C. R. Acad. Sci. Paris,* 283C, 95–97, 1976.

[16] Thacher, H. C., Jr., "The dielectric properties of dispersed liquids. I. The theory of the dielectric constant," *J. Phys. Chem.*, 56, 795–797, 1952.

[17] Grosse, C., and J. L. Greffe, "Influence du champ appliqué sur la permittivité d'une émulsion," *C. R. Acad. Sci.*, 283C, 159–161, 1976.

[18] Meredith, R. E., and C. W Tobias, "Resistance to potential flow through a cubic array of spheres," *J. Appl. Phys.*, 31, 1270–1273, 1960.

[19] de La Rue, R. E. and C. W. Tobias, "The conductivity of dispersions," *J. Electrochem. Soc.* 106, 804–809, 1959.

[20] Eichbaum, B. R., "The dielectric behavior of solids embedded in a homogeneous medium," *J. Electrochem. Soc.*, 106, 804–809, 1959.

[21] Lord Rayleigh, "On the influence of obstacles arranged in rectangular order upon the properties of a medium," *Phys. Magn.*, 34, 481–502, 1892.

[22] Wiener, O., "Die theorie des Mischkorpers fur das Feld der Statonären Stromüng," *Abh. Math. Phys. sach Wiess*, 32, 509–604, 1912.

[23] Mosotti, O. F., "Discussione analitica sull' influenza che l'azione di unmezzo dielettrico ha sulla distriuzzione dell' electtricita alla superficiedi piu corpi electrrici deseminati in esso," *Mem. Di. Matem.*

*e Fisica di Modena,* **24**, 49–74, 1846.

[24] Clausius, R., "Die Mechanishe Wärmetheorie Zweite Auflage, Abschnitt III," Druck und Verlag, Braunshweig 62–97, 1876.

[25] Onsager, L., "Electric moments of molecules in liquids," *J. Amer. Chem. Soc.,* **58**, 1486–1493, 1936.

[26] Wagner, K. W., "Erklarung der dielektrischen Nachwirkungsvorgänge auf Grund Maxwellscher Vorstellungen," *Arch. Electrotech.,* **2**, 371–387, 1914.

[27] Bruggeman, D. A. G., "Berechnung verschiedener physikalischer Konstanten von heterogen Substanzen I. Dielektrizitätskonstanten und leitfähig keiten der Misch köper aus isotropen Substanzen," *Ann. der Phys.,* **24**, 636–664, 1935.

[28] Hanai, T., "Theory of the dielectric dispersion due to the interfacial polarization and its application to emulsions," *Kolloid Zeitschrift,* **171**, 23–31, 1960.

[29] Kubo, M., and S. Nakamura, "Dielectric constant of dispersions of spherical particles," *Bull. chem. Soc. Jap.,* **26**, 318–322, 1953.

[30] Bottcher, C. J. F., "The dielectric constant of crystalline powders," *Reç. Trav. chim.,* **64**, 47–51, 1945.

[31] Lichtenecker, K., and K. Rother, "Die Herleitung das logarithmischen Mischungsgesetzes aus allgemeinen Prinzipien der Stationären Strömung," *Phys. Zeitschr.,* **32**, 255–260, 1931.

[32] Landau, L., and F. Lifshitz, *Electrodynamique des milieux continus,* 68–70, Ed. M. I. R., Moscow, 1969.

[33] Looyenga, H., "Dielectric constants of heterogeneous mixtures," *Physica,* **31**, 401–406, 1965.

[34] Lorenz, L., "Ueber die Refractionsconstante," *Annalen der physik und chimie,* Leipzig, **11**, 70–103, 1880.

[35] Lorentz, H. A., *The Theory of Electrons: 2nd Ed.,* B. G. Teubner, Leipzig, 1916.

[36] Higuchi, W. I., "A new relationship for the dielectric properties of two phase mixtures," *J. of Phys. Chem.,* **62**, 649–653, 1958.

[37] Reynolds, J. A., and J. M. Hough, "Formulae for dielectric constants of mixtures," *Proc. Phys. Soc.,* **70**(B), 769–775, 1957.

[38] Brown, W. F., Jr., "Solid mixtures permittivities," *J. Chem. Phys.*, **23**, 1514–1517, 1955.

[39] de Loor, G. P., "Method of obtaining information and the internal dielectric constant of mixtures," *Apll. Sc. Res.*, **3(B)**, 479–481, 1954.

[40] Kirwood, J. G., "Theory of solutions of molecules containing widely separated charges with special application to zwitterions," *J. Chem. Phys.*, **2**, 351–361, 1934.

[41] Tinga, W. R., W. A. G. Uoss, and D. F. Blossey, "Generalized approach to multiphase dielectric mixture theory," *J. Appl. Phys*, **44**, 3897–3902, 1973.

[42] Kirwood, J. G., "The dielectric polarization of polar liquids," *J. Chem. Phys.*, **7**, 911–919, 1939.

[43] Frolich, H., *Theory of Dielectrics*, Oxford University Press, London, 1958.

[44] Barriol, J., and J. L. Greffe, "Relations entre le modéle microscopique des diélectriques polarisables et le modéle macroscopique," *I. J. Chim. Phys.*, **66**, 154–158, 1969.

[45] Pearce, C. A. R., "The permittivity of two phase mixtures," *British J. of Appl. Phys.*, **6**, 358–361, 1955.