

Double Dielectric Relaxation of Non-Confocal Membrane-Covered Ellipsoidal Particle Suspensions

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The complex dielectric constant of suspensions of membrane-covered ellipsoidal particles is formulated in terms of the complex dielectric constant of the interior, the membrane and the medium, the volume ratios p and q , and the shape factors n_1 and n_2 . It is not necessary for the two ellipsoidal interfaces (one between the interior and the membrane, the other between the membrane and the medium) to be confocal, nor for the thickness of the membrane to be uniform. The result is factorized to demonstrate double relaxation.

In addition, the blurring mechanism of multiple relaxation is naively explained.

Various formulae^{1–4} have been developed for the dielectric properties of inhomogeneous mixtures and applied to actual cases in the past. Examples of these can be seen for the case of spherical particle suspensions⁵ and ellipsoidal particle suspensions^{5,6}. However, in biological applications the membrane must also be taken into account because many of the behavioral characteristics of biological cell suspensions have been attributed to it. Pauly and Schwan⁷ have made a general calculation on suspensions of spherical particles covered by conducting membranes. In this paper, Sillars'⁶ result for suspensions of ellipsoidal particles without membranes is extended for the case of suspensions of membrane-covered ellipsoidal particles. This is done in the same manner as the analysis of Pauly and Schwan.

The model configuration is shown schematically in Figure 1. It is assumed that the particles align in the direction of the applied field. Although uniform thickness of the membrane is assumed, this restriction is not necessary. It will also be seen later that the effects caused by different locations of the centers of these two ellipsoidal structures can be neglected; that is, the analysis presented here will also apply to the configuration of Fig. 2, which

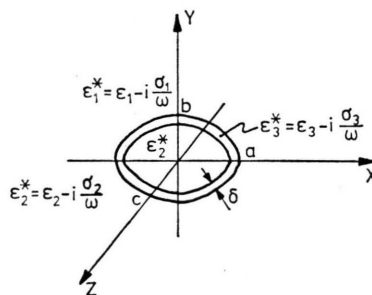


Fig. 1. Model configuration.

is different from that of Fig. 1 by a parallel shift of the major axes. As the only restriction on the model the long axes of the two (outer and inner) ellipsoidal structures of a particle have to be parallel.

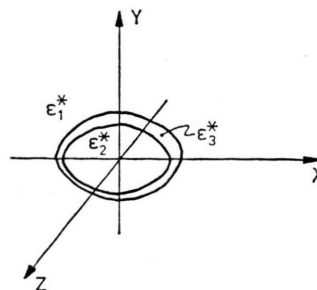


Fig. 2. Possible configuration.

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The complex permittivity ϵ^* of an ellipsoidal particle suspension can be calculated from the



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equation ³⁻⁷:

$$\frac{\varepsilon^* - \varepsilon_1^*}{n_1 \varepsilon_1^* + (\varepsilon^* - \varepsilon_1^*)} = p \frac{\varepsilon_{23}^* - \varepsilon_1^*}{n_1 \varepsilon_1^* + (\varepsilon_{23}^* - \varepsilon_1^*)}, \quad (1)$$

where ε_1^* is the complex permittivity of the suspending medium, ε_{23}^* is the equivalent complex permittivity of the membrane-covered particle, n_1 is given by

$$n_1 = 4\pi \int_0^\infty ds \left/ \left[\{ (a+\delta)^2 + s \} \cdot \frac{\sqrt{\{ (a+\delta)^2 + s \} \{ (b+\delta)^2 + s \} \{ (c+\delta)^2 + s \}}}{2\pi(a+\delta)(b+\delta)(c+\delta)} \right] \right.$$

and p is the fractional volume occupied by the particles in the suspension. In the same manner

as given by Pauly and Schwan⁷ for suspensions of spherical particles, the equivalent complex permittivity ε_{23}^* is given by the equation

$$\frac{\varepsilon_{23}^* - \varepsilon_3^*}{n_2 \varepsilon_3^* + (\varepsilon_{23}^* - \varepsilon_3^*)} = q \frac{\varepsilon_2^* - \varepsilon_3^*}{n_1 \varepsilon_3^* + (\varepsilon_2^* - \varepsilon_3^*)}, \quad (2)$$

where ε_2^* and ε_3^* are the complex permittivities of the membrane and the inner particle, respectively, n_2 is given by

$$n_2 = 4\pi \int_0^\infty ds \left/ \left\{ (a^2 + s) \frac{\sqrt{(a^2 + s)(b^2 + s)(c^2 + s)}}{2\pi a b c} \right\} \right.$$

and q is the ratio of the volume of the particle without the membrane to its volume including the membrane.

The complex permittivity of the suspension is obtained by solving Eq. (2) for ε_{23}^* , substituting the result into Eq. (1) and then solving for ε^* . The result is given by the equation

$$\begin{aligned} \varepsilon^* &= \varepsilon_1^* \{ n_1 [p^{-1} (n_2 (\varepsilon_1^* / \varepsilon_3^*) \{ q^{-1} [n_1 ((\varepsilon_2^* / \varepsilon_3^*) - 1)^{-1} + 1] - 1\}^{-1} + 1] - 1]^{-1} + 1 \} \\ &= \frac{(1-q)(n_1 - 1 + p - n_1 p) \varepsilon_1^{*2} \varepsilon_2^* + (1-p + n_1 p)(1-q + n_2 q) \varepsilon_1^* \varepsilon_2^* \varepsilon_3^*}{(1-q)(n_1 - 1 + p) \varepsilon_1^* \varepsilon_2^* + (1-p)(1-q + n_2 q) \varepsilon_2^* \varepsilon_3^*} \\ &\quad + \frac{(n_1 - 1 + q)(n_1 - 1 + p - n_1 p) \varepsilon_3^* \varepsilon_1^{*2} + (1-p + n_1 p)(n_1 - 1 + q - n_2 q) \varepsilon_1^* \varepsilon_3^{*2}}{(n_1 - 1 + p)(n_1 - 1 + q) \varepsilon_3^* \varepsilon_1^* + (1-p)(n_1 - 1 + q - n_2 q) \varepsilon_3^{*2}}. \end{aligned} \quad (3)$$

Although it is intuitively obvious, it should be noted that Eq. (3) is easily reducible to special simpler cases:

- (i) By setting $p = 0$, we get $\varepsilon^* = \varepsilon_1^*$,
- (ii) By setting $p = 1$, we get $\varepsilon^* = \varepsilon_{23}^*$,
- (iii) By setting $p = q = 1$, we get $\varepsilon^* = \varepsilon_2^*$,
- (iv) By setting $p = 1$, $q = 0$, we get $\varepsilon^* = \varepsilon_3^*$.

These are useful checks on the consistency of the calculation. Furthermore, by setting $n_1 = n_2 = 3$ in Eq. (3), we get the Pauly-Schwan expressions for spherical particle suspensions⁷.

Equation (3) is then rewritten as

$$\varepsilon^* = \varepsilon_\infty + \frac{\Delta \varepsilon_1}{1 + i w \tau_1} + \frac{\Delta \varepsilon_2}{1 + i w \tau_2} - i \frac{\sigma_0}{w} \quad (4)$$

where

$$\tau_1 = (C + \sqrt{C^2 - 4AB}) / (2B),$$

with

$$\begin{aligned} A &= (1-q)(n_1 - 1 + p) \varepsilon_1 \varepsilon_2 + (1-p)(1-q + n_2 q) \varepsilon_2 \varepsilon_3 + (n_1 - 1 + p)(n_1 - 1 + q) \varepsilon_3 \varepsilon_1 \\ &\quad + (1-p)(n_1 - 1 + q - n_2 q) \varepsilon_3^2, \\ B &= (1-q)(n_1 - 1 + p) \sigma_1 \sigma_2 + (1-p)(1-q + n_2 q) \sigma_2 \sigma_3 + (n_1 - 1 + p)(n_1 - 1 + q) \sigma_3 \sigma_1 \\ &\quad + (1-p)(n_1 - 1 + q - n_2 q) \sigma_3^2, \end{aligned}$$

$$\tau_2 = (C - \sqrt{C^2 - 4AB}) / (2B),$$

$$\varepsilon_\infty = D/A,$$

$$\sigma_0 = G/B,$$

$$\begin{aligned} \Delta \varepsilon_1 &= \frac{1}{2} \left(\frac{E}{B} - \frac{D}{A} - \frac{CG}{B^2} \right) + \frac{1}{2\sqrt{C^2 - 4AB}} \\ &\quad \cdot \left(\frac{CE}{B} - \frac{C^2 G}{B^2} - 2F + \frac{CD}{A} + \frac{2AG}{B} \right), \end{aligned}$$

$$\begin{aligned} \Delta \varepsilon_2 &= \frac{1}{2} \left(\frac{E}{B} - \frac{D}{A} - \frac{CG}{B^2} \right) - \frac{1}{2\sqrt{C^2 - 4AB}} \\ &\quad \cdot \left(\frac{CE}{B} - \frac{C^2 G}{B^2} - 2F + \frac{CD}{A} + \frac{2AG}{B} \right), \end{aligned} \quad (5)$$

$$\begin{aligned}
C &= (1-q)(n_1-1+p)(\varepsilon_1\sigma_2+\varepsilon_2\sigma_1) + (1-p)(1-q+n_2q)(\varepsilon_2\sigma_3+\varepsilon_3\sigma_2) \\
&\quad + (n_1-1+p)(n_1-1+q)(\varepsilon_3\sigma_1+\varepsilon_1\sigma_3) + (1-p)(n_1-1+q-n_2q)2\varepsilon_3\sigma_3, \\
D &= (1-q)(n_1-1+p-n_1p)\varepsilon_1^2\varepsilon_2 + (1-p+n_1p)(1-q+n_2q)\varepsilon_1\varepsilon_2\varepsilon_3 + (n_1-1+q) \\
&\quad \cdot (n_1-1+p-n_1p)\varepsilon_1^2\varepsilon_3 + (1-p+n_1p)(n_1-1+q-n_2q)\varepsilon_1\varepsilon_3^2, \\
E &= (1-q)(n_1-1+p-n_1p)(2\varepsilon_1\sigma_2+\varepsilon_2\sigma_1) + (1-p+n_1p)(1-q+n_2q)(\varepsilon_1\sigma_2\sigma_3+\sigma_1\varepsilon_2\sigma_3+\sigma_1\sigma_2\varepsilon_3) \\
&\quad + (n_1-1+q)(n_1-1+p-n_1p)(\varepsilon_3\sigma_1^2+2\varepsilon_1\sigma_1\sigma_3) + (1-p+n_1p) \\
&\quad \cdot (n_1-1+q-n_2q)(\varepsilon_1\sigma_3^2+2\varepsilon_3\sigma_1\sigma_3), \\
F &= (1-q)(n_1-1+p-n_1p)\varepsilon_1(\varepsilon_1\sigma_2+2\varepsilon_2\sigma_1) + (1-p+n_1p)(1-q+n_2q) \\
&\quad \cdot (\sigma_1\varepsilon_2\varepsilon_3+\varepsilon_1\sigma_2\varepsilon_3+\varepsilon_1\varepsilon_2\sigma_3) + (n_1-1+p-n_1p)(n_1-1+q)\varepsilon_1(2\varepsilon_3\sigma_1+\varepsilon_1\sigma_3) \\
&\quad + (1-p+n_1p)(n_1-1+q-n_2q)\varepsilon_3(2\varepsilon_1\sigma_3+\varepsilon_3\sigma_1), \\
G &= (1-q)(n_1-1+p-n_1p)\sigma_1^2\sigma_2 + (1-p+n_1p)(1-q+n_2q)\sigma_1\sigma_2\sigma_3 + (n_1-1+q) \\
&\quad \cdot (n_1-1+p-n_1p)\sigma_1^2\sigma_3 + (1-p+n_1p)(n_1-1+q-n_2q)\sigma_1\sigma_3^2. \tag{6}
\end{aligned}$$

Equation (1) can also be rewritten as

$$\frac{\varepsilon^*}{\varepsilon_1^*} = n_1 \left\{ p^{-1} \left[n_1 \left(\frac{\varepsilon_{23}^*}{\varepsilon_1^*} - 1 \right)^{-1} + 1 \right] - 1 \right\}^{-1} + 1. \tag{7}$$

This expression of $\varepsilon^*/\varepsilon_1^*$ as a function of $\varepsilon_{23}^*/\varepsilon_1^*$ suggests, since ε_1^* is supposed to be isotropic, that, if we are only interested in isotropic results for ε^* , it is sufficient to assume ε_{23}^* to be isotropic. This justifies the procedure employed to obtain the equivalent complex permittivity of the combination of the interior and the membrane (i.e., the discussion of the combination of the interior and the membrane in a hypothetical medium of the same substance as the membrane).

To retrace the procedure to obtain Eq. (1), it resulted, as is customary from equating the potential (at some arbitrary point P) due to an aggregate of small ellipsoidal particles and the potential due to an imaginary equivalent ellipsoid of those mixtures having the desired dielectric properties:

$$\frac{\varepsilon^* - \varepsilon_1^*}{n_1 \varepsilon_1^* + (\varepsilon^* - \varepsilon_1^*) \frac{l a'}{4 \pi} n_1} = P \frac{\varepsilon_{23}^* - \varepsilon_1^*}{n_1 \varepsilon_1^* + (\varepsilon_{23}^* - \varepsilon_1^*)}, \tag{8}$$

where

$$l a' = \int_0^\infty \frac{ds}{\frac{(a'^2+s)V(a'^2+s)(b'^2+s)(c'^2+s)}{2 \pi a' b' c'}}$$

corresponds to the shape of the above ellipsoidal volume of mixtures. Then, Sillars' next procedure is

to assume that $(\varepsilon^* - \varepsilon_1^*)(l a'/4 \pi) n_1$ is negligibly small compared to $n_1 \varepsilon_1^*$. However, if we rewrite Eq. (8) as

$$\begin{aligned}
&\frac{\varepsilon^* - \varepsilon_1^*}{n_1 \varepsilon_1^* + (\varepsilon^* - \varepsilon_1^*) + (\varepsilon^* - \varepsilon_1^*) \left[\left(\frac{l a'}{4 \pi} \right) n_1 - 1 \right]} \\
&= P \frac{\varepsilon_{23}^* - \varepsilon_1^*}{n_1 \varepsilon_1^* + (\varepsilon_{23}^* - \varepsilon_1^*)}, \tag{9}
\end{aligned}$$

and neglect $(\varepsilon^* - \varepsilon_1^*)[(l a'/4 \pi) n_1 - 1]$ compared to $n_1 \varepsilon_1^* + (\varepsilon^* - \varepsilon_1^*)$, Eq. (1) results. We recognize here that the shape of the whole mixture is usually taken rather arbitrarily. (In case of spherical particle suspensions, there is no guarantee that the whole mixture can be represented by a spherical volume because of the directional field.) However, we note that, if our whole system is represented by the similarly shaped ellipsoid as an individual ellipsoid, $(l a'/4 \pi) n_1 - 1 = 0$. Namely Sillars' approximation is based on the assumption that $\varepsilon^* \cong \varepsilon_1^*$, whereas ours is based on the assumption that $(l a'/4 \pi) n_1 \cong 1$ in addition to $\varepsilon^* \cong \varepsilon_1^*$. Even if we set $n_1 = 3$ in Sillars' result we cannot create spherical cases unlike ours. Thus we really did not assume that the whole mixture can be precisely represented by an ellipsoid of certain axial ratios but we only assumed that such axial ratio is nearly that of an individual ellipsoid.

The factorization adopted here is a little different from that of Pauly and Schwan⁷. The combination of parameters they obtained is not unique and there are also some non-realistic features such as $\sigma_{10} \varepsilon_{10} < 0$, etc. In order for τ to be the same as

to the one normally discussed, $C^2 - 4AB > 0$ must be satisfied. If $C^2 - 4AB = 0$, it will be reduced to a single relaxation. In a dielectric relaxation spectrum, we don't observe the Cotton effect and we rule out $C^2 - 4AB < 0$ overall.

Although we have given an actual example of double relaxation, such a situation may not be easily observable. The normalized experimental plottings should be carefully compared with the theoretical plottings to make sure that there are no systematic deviations, before declaring a single relaxation mechanisms.

Blurring of multiple relaxation can be explained by the use of piecewise-linear approximations to a curve for a single relaxation. Figure 3 shows such an approximation. The straight lines are the zero- and infinite-frequency asymptotes and a tangent to the curve at the relaxation frequency. As the simplest case, if one adds two relaxations that are characterized by the same increment, but by different relaxation frequencies one obtains a curve which can be classified into one of three cases, which are shown in Figs. 4, 5 and 6. If the two frequencies are widely separated, the double relaxation will be apparent (Figure 4). If they are different by some critical multiple (it happens to be the number e^2), the plot will actually appear to

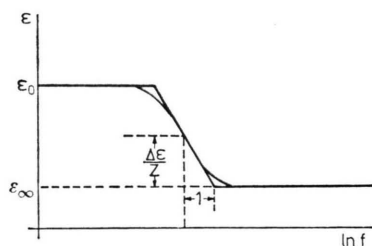


Fig. 3. Piecewise-linear approximation.
(Read 2 instead of Z .)

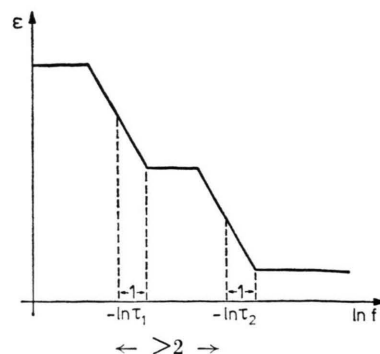


Fig. 4. Separated case of double relaxation.

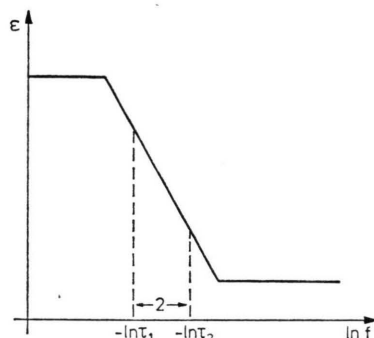


Fig. 5. Critical case of double relaxation.

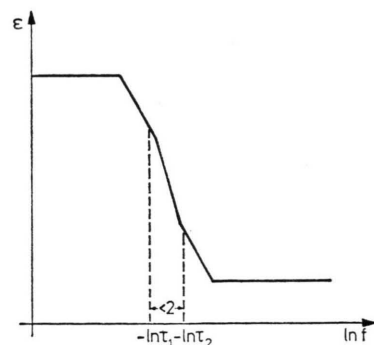


Fig. 6. Overlapped case of double relaxation.

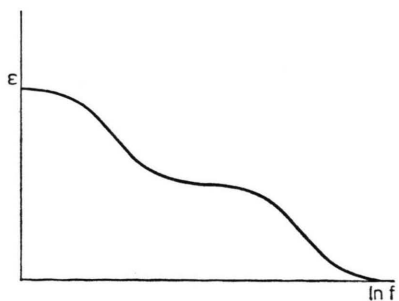


Fig. 7 a

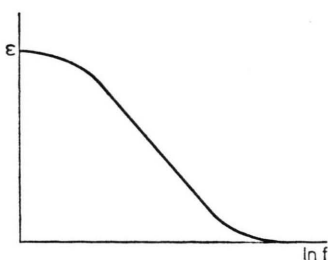


Fig. 7 b

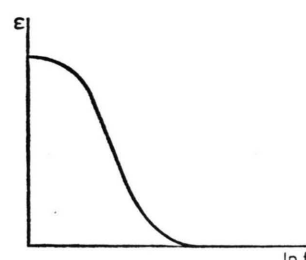


Fig. 7 c

Fig. 7. Example of a) the separated, b) the critical, and c) the overlapped case of double relaxation.

indicate a single relaxation with twice the increment (Figure 5). If they are closer than this critical distance, the plot is more complicated (Figure 6). As an example,

$$\epsilon' = \epsilon_{\infty} + \frac{\Delta\epsilon_1}{1 + w^2 \tau_1^2} \frac{\Delta\epsilon_2}{1 + w^2 \tau_2^2} +$$

is calculated for $\epsilon_{\infty} = 0$, $\Delta\epsilon_1 = \Delta\epsilon_2 = 0.5$ with differing values of τ_1 and τ_2 , corresponding to the above three cases, and the semilogarithmic plots

of ϵ' vs w are shown in Figs. 7, 8 and 9. In Fig. 7, which corresponds to the case of Fig. 4, double relaxation is clearly visible. In Fig. 7, which corresponds to the case of Fig. 5, you can hardly tell the difference from single relaxation with twice the increment. In Fig. 9, which corresponds to the case of Fig. 6, unlike the piecewise approximation the actual plotting does not show such zig-zagging and looks like a single relaxation, although the slope looks a bit steep.

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