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and
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ABSTRACT

Precise conductivity measurements on models sectioned out from a cubic lattice of spheres in a continuous medium, indicate that the effective conductance of such a system deviates from the values predicted by Lord Raleigh's analytic solution of this potential distribution problem. Deviations become particularly significant when the spheres approach close packing, and when the conductance of spheres is much greater than that of the continuum. By use of a different function for potential, and by consideration of higher terms in the series expression for the potential in the continuous phase, Rayleigh's results are modified, yielding an analytical expression that represents effective conductance satisfactorily in the concentration region approaching close packing.

* Work done under the auspices of the U. S. Atomic Energy Commission.

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INTRODUCTION

Interest in the classical problem of evaluating the effective conductance k_m , in a uniform medium of conductance k_c that is interrupted by discrete regions of known shape characteristics and of conductance k_d has been renewed in recent years.¹⁻⁵ Paralleling the exact treatment by Maxwell⁶ valid for very dilute dispersions of spheres, Fricke⁷ developed correct relations for the cases when the dispersed phase consists of spheroids.

When the obstacles are no longer very small in comparison to the distance between them, the effects of fields around each particle on each other must further be taken in account. Lord Rayleigh⁸ considered the case of a cubic array of uniform size spheres, and took into account the effect on the potential in the neighborhood of a sphere by 248 of its closest neighbors (lying within the first 15 shells around a central sphere). In essence, Rayleigh solved the Laplace equation for the potential inside and about a sphere by using the principle of superposition to take into account the effects of surrounding spheres on the field in the neighborhood of the central sphere.

The resulting final equation, expressing the conductivity of the mixture in terms of the conductivities of the two phases and the volume fraction:

$$K_m = \frac{\frac{2 + K_d}{1 - K_d} - 2f - 0.525 \frac{3 - 3K_d}{4 + 3K_d} f^{10/3}}{\frac{2 + K_d}{1 - K_d} + f - 0.525 \frac{3 - 3K_d}{4 + 3K_d} f^{10/3}} \quad * \quad (1)$$

*This equation includes a numerical correction introduced by Runge,⁹ the coefficient 0.525 replaces 1.65 in the denominator, correcting for the omission of a factor of $1/\pi$ in Rayleigh's derivation.

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where, $K_d = \frac{k_d}{k_c}$, $K_m = \frac{k_m}{k_c}$, f = volume fraction of discontinuous phase

is plotted in Fig. for $K_d \rightarrow \infty$ and for $K_d = 0$.

Inspection of equation 1 reveals that it reduces to Maxwell's relation when $f \rightarrow 0$:

$$K_m = \frac{K_d + 2 - 2f(1 - K_d)}{K_d + 2 + f(1 - K_d)} \quad (2)$$

indicating that at this lower limit the solution becomes exact. With increasing f and also with K_d , the discrepancy between the Maxwell relation and Rayleigh expression becomes increasingly significant. Of particular interest is the region of volume concentrations when the spherical particles in the cubic lattice nearly touch each other. At $f = 0.5236$, the spheres are in point contact, and, for $K_d \rightarrow \infty$ therefore, the effective conductance should approach infinity also. Obviously this condition is approached asymptotically as the volume fraction of the discontinuous phase nears this limit in volume fraction.

These qualitative conditions, however, are not satisfied by Rayleigh's equation, neither has Rayleigh elaborated on this point in his definitive work on the subject. To obtain information about this critical region of volume concentrations an experimental investigation was undertaken, and the steps involved in the mathematical development by Rayleigh were reevaluated.

EXPERIMENTAL

Experimental studies on ordered arrangements of spheres were previously performed by Slawinski,¹⁰ Pearce,¹¹ and Mashovets.¹² Findings of these authors on identical models are not in good agreement. The experimental techniques employed and the analysis of data in all three cases point to questions left unresolved.

The conductivity cell used for this study consisted of a unit of cubical geometry defined by lucite walls and silver-plated copper electrodes. Two of these cells were used; one cell was designed to act as a reference unit and to give a measurement of the conductivity of continuous phase or electrolyte.

The overflow outlets and the electrode spacing was such that each cell had the internal dimensions of 5" x 5" x 5" (see Figure 1).

Two carefully machined hemispheres were constructed for each run. representative of a volume packing. For the case of a nonconducting dispersed phase the material of construction was brass. The machining was of such precision that the difference between the volumes of any pair of hemispheres was less than 0.1%. Furthermore, the volume of any hemisphere as calculated from its measured radius was in agreement with its volume as calculated from its measured diameter to within 0.1%. Thus, the hemispheres that formed a pair were not only equal in size, but were also true in shape for all practical purposes. Threaded screw holes were placed in the center of the flat sides of the hemispheres and were matched with holes in the center of the electrode surfaces. The objects to be studied were locked flush against the electrodes by means of a locking screw.

The conductivity bridge used in this study contained components that were symmetrically shielded and arranged to cover from 0.1 to 100 kc with less than 1% absolute error.

Tap water was used as the electrolyte in this study, and prior to making any measurements, the water was circulated between the working cell and the reference cell and allowed to come to equilibrium at room temperature. The liquid level in both cells was carefully brought up to a standard reference mark by using a hypodermic syringe.

Conductance values obtained with a set of brass hemispheres are given in Table I as a function of bridge frequency. From these data it is evident that, for studies involving clean brass and tap water, polarization can continue to be a source of error up to relatively high frequencies. Pearce's data, taken on a similar model at 0.4 kc, may consequently be considered to be in error by as much as 25%.

The results are given in Table I and Fig. 3. At least four measurements were made for every run or data point that appears in Table I. The typical standard deviation for data taken at each volume fraction is less than 1%.

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Table I

Conductivity data on dispersions of spheres arranged in cubic arrays		
<u>$K_d = 0$</u>		
Dia. in inches	Vol. fract.	K_m
1.993	0.0332	0.9609
3.468	0.1747	0.7649
3.959	0.2600	0.6510
4.976	0.5161	0.3520
<u>$K_d = \infty$</u>		
Dia. in inches	Vol. fract.	K_m
1.993	0.0332	1.114
3.468	0.1747	1.659
3.957	0.2595	2.141
4.487	0.3785	3.008
4.726	0.4421	3.905
4.976	0.5161	7.570

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Table II

Data on brass spheres as a function of
frequency ($f = 0.5161$, dia. = 4.976")

<u>Freq.</u> <u>in kc</u>	<u>K_m</u>
0.40	5.7
1.00	6.9
10.00	7.5
50.00	7.6
90.00	7.6

THEORETICAL

In the original work by Rayleigh, terms higher than those involving the cube of the distance were omitted from the Legendre polynomials expressing the potential about the point of origin.* This is a perfectly reasonable and acceptable measure, one however, which should be subjected to scrutiny in regards to limitations it may have introduced.

In the following, the technique of Rayleigh's derivation is retained, however, a different series expansion for the function representing potential is employed.

Consider a cubical lattice of spheres oriented in such a manner that the field E_0 is pointing in the x direction and is perpendicular to a principal plane of the lattice (Fig. 2). If the shortest distance between spheres is α then a unit cell consists of a cube with edge length equal to α with a sphere of radius $\underline{a}$ in its center. Let the center of a sphere at point P be chosen as the origin for rectangular coordinates and let θ be an angle in the xy plane. Symmetry considerations require that the potential be reversed when $(\pi - \theta)$ is substituted for θ , and require also that the results be independent of angle in the yz plane. The expressions for the potential in the continuous phase around P and in the dispersed phase which includes P are thus expansions in odd Legendre polynomials P_{2n-1} :

$$V_c = A_0 + \sum_{n=1}^{n=\infty} (A_{2n-1} r^{2n-1} + B_{2n-1} r^{-2n}) P_{2n-1} \quad ** \quad (3)$$

$$V_d = \sum_{n=1}^{n=\infty} (C_{2n-1} r^{-2n}) P_{2n-1} \quad (4)$$

* Eq. 61, page 494 Ref. (8).

** The expressions for the potential given in Eqs. (3) and (4) are of a different form from the relations used by Lord Rayleigh. In his work he used series expansions which result in changing the P_{2n-1} term to a Y_{2n-1} , where

$$P_n = \frac{1.3.5 \dots (2n-1)}{n!} Y_n$$

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At the interface between the dispersed and continuous phases, the potential and current must be continuous. Using these boundary conditions, one obtains for the constants in Eq. (3),

$$A_n = \frac{K_d + (n+1)/n}{1 - K_d} a^{-(2n+1)} B_n \quad (5)$$

An expression for the conductivity of the mixture may be obtained by applying Green's Theorem to the boundary of the continuous medium in the unit cell. If U and V are harmonic functions, we may write

$$\int_S \left(U \frac{\partial V}{\partial n} - V \frac{\partial U}{\partial n} \right) dS = 0. \quad (6)$$

More specifically, we set $V = V_c$ and $U = r \cos(\theta) = x$. The above integral now has no contribution from the sides of the cube parallel to the field. Along the faces normal to the direction of the field, the terms in the above integral have the values of $I\alpha$ and $V' \alpha^2$ respectively. Here I is the total current crossing the unit cell and V' is the potential drop through the unit cell. Along the spherical boundary, the direction of the normal is negative to the radius vector and Eq. (7) becomes

$$V' \alpha^2 - I\alpha = 2\pi a^2 \int_0^\pi [V_c - a(\partial V_c / \partial r)_{r=a}] \cos(\theta) \sin(\theta) d\theta. \quad (7)$$

When Eq. (3) is substituted into (6) and the integral is evaluated term by term, it is found that the only nonzero value is $4\pi B_1$. Then, by Green's Theorem

$$I\alpha - V' \alpha^2 + 4\pi B_1 = 0. \quad (8)$$

The above equation may be rearranged to give the specific conductivity of the mixture, i.e.,

$$K_m = I/V' \alpha = (1 - 4\pi B_1/E_0 \alpha^3). \quad (9)$$

V has been replaced by $E_0 \alpha$ in the last term. This identity is valid because the drop in potential across the cell is equal to the line integral of the field between the faces of the cube.

For further development one must obtain a value for $B_1/E_0 \alpha^3$. An approximate value for this term may be arrived at in the following manner:

Note that the potential around P, when P is not included, is given by Eq. (3) with terms containing B omitted, i.e.,

$$V_c = A_0 + \sum_{n=1}^{n=\infty} (A_{2n-1} r^{2n-1})_{P_{2n-1}} \quad (10)$$

This same potential, however, may be regarded as due to the original field plus sources of potential at each of the neighboring spheres (P not included), i.e.,

$$V_c = E_0 x + \sum_{n=1}^{n=\infty} \sum_{i=1}^{i=\infty} B_{2n-1} r_i^{-2n} P_{2n-1,i} \quad (11)$$

In this latter expression, the summation in i extends over all spheres in the mixture except the sphere P which is located at the center of the coordinate system. The radius vector and the Legendre Polynomials that appear in this relation are understood to be evaluated with an origin at the i th sphere. That is, if r is a radius vector with respect to the center of the sphere at P and ξ_i , η_i , and ζ_i are the coordinates of the i th sphere with respect to P, then we have

$$x_i = x - \xi_i, \quad y_i = y - \eta_i, \quad z_i = z - \zeta_i \quad (12)$$

and

$$r_i^2 = (x - \xi_i)^2 + (y - \eta_i)^2 + (z - \zeta_i)^2 \quad (13)$$

For convenience let us also set

$$\rho_i^2 = \xi_i^2 + \eta_i^2 + \zeta_i^2, \quad (14)$$

so that when r is zero we have

$$r_i = \rho_i \quad (15)$$

with respect to the origin centered at P.

Combining Eqs. (10) and (11) we obtain

$$\begin{aligned}
 A_0 + \sum_{n=1}^{\infty} (A_{2n-1} r^{2n-1}) P_{2n-1} \\
 = E_0 x + \sum_{n=1}^{\infty} \sum_{i=1}^{\infty} (B_{2n-1} r_i^{-2n}) P_{2n-1,i} \quad (16)
 \end{aligned}$$

The next step in evaluating $B_i/E_0 \alpha^3$ is to take successive derivatives of Eq. (16) with respect to x and evaluate the results at the point P . In performing this latter operation we note that the point (x_i, y_i, z_i) becomes the point (ξ_i, η_i, ζ_i) and r_i is replaced by ρ_i . The Legendre polynomials, $P_{2n-1,i}$ become functions of ξ_i/ρ_i . Noting also that

$$\frac{\partial}{\partial x} (r^{2n-1} P_{2n-1}) = (2n-1) r^{2n-2} P_{2n-2} \quad (17)$$

and

$$\frac{\partial}{\partial x} (r^{-2n} P_{2n-1}) = - (2n) r^{-2n-1} P_{2n} \quad (18)$$

we find that the first five derivatives yield

$$A_1 - E_0 = - (2n) B_{2n-1} \rho_i^{-2n-1} P_{2n,i} \quad (19)$$

$$6A_3 = - (2n)(2n+1)(2n+2) B_{2n-1} \rho_i^{-2n-3} P_{2n+2,i}$$

$$120A_5 = - (2n)(2n+1)(2n+2)(2n+3)(2n+4) B_{2n-1} \rho_i^{-2n+5} P_{2n+4,i}$$

where summations in n and i extend from 1 to ∞ .

The coordinates of all spheres, with respect to the sphere at P , are of the form $l\alpha, m\alpha, n\alpha$, where l, m , and n are integers. If α is chosen as a unit distance, then we may write

$$\sum_{i=1}^{i=\infty} \frac{\rho_i^{-2n-1}}{\rho_i} P_{2n,i} = \alpha^{-2n-1} S_{2n}, \quad (20)$$

where S_{2n} is now purely numerical and represents a sum over all spheres except the one at P, e.g.,

$$S_2 = \sum_{i=1}^{i=\infty} \frac{2 \xi_i^2 - \eta_i^2 - \zeta_i^2}{2 \rho_i^5} \quad (21)$$

Noting that the A's may be expressed in terms of B's by use of Eq. (5), we may generate an n-by-n matrix in terms of S's and the unknown B's. Thus, by substitution of Eq. (20) into the relations given under Eq. (19), we obtain $A_1, A_3, A_5, \dots$ in terms of $S_2, S_4, S_6, \dots$. Rayleigh considered only A_1 and A_3 in terms of S_2 and S_4 . In the present development we are going to consider the next higher terms also, and obtain:

$$A_1 - E_0 = -2B_1 S_2 \alpha^{-3} - 4B_3 S_4 \alpha^{-5} - 6B_5 S_6 \alpha^{-7}, \quad (22)$$

$$A_3 = -4B_1 S_4 \alpha^{-5} - 20B_3 S_6 \alpha^{-7}, \quad (23)$$

$$A_5 = -6B_1 S_6 \alpha^{-7}. \quad (24)$$

Lord Rayleigh has evaluated S_2 and S_4 for a medium which is infinitely more extended in the direction of the field. His results are:

$$S_2 = 2\pi/3 \quad (25)$$

and

$$S_4 = 3.11. \quad (26)$$

To evaluate S_6 , we use Eq. (20) and thereby obtain:

$$S_6 = \sum_{i=1}^{i=\infty} \frac{231 \xi_i^6 - 315 \xi_i^4 \rho_i^2 + 105 \xi_i^2 \rho_i^4 - 5 \rho_i^6}{16 \rho_i^{13}} \quad (27)$$

Numerical evaluation of this sum yields

$$S_6 = 0.576 \quad (28)$$

We are now in the position to express all variables in terms of K_d and f ; combining Equations (5), (9), (22), (23), (24), (25), (26), (28) and considering that

$$f = (4\pi/3)(a/\alpha)^3 \quad (29)$$

the relation for the effective conductivity of the mixture is obtained:

$$K_m = 1 - \frac{3f}{\frac{2 + K_d}{1 - K_d} + f - \frac{1.315f^{10/3}}{\frac{(4/3 + K_d)}{1 + K_d} + 0.409f^{7/3}} - \frac{0.016(1 - K_d)}{(6/5) + K_d} f^{14/3}} \quad (30)$$

It may be shown that the last term in the denominator of Eq. (30) is negligible for all values of K_d , and for all $f < 0.5236$ (the volume fraction corresponding to maximum packing.) Neglecting this term, and rearranging Eq. (30), we obtain our final result in a form similar to that presented by Rayleigh:

$$K_m = \frac{\frac{2 + K_d}{1 - K_d} - 2f + 0.409 \frac{6 + 3K_d}{4 + 3K_d} f^{7/3} - 2.133 \frac{3 - 3K_d}{4 + 3K_d} f^{10/3}}{\frac{2 + K_d}{1 - K_d} + f + 0.409 \frac{6 + 3K_d}{4 + 3K_d} f^{7/3} - 0.906 \frac{3 - 3K_d}{4 + 3K_d} f^{10/3}} \quad (31)$$

Then, for the case of a nonconducting dispersed phase, we obtain

$$K_m = \frac{2 - 2f + 0.6135f^{7/3} - 1.600f^{10/3}}{2 + f + 0.6135f^{7/3} - 0.6795f^{10/3}} \quad (32)$$

and when the conductivity of the dispersed phase is very much larger than that of the continuous phase,

$$K_m = \frac{1 + 2f - 0.409f^{7/3} - 2.133f^{10/3}}{1 - f - 0.409f^{7/3} - 0.906f^{10/3}} \quad (33)$$

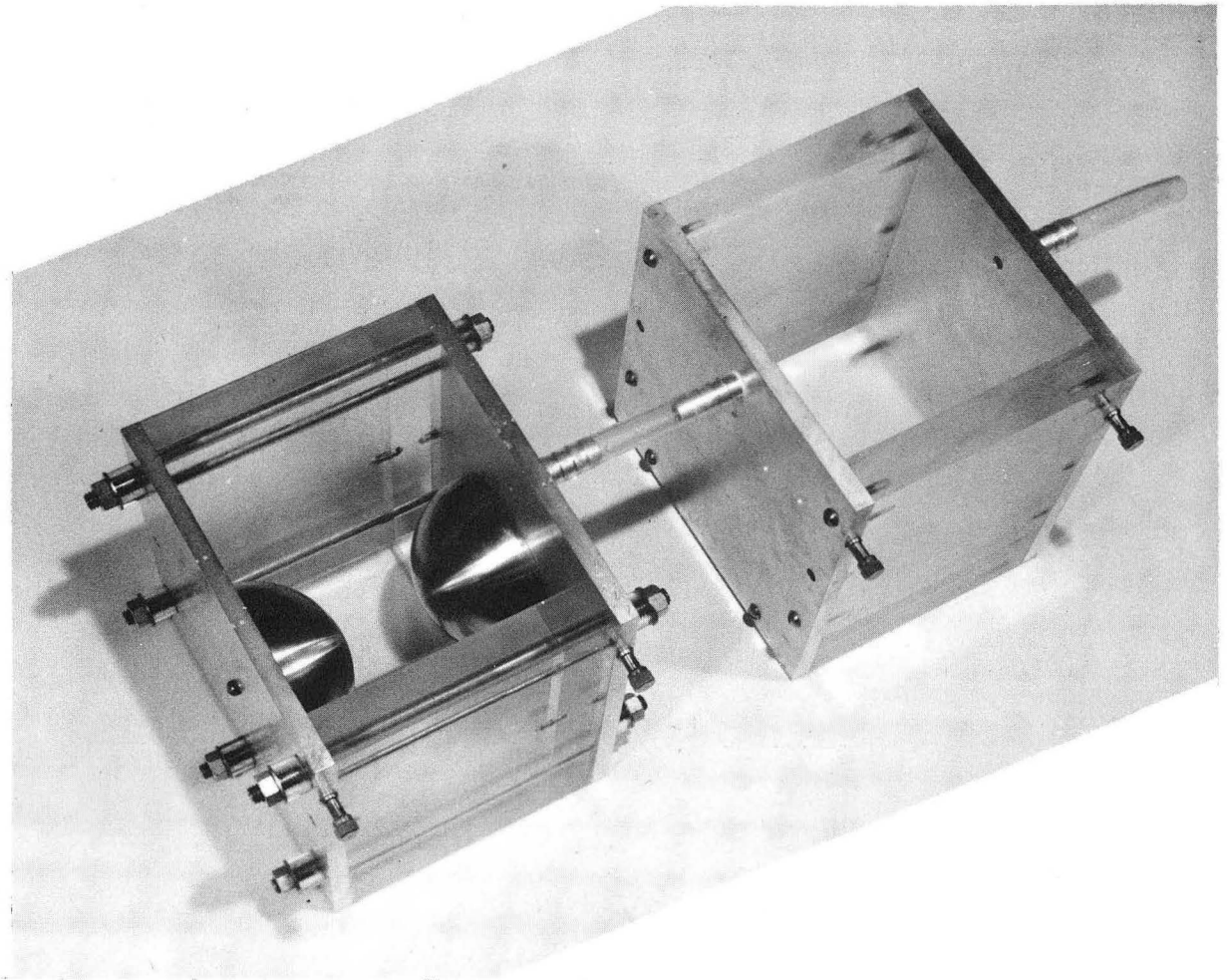
DISCUSSIONS AND CONCLUSIONS

Graphical representations of Equations (32) and (33) are given in Fig. 3 and 4, together with the curves corresponding to Rayleigh's original equations, and to Maxwell's equations. The experimental point presented in Table I lie very close to the "modified Rayleigh relations", except for the conductivity corresponding to $K_d \rightarrow \infty$ and $f = 0.5161$, which is well above the value predicted by the new equation proposed. This behavior is not surprising in view of the neglect of still higher terms in Eq. (19). It should be noted the inclusion of the term involving S_6 has actually introduced a lower order term in the volume fraction than the last one given by Rayleigh. The coefficients are such, however, that both the terms in $f^{7/3}$ and $f^{10/3}$ are of the same order of magnitude, and thus if one is used, both must be used. It must further be noted that the simple elimination of the term in $f^{7/3}$ from Eq. (31) does not cause the relation to reduce to Rayleigh's equation. This is a consequence both of the steps involved in rearranging Eq. (30), and of the changes caused by the more rapidly converging series introduced in Equations (3) and (4).

In the preceding section we have presented a modified derivation of Rayleigh's equation for the conductivity of a cubic array of spheres in a continuum. The agreement with experimental data is very satisfactory. The influence of close neighbouring particles on the field that exists when they are distant is much larger than predicted by the original Rayleigh equation. The degree of improvement over the original Rayleigh equation is obvious in principle, and not negligible for practical purposes.

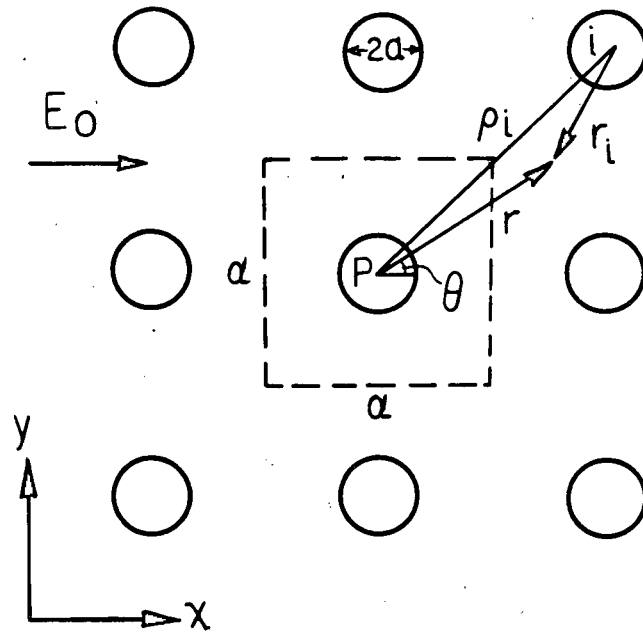
REFERENCES

1. D. Cornell and D. L. Katz, Ind. Eng. Chem. 45, 2145 (1953).
2. R. H. Wang and J. G. Knudsen, Ind. Eng. Chem. 50, 1667 (1958).
3. R. M. De La Rue and C. W. Tobias, J. Electrochem. Soc. 106, 827 (1959).
4. L. Topper, Ind. Eng. Chem. 47, 1377 (1955).
5. D. A. deVries, Ind. Eng. Chem. 49, 1936 (1957).
6. J. C. Maxwell, A Treatise on Electricity and Magnetism, Second Edition, Vol. 1 (Clarendon Press, Oxford, 1881) p. 435.
7. H. Fricke, Phys. Rev. 24, 575 (1924).
8. Lord Rayleigh, Phil. Mag. 34, 481 (1892).
9. I. Runge, Z. Techn. Phys. 6, 61 (1925).
10. A. Slawinski, J. Chem. Phys. 23, 710 (1926).
11. C. A. R. Pearce, Brit. J. Appl. Phys. 6, 113 (1955).
12. V. P. Mashovets, J. Appl. Chem. U.S.S.R. (English Translation) 24, 391 (1951).



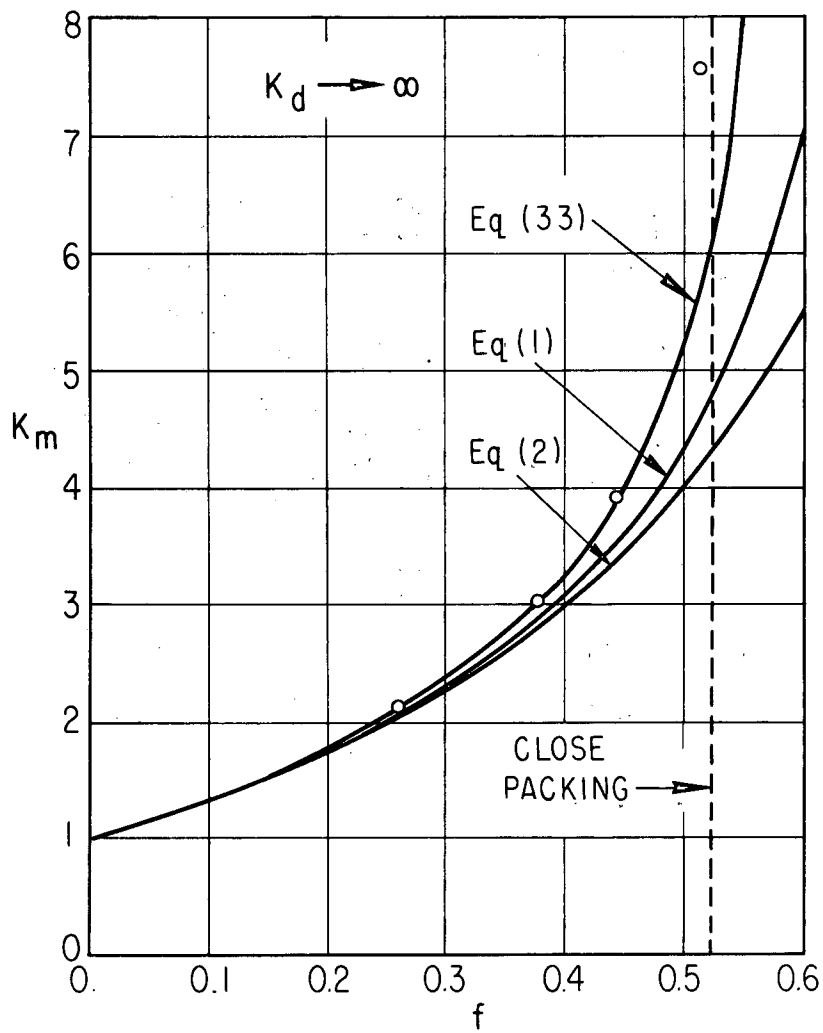
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Fig. 1. A view of the cells used in measurements on the ordered arrangements of spheres.



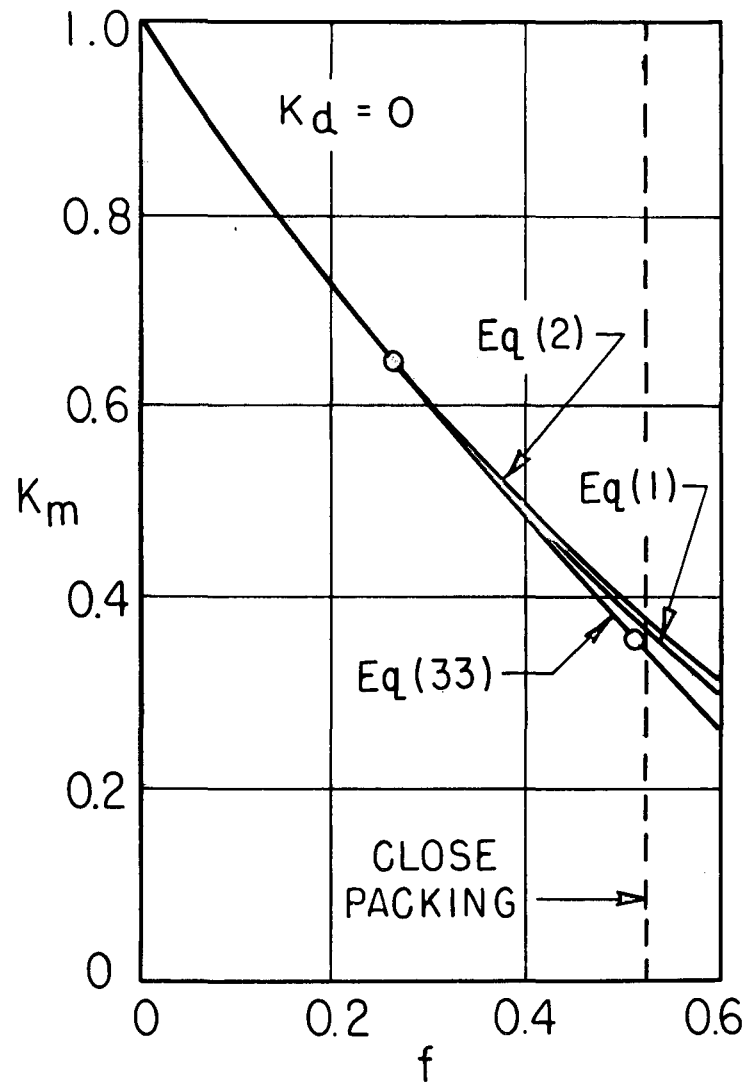
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Fig. 2. Section of three dimensional lattice of spheres.



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Fig. 3. Comparison of equations by Rayleigh (1), Maxwell (2), and present authors [data as circles; Eq. (33)].



MU-18344

Fig. 4. Comparison of equations by Rayleigh (1), Maxwell (2), and present authors [data as circles; Eq. (33)].

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