The Dielectric Behavior of Colloidal Particles with an Electric Double-Layer

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The dielectric behavior of colloidal particles is treated mathematically. The particles are assumed to be spheres and the electric double-layer is represented by a concentric conducting shell. Assuming that the conductivity of the shell is large compared with that of the particle and that its thickness is small compared with the radius of the particle, the relaxation time in sec. is given by $3\,\epsilon\alpha/8\pi c^2\lambda_2 d$ where ϵ is the dielectric constant of the material of the particle, a its radius in cm, c the ratio of the e.m.u. to the e.s.u., λ_2 the conductivity of the shell in e.m.u., and d its thickness in cm. A distribution of particle size is assumed, and by the use of Wagner's treatment of non-homogeneous media expressions are obtained for the capacity and power factor as functions of the frequency. It is thus shown that the dielectric behavior predicted by Wagner for an assemblage of spheres having different specific conductivities may also result from an assemblage of colloidal particles of non-uniform size.

INTRODUCTION

A CONSIDERABLE number of theories have been proposed in explanation of the mechanism of power loss in liquid and solid dielectrics under alternating electric stress. Some materials behave in a simple manner in that the power loss can be calculated from the dielectric constant and the direct-current conductivity. Many materials are not so simple and the theories proposed for them follow one of two general lines. They consider either that the material is made up of a mixture of substances which separately behave in a simple manner, or that the material itself has an inherently complex behavior.

The theories dealing with the complex behavior of the material are based on the assumption of anomalous conductivity, dielectric hysteresis, or, more recently, the rotation of dipoles acted upon by viscous forces as treated by Debye.[1]

Maxwell[2] treated the case of a non-homogeneous material consisting of layers of simple dielectrics with different dielectric constants and conductivities and showed that an absorption current was to be expected. Grover[3] has shown that this would result in a change of the dielectric constant with frequency and a power factor different from that which would be calculated using the direct-current resistance.

[1] P. Debye, "Polar Molecules," Chemical Catalog Co., p. 77, New York, 1929.

[2] J. C. Maxwell, "Treatise on Electricity and Magnetism," Oxford University Press, New York, 1928.

[3] F. W. Grover, Bull. Bur. Stand. **7,** 519 (1911).

By assuming the material to be made up of elements of different relaxation times, whose nature is no more specifically described, von Schweidler[4] has shown that the dielectric behavior of certain materials can be explained. Using the experimentally determined charge and discharge currents, he has developed by means of the superposition principle (Hopkinson-Curie) expressions for the behavior of the power factor and capacity as functions of frequency.

Wagner[5] has considered a distribution law for the time constants proposed by von Schweidler and then has made use of this distribution in an extension of Maxwell's theory[6] in which the medium is supposed to consist of spheres of differing conductivities imbedded in a non-conducting medium. It should be remarked that the radii of the spheres play no part in the expression for the time constants of the material.

Murphy and Lowry[7] have proposed a mechanism to explain power loss in solid and liquid dielectrics. They assume (a) that the material contains insulating particles on which are adsorbed ions of both charges, (b) that under
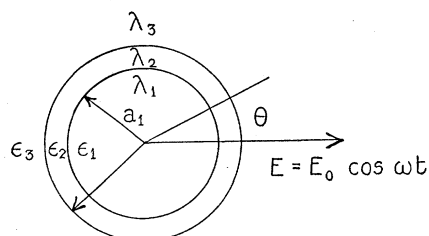

Fig. 1. Model of colloidal particle.

the influence of a field an ion can move freely over the surface, (c) that the ion cannot leave the surface until a critical voltage is attained, and (d) that the concentration of ions decreases at increasing distance from the interface. They consider that the particle alone is electrically equivalent to a pure capacity and that the ions beyond the interface are equivalent to parallel capacities with series resistances of different values, and therefore with different relaxation times. They then set up expressions for the capacity and power factor of such a system of condensers, but the constants which are involved are not determined.

THEORY

We shall here consider a mechanism somewhat similar to that of Murphy and Lowry. The dielectric is assumed to consist of poorly conducting particles surrounded by ionic atmospheres and imbedded in a non-conducting medium. We wish to consider the effect of the size of the particles upon the power factor and dielectric constant. For the purpose of mathematical treatment the particles are represented by spheres and the ionic atmospheres by concentric shells of a certain conductivity. The model is drawn in Fig. 1 and corre-

[4] E. von Schweidler, Ann. d. Physik 24, 711 (1907).

[5] K. W. Wagner, Ann. d. Physik 40, 817 (1913).

[6] K. W. Wagner, Arch. Elektr. 2, 371 (1914).

[7] E. J. Murphy and H. H. Lowry, J. Phys. Chem. 34, 598 (1930).

sponds roughly to the accepted picture of colloidal particles possessing an electric double-layer. The conductivity of the atmosphere surrounding a colloidal particle undoubtedly varies with the distance from the surface but it is here considered to be lumped into an equivalent conducting layer of a certain thickness.

Wagner has treated a system of conducting spheres in a non-conducting medium. Use will be made of this treatment, which gives expressions for the capacity and power factor, by showing that our model is equivalent to a conducting sphere the conductivity of which depends on the constants of the model. By assuming that the conductivity of the spheres varies in a certain way about a most probable conductivity, Wagner obtained expressions for the power factor and dielectric constant of the system which are functions of the frequency. These expressions give curves which are typical of a great many dielectric materials. It is here shown that a similar sort of behavior would be displayed by a dielectric containing spheres of different radii, each surrounded by a conducting shell. Such a system corresponds roughly to the structure of colloidal dispersions.

An outline of the argument to be used follows. The material is supposed to consist of spheres as shown in Fig. 1. The central sphere of radius a_1, has a conductivity of λ_1 and a dielectric constant, ϵ_1. The concentric shell has a radius a_2, conductivity λ_2, dielectric constant ϵ_2, and the outside medium has conductivity and dielectric constant respectively, λ_3, and ϵ_3.

The dielectric constant and conductivity are combined into a complex conductivity to be represented by $\Lambda = \lambda + i\omega\epsilon/4\pi c^2$, where i is $(-1)^{1/2}$, c the ratio of the e.m.u. to the e.s.u. and $\omega/2\pi$ is the frequency. This sphere with its shell is shown to be equivalent to a single sphere of complete conductivity $\overline{\Lambda}$. It is found that $\overline{\Lambda}$ is a function of Λ_1, Λ_2, and the ratio a_2/a_1, and is independent of the conductivity of the medium, Λ_3. The fact that the equivalence is independent of Λ_3 makes it possible to substitute in Wagner's expression for the conductivity of a single sphere, an expression which involves the conductivities of the sphere and the shell and their respective radii. In this way Wagner's work can be taken over directly. By the use of simplifying assumptions and approximations it is possible to get the equivalent conductivity in terms of a single expression, and then by considering a distribution of particle size, rather than a distribution of conductivity as Wagner did, we obtain expressions for the power factor and the capacity as functions of the frequency.

We will now take up the argument in detail. Referring to Fig. 1, let the potentials in the three media be V_k, where $k = 1, 2, 3$; the corresponding electric field strengths are then

$$E_k = - \text{grad } V_k. \tag{1}$$

We consider the sphere immersed in a uniform alternating electric field, the direction of which is along the z axis; the field is accordingly axially symmetric about this axis. Since there are no free charges in the various media the V_k must satisfy Laplace's equation

$$\Delta V_k = 0 \tag{2}$$

and in virtue of the axial symmetry may, on choosing polar coordinates with z axis as pole, be taken in the form

$$V_k = \sum_{n=0}^{\infty}(A_{kn}r^n + B_{kn}r^{-(n+1)})P_n(\cos\theta) \tag{3}$$

where $P_u(\cos\theta)$ is the nth Legendre polynomial.

The boundary conditions to be satisfied by the V_k are as follows: (a) the field must become uniform as $r\rightarrow\infty$, i.e., $\boldsymbol{E}_3\rightarrow(0, 0, E_0\,e^{i\omega t})$. But this requires that

$$A_{31} = -E_0 e^{i\omega t}; \quad A_{3n} = 0(n > 1) \tag{4}$$

to which we may add the normalizing condition

$$A_{30} = 0. \tag{5}$$

(b) V_1 can have no singularity at the origin, whence

$$B_{1n} = 0 \tag{6}$$

for all n. (c) The potentials must be continuous at the boundaries $r = a_1,\ a_2$ of the spherical shell, i.e.,

$$V_3(a_2) = V_2(a_2); \quad V_2(a_1) = V_1(a_1). \tag{7}$$

Finally, the normal component *total* current

$$\boldsymbol{i}_k = \left(\lambda_k + \frac{i\omega\epsilon_k}{4\pi c^2}\right)\boldsymbol{E}_k = \Lambda_k\boldsymbol{E}_k \tag{8}$$

must be continuous at the boundaries, i.e.,

$$\Lambda_3\frac{\partial V_3}{\partial r} = \Lambda_2\frac{\partial V_2}{\partial r} \text{ for } r = a_2$$

$$\Lambda_2\frac{\partial V_2}{\partial r} = \Lambda_1\frac{\partial V_1}{\partial r} \text{ for } r = a_1 \tag{9}$$

Conditions (4)–(9) are readily solved for the constants A_{kn}, B_{kn} of Eq. (3); since we are only interested in the region exterior to the sphere we only write down the results referring to this medium:*

$$B_{31} = \frac{(\Lambda_3 - \Lambda_2)(2\Lambda_2 + \Lambda_1)a_2{}^3 + (\Lambda_2 - \Lambda_1)(\Lambda_3 + 2\Lambda_2)a_1{}^3}{(2\Lambda_2 + \Lambda_1)(2\Lambda_3 + \Lambda_2)a_2{}^3 + 2(\Lambda_2 - \Lambda_1)(\Lambda_3 - \Lambda_2)a_1{}^3}a_2{}^3A_{31}$$

$$B_{3n} = 0 \quad (n \neq 1). \tag{10}$$

Following Wagner we ask whether it is possible to describe this field as due to a single sphere of radius a_2 and complex conductivity $\bar{\Lambda}$ immersed in

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* These results as well as (11) and (12) below may be taken directly from J. C. Maxwell, "Electricity and Magnetism" 3rd Ed. Vol. 1, pp. 437–438 (Oxford 1892) (in particular, from Eqs. (6), (10), and (11)) on noting that the mathematical problem here involved is equivalent to his on replacing the (real) specific resistance k by the reciprocal of the complex conductivity Λ.

a medium of complex conductivity. Under the same conditions as those for the double sphere the potential exterior to the single sphere will be given by

$$V_3 = A_{31}\left(r + \frac{a_2{}^3}{r^2} \frac{\Lambda_3 - \bar{\Lambda}}{2\Lambda_3 + \bar{\Lambda}}\right)\cos\theta. \tag{11}$$

Equating the two expressions (3) and (11) for V_3 and solving for $\bar{\Lambda}$ we find

$$\bar{\Lambda} = \frac{(2\Lambda_2 + \Lambda_1)a_2{}^3 - 2(\Lambda_2 - \Lambda_1)a_1{}^3}{(2\Lambda_2 + \Lambda_1)a_2{}^3 + (\Lambda_2 - \Lambda_1)a_1{}^3}\Lambda_2. \tag{12}$$

The double sphere is therefore equivalent to a single sphere whose conductivity is given by the last equation, expressing the conductivity of the latter in terms of the conductivities and radii of the former. This equivalence is perfectly general and does not depend on the medium surrounding the spheres since Λ_3 no longer appears. Wagner derived expressions for the capacity and power factor of an assemblage of single spheres and from the above argument we see that exactly the same electrical behavior results from an assemblage of spheres with shells. We could at any point in Wagner's discussion substitute for the conductivity of his single spheres by means of Eq. (12).

For our purposes, however, it is convenient to introduce at this point some simplifying assumptions. We assume (A) that the conducting shell is thin compared with the radius of the sphere and that its thickness d is constant, i.e.,

$$d/a \ll 1 \text{ and } a_2 = (a_1 + d) \tag{13}$$

(B) that Λ_2 is large compared with Λ_1 or

$$|\Lambda_2/\Lambda_1| \ll 1. \tag{14}$$

On dividing numerator and denominator of Eq. (12) by $2\Lambda_2 a_1{}^3$, substituting from Eq. (13) for $a_2{}^3$ and expanding, neglecting higher powers of d/a_1, and dropping the subscript of a, we have

$$\bar{\Lambda} = \frac{(1 + \Lambda_1/2\Lambda_2)(1 + 3d/a) - (1 - \Lambda_1/\Lambda_2)}{(1 + \Lambda_1/2\Lambda_2)(1 + 3d/a) + \frac{1}{2}(1 - \Lambda_1/\Lambda_2)}\Lambda_2. \tag{15}$$

Expanding and neglecting the product of the small quantities Λ_1/Λ_2 and d/a, we have

$$\bar{\Lambda} = \frac{3\Lambda_1/2 + 3d\Lambda_2/a}{3/2 + 3d/a} \tag{16}$$

$$\bar{\Lambda} = \Lambda_1 + 2d\Lambda_2/a. \tag{17}$$

We now have this simple expression in place of the more complicated Eq. (12) giving the conductivity of the equivalent single sphere and will use it to substitute in Wagner's equations. He gives for the relaxation time of the single sphere

$$\frac{\bar{\epsilon} + 2\epsilon_3}{4\pi c^2(\bar{\lambda} + 2\lambda_3)}. \tag{18}$$

For the relaxation time of our model we obtain by the indicated substitution

$$T = \frac{\epsilon_1 + 2d/a + 2\epsilon_3}{4\pi c^2(\lambda_1 + 2d\lambda_2/a + 2\lambda_3)} \cdot \tag{19}$$

Further simplification is obtained by following Wagner in assuming that $\epsilon_1 = \epsilon_3$ and in addition that the conductivity of the shell in relation to the sphere is so large that λ_1 can be neglected with respect to $2\lambda_2 d/a$ and that $\epsilon_2 d/a \ll \epsilon_1$. We have, then

$$T = \frac{3\epsilon_1 a}{8\pi c^2 \lambda_2 d} \tag{20}$$

for the relaxation time of a non-conducting sphere surrounded by a thin concentric conducting shell.*

Now in order to interpret the experimental facts for many materials it has been shown by von Schweidler[4] and others that it is necessary to assume that the materials are made up of an assemblage of elements having different relaxation times. Since the relaxation time in Wagner's expression, Eq. (18), does not depend on the radii of his spheres, he considers that the variation in T is due to a variation of conductivity. As the radius appears in our expressions for the relaxation time, Eqs. (19) and (20), we shall consider the variation in T to be due to a variation in the radius. We thus depend on the variation of particle size rather than inhomogeneity in particle constitution for the necessary distribution of relaxation times.

The next step is to choose some function to represent the distribution of particle size. Wagner gives reasons for assuming that the conductivities of the spheres differ in such a way that the relaxation times are distributed according to a logarithmic error function and then uses the analysis of his earlier paper[5] in which such a distribution was taken. Since there is no general function expressing the distribution of particle size in colloidal dispersions we will choose a function which, while representing approximately the distribution in typical colloids, gives the same distribution of relaxation times as used in Wagner's treatment. Such a function results if we assume that the volume per cc occupied by spheres of radius between a and $a+da$ is given by

$$dV_a = \frac{Vb}{(\pi)^{1/2}} \frac{1}{a} e^{-(b \log a/a_0)^2} da \tag{21}$$

where V is the total volume per cc occupied by the spheres and b is a constant which determines the density of grouping about a most probable radius a_0. Curves illustrating this function are given in Fig. 2. The general shape is characteristic of the distribution found for small particles.[8]

* The more complete theory of the relaxation times for our model leads to two such times which in the approximation $d/a \ll 1$ here considered are given by Eq. (20) and $\epsilon/4\pi c^2\lambda$. But the effect of this second term is negligible in comparison to that of the first in our case, for in addition to being short in comparison with (20) it appears with an initial amplitude of relative order $d/3a$.

[8] See for example, R. P. Loveland and A. P. H. Trivelli, J. Franklin Inst. **204**, 193 (1927); S. Odén, Chap. 58, "Colloid Chemistry," J. Alexander, Chemical Catalog Co., New York; J. B. Nichols, Physics **1**, 254 (1931).

We wish to show that the particle size distribution, Eq. (21), gives the time constant distribution assumed by Wagner. Eq. (21) can be written thus

$$dV_a = (Vb/\pi^{1/2})e^{-(b\log a/a_0)^2}d\log a/a_0 \tag{22}$$

which, on substituting for a in terms of T by Eq. (20), becomes

$$dV_a = (Vb/\pi^{1/2})e^{-(b\log T/T_0)^2}d\log T/T_0 \tag{23}$$

Wagner's Eq. (44)[6] gives for the distribution of the volumes occupied by the single spheres of different time constants.

$$3dV_a = (Kb/\pi^{1/2})e^{-(b\log T/T_0)^2}d\log T/T_0 \tag{24}$$

where K is a constant (Nachwirkungskonstant)* appearing in his first treatment of a distribution of time constants[5] and is defined as follows: When a
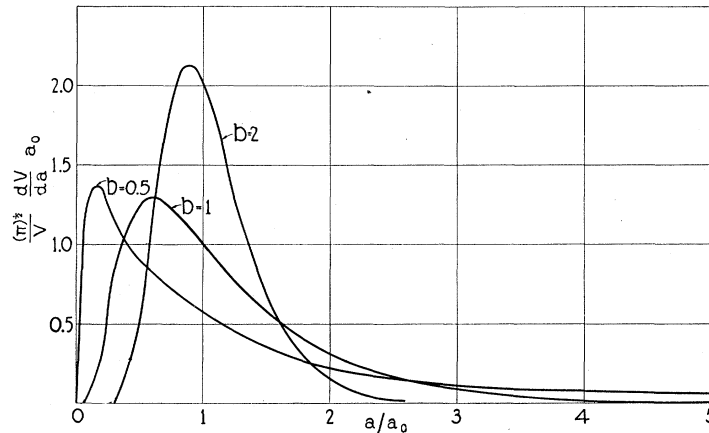

Fig. 2. Assumed volume distribution of particle size.

field is impressed on an imperfect dielectric the electric displacement after a long time, D_∞, is greater than the initial displacement, D_0, and is given by

$$D_\infty = D_0(1 + K). \tag{25}$$

Comparing Eqs. (23) and (24) we see that Wagner's equations may be applied to our case if we substitute $3V$ for k. In his treatment the capacity at any frequency is given by $C+\Delta C$ where C is the capacity at infinite frequency. Making the substitution for k, his equation becomes

$$\frac{\Delta C}{C} = \frac{3Vb}{\pi^{1/2}}e^{-b^2z_0^2}\int_0^\infty e^{-b^2u^2}\frac{\cos(2b^2z_0-1)u}{\cos u}du \tag{26}$$

and for the power factor, $\tan\phi$,

$$\left(1+\frac{\Delta C}{C}\right)\tan\phi = \frac{3Vb}{\pi^{1/2}}e^{-b^2z_0^2}\int_0^\infty \frac{e^{-b^2u^2}\cos 2b^2z_0u}{\cos u}du. \tag{27}$$

Here

$$z = \log T/T_0, \quad z_0 = \log T_0, \quad \text{and} \quad z+z_0 = u,$$

* See "Elektrophysik der Isolierstoffe," A. Gemant, Julius Springer, Berlin, 1930, p. 95, for amplification of the meaning of this constant and also on the pages following for calculation of the relaxation time by a method similar to Wagner's.

Tables and curves illustrating these equations are given in Wagner's paper.[5] In Figs. 3 and 4 are reproduced his curves for capacity and power factor as functions of frequency.

It is of interest to see the order of magnitude to be expected for the value of T_0. Eq. (20) becomes

$$T_0 = 1.33(a/d)\epsilon_1(1/\lambda_2')10^{-13} \tag{28}$$

where λ_2' is expressed in reciprocal ohms. If we assume the electric double-layer[9] of the order of 10^{-7} cm in thickness, a particle radius of 10^{-5} cm, and a conductivity of 10^{-3}, then the relaxation time will be 1.33×10^{-8}. We should not expect the conductivity to be greater than that of a strong acid in aqueous solution, i.e., of the order of 1 and it will probably be less than that. With this value of T_0, a decrease in the dielectric constant and an increase in the power factor should be observed in the range of the high radio frequencies, i.e.,
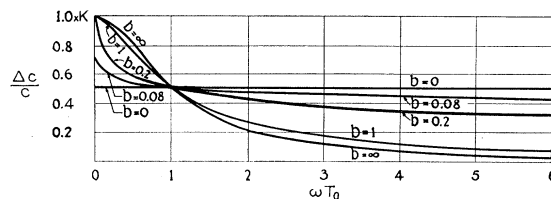
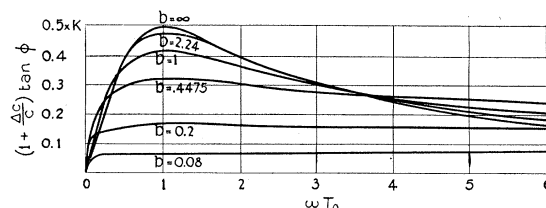

Fig. 3. Capacity increment as a function of ωT_0.

Fig. 4. Power factor as a function of ωT_0.

at about 10^7. In many cases the particle size may be larger than 10^{-5} cm, and as we see from the above expression, the relaxation time increases with increasing particle size, so that for particle sizes of the order of 10^{-4} cm the whole region of anomalous behavior would fall in the range of frequencies in which measurements can easily be made.

In some cases the relaxation time may be so short that it will be experimentally impossible to determine C, the capacity at infinite frequency. In order to make use of Eqs. (26) and (27) this quantity must be known. However, it should be possible to calculate C from the dielectric constants of the medium and the material of the spheres. Methods of doing this are discussed by Piekara.[10]

It should be pointed out that the assumptions made in simplifying Eq. (12) place certain limitations on the applicability of the simple expression

[9] T. Svedberg, "Colloid Chemistry," p. 195, Chemical Catalog Co., New York, 1924.
[10] A. Piekara, Phys. Zeits. **31,** 579 (1930).

for the relaxation time which results, Eq. (20). For small particle sizes of the order of 10^{-7} cm it has been estimated that the thickness of the ionic layer is of the same order as the particle radius.[11] We have assumed that d/a is less than one, so that we can apply our expressions only to the larger particles. Since we have assumed the particles to be relatively non-conducting the results will not be applicable to dispersions of colloidal metals. We have tacitly assumed in expression (14) that

$$\omega\epsilon_1/4\pi c^2\lambda_2 \ll 1$$

or in using Eq. (20) we must have

$$(2/3)\omega Td/a \ll 1.$$

We have assumed d/a small so that the expressions are valid for a frequency as high as $1/T$ and for frequencies above this the validity will depend on the value of d/a.

Speculations of a qualitative nature have often been made as to the effect of adsorbed ions on the alternating current losses in liquid and solid dielectrics and of the effect of colloidal particles on these losses in transformer oils. With the aid of Eq. (20) we can obtain quantitative expression for the frequency at which the maximum power loss is to be expected for one model. For other spherical models with different conditions of shell thickness, conductivity, etc., a similar procedure might be undertaken to obtain the relaxation time by use of the general Eq. (12) and substitution in Wagner's expression for the relaxation time, Eq. (18). In view of the impossibility of obtaining a rigorous mathematical representation of the form of the conducting surfaces, their conductivities, etc. in the case of solid dielectrics and of the lack of knowledge of the nature of the electric double-layer in colloids it does not seem worth-while to undertake the expression of the relaxation time for more general cases of the spherical model. It is evident from the expressions obtained for the model treated in detail that in addition to the recognized effect of the volume concentration and conductivity of impurities on the dielectric behavior, the effect of size is also of importance in certain cases.

In addition to providing an interpretation of dielectric behavoir, this analysis provides means for investigating colloidal structure. For example an indication of the degree of uniformity of particle size could be obtained from the shape of the power factor vs. frequency curve, or the position of a maximum in this curve would give the most frequent relaxation time giving definite relationship between the particle radius, the thickness of the ionic atmosphere and its conductivity.

In conclusion one of the authors (J.B.M.,Jr.) wishes to express his appreciation of the encouragement and helpful criticism which he has received from Dr. E. O. Kraemer during the preparation of this paper.

[11] A. Tiselius, Diss., Upsala, 1930.