THE UNIVERSITY OF MICHIGAN

INDUSTRY PROGRAM OF THE COLLEGE OF ENGINEERING

LIGHT-SCATTERING BY VERY DENSE MONODISPERSIONS OF LATEX PARTICLES

Stuart W. Churchill
G. C. Clark
C. M. Sliepcevich

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INTRODUCTION

The intensity of radiation within or at the boundaries of a dispersion of uniformly sized, nonabsorbing spheres can be described in terms of the angular distribution for single scattering, the dimensions of the dispersion expressed in mean free paths for scattering, the source distribution, and the boundary conditions. The mean free path for scattering

$$l_s = 1/N\sigma_s = 4/NK_s\pi d^2 \tag{1}$$

where N is the number of spheres per unit volume, σ_s is the scattering cross section, K_s is the scattering coefficient (the ratio of the scattering to the geometrical cross section), and d is the diameter of the spheres.

If the spheres are sufficiently far apart, the angular distribution for single scattering and the scattering coefficient are functions only of n, the refractive index of the sphere relative to the surrounding medium, and $\alpha = \pi d/\lambda$, where λ is the wavelength of the radiation in the continuous medium. It is then possible to scale a dispersion in terms of mean free paths if the same n and α are established as illustrated by Scott and co-workers.[1,2]

Sinclair[3] stated without documentation that optical interference between particles would be expected if the particles were less than 5 diameters apart. No measurements of interference or theoretical expressions for the effect have been found in the literature.

The objective of this investigation was to determine the separation distance at which interference becomes appreciable and to measure of the magnitude of the effect. Several possible methods of investigation were considered:

(i) Development of theoretical expressions for the two-body and multiple-body problems.

(ii) Measurement of the radiant field around a set of two or more spheres with dimensions of the order of millimeteres, using a beam of millimeter waves.

(iii) Measurement of the transmission of a beam of monochromatic light through dense dispersions with particle concentration as a variable.

Method (iii) was chosen because of its comparative simplicity and the more direct applicability of the results.

EXPERIMENTAL

APPARATUS

The equipment consisted of a source and collimating system, a receiver and amplifying unit, and a cell and traversing mechanism, all located in a dehumidified dark room at 18°C.

The source was a 50-candlepower, auto-headlight bulb operated with a regulated power supply. The light beam was monochromaticized with interference filters, yielding a transmission of 45% at 5460 ± 150°A and a band width of 120-140°A at the 22.5% transmission points.

The collimating system is shown in Figure 1. Diaphragms D_1 and D_2 reduced the stray light reaching the collimating lens and diaphragm D_3 limited the size of the collimated beam. The condensing lens L_1 and L_2 had focal lengths of 150 and 100 mm, respectively. The shutter was closed except during measurements. The collimating lens L_3 was an achromatic, coated, telescope objective, 51 mm in diameter and 191.5 mm in focal length. With a 1/16-mm pinhole P the final beam had a dimaeter of 32 mm and a divergence of only 14.2 min. Such a high degree of collimation was not necessary for the transmission measurements but was desirable for the determination of particle concentration.

The Du Mont 6291 photomultiplier used as a receiver is a ten-stage multiplier, 38 mm in diameter, with a flat, end-window type photo-cathode. The photocathode has a S-11 response characteristic; the maximum response is at λ = 4400 ± 250°A with 10% of the maximum response at λ = 3250 ± 250°A and 6175 ± 275°A. Voltage from a variable power supply was fed to the photomultiplier through a step attenuator with resistances chosen to give an amplification of about 3:1 per step. The anode current was determined by measuring the potential drop across a 1000 Ω resistor. The amplified signal was fed to the Y channel of an X-Y recorder.

The cell is shown in Figure 2. The fixed part of the cell served as the receiver housing and as the upper boundary of the dispersion. The photomultiplier was optically coupled to the upper glass window of the cell with immersion oil. The movable part of the cell was attached to a plat-form which travelled on a screw turned by a hand crank. The screw was geared to a Helipot which served as a potentiometer with the output fed through a cathode follower to the X channel of the recorder. The recorder thus produced a continuous record of transmission as a function of cell thickness. As the cell thickness decreased, the excess dispersion flowed

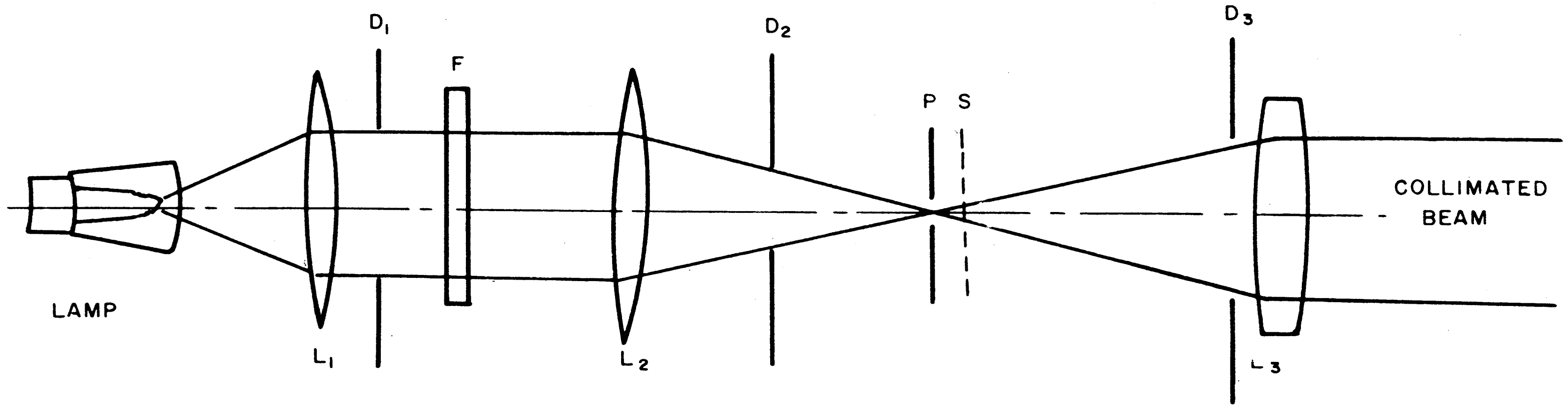

Figure 1. Schematic Diagram of Collinating System

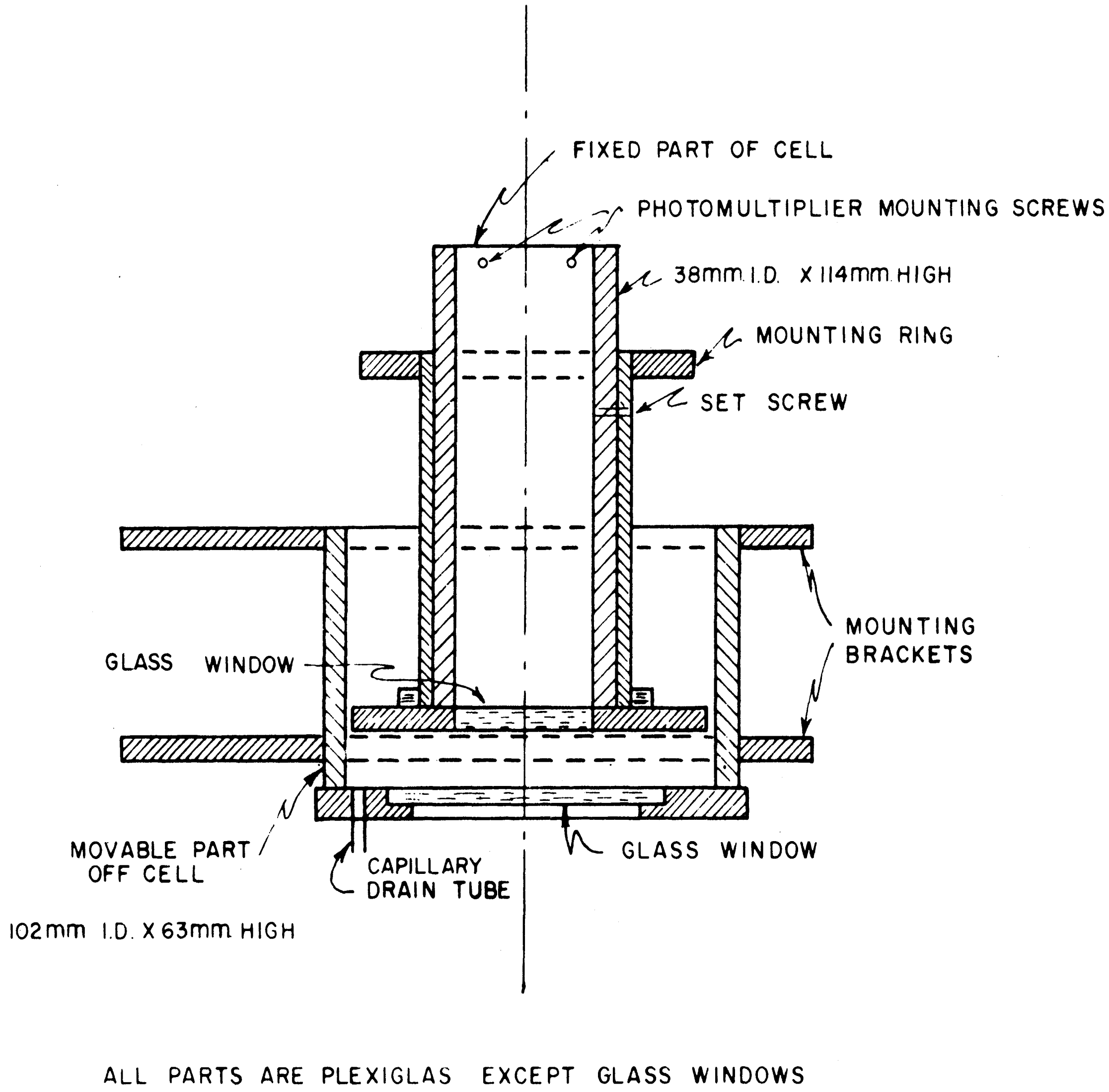

Figure 2. Experimental All

up around the lower plate of the fixed part of the cell and was thus optically decoupled from the dispersion remaining in the cell. All cell surfaces except the receiver window and the portion of the source window illuminated by the incident beam were painted with flat, black, acrylic resin.

For determination of the particle concentration a camera with an achromatic, coated, telescope objective lens, 83 mm in diameter and 914 mm in focal length, was located at the outlet window of the cell. A pinhole in the back of the camera opened to an opal glass optically coupled to the window of the photomultiplier. This receiver system was surrounded by a black, light-tight housing.

MATERIALS

The dispersions were prepared from very uniformly sized polystyrene-latex spheres supplied by the Dow Chemical Company, Midland, Michigan. One batch had a mean diameter of 0.814μ with a standard deviation of 0.011μ; the other, a mean diameter of 1.171μ with a standard deviation of 0.013μ. At λ = 5460°A (in air), the latex has a refractive index of 1.205 with respect to water and a negligible absorptivity. The spheres are stable in water, and, since they are charged, do not agglomerate.

PROCEDURE

After optical alignment, the cell was closed to a thickness of about 0.5 mm and the Helipot shaft was adjusted to indicate a zero signal on the X channel of the recorder. About 50 ml of distilled water were added to the cell and the cell was opened until full deflection occurred on the X channel, corresponding to a cell thickness of about 4 mm. The amplified photomultiplier signal was then recorded as the cell was slowly closed to a zero signal on the X channel. This experiment provided the reference signal I_o for calculation of the transmission.

After cleaning and drying the cell, 50 ml of a concentrated dispersion were added and the photomultiplier signal was again recorded as the cell was closed. The concentrated dispersion was next withdrawn from the cell to a reservoir, diluted with a measured quantity of water, mixed and returned to the cell, and a new traverse was carried out. Tests were made at twelve stages of dilution over a 10:1 range of concentration. All traverses were repeated as necessary to assure reproducibility and complete mixing.

DETERMINATION OF PARTICLE CONCENTRATION AND SEPARATION

Samples of the dispersion were withdrawn at the end and at two intermediate stages of dilution. After great dilution, traverses were made on these samples with the camera between the cell and the photomultiplier. The particle concentration was determined from these data and the modified form of the Bouguer-Beer law:

$$- dI_1 = RN\sigma_s I_1 dl \qquad (2)$$

where I is the collimated radiant flux density, R is a correction factor for the finite angle subtended by the receiver, and l is distance. Eqn. (2) can be integrated and rearranged in the form

$$\ln (I_o/I) = RN\sigma_s(l_m + l_o) \qquad (3)$$

where l_o is the unknown reference thickness for which the X channel of the recorder was set to zero, and $l_m = (l - l_o)$ is the measured distance.

$RN\sigma_s$ and l_o were calculated from Eqn. (3) and the data by least squares. $N\sigma_s$ was then calculated taking R = 0.998, corresponding to the angle of 47.8 min subtended by the receiver, N = 1.205 and the appropriate value of α. It should be noted that in water, and hence in this value of α, $\lambda = \lambda_{air}/n_{water} = 5460/1.33 = 4105°A$. N was in turn calculated using the theoretical values of 2.48 and 3.57 for K_s for the 0.814 and 1.171μ particles, respectively. The volume fraction of solids x $= N\pi d^3/6$ was next calculated from the known particle diameters.

The centre-to-centre distance between particles was calculated from the following expression for a rhombohedral array:

$$\delta = (\sqrt{2}/N)^{1/3} = (\pi/3\sqrt{2}x)^{1/3}\, d \qquad (4)$$

Since the particles are charged, this arrangement, which gives the maximum possible distance between particles for a given concentration, may be approached as the particle concentration increases to the limit. This limit for $\delta = d$ is $N = \sqrt{n}/d^3$ and the corresponding maximum x is $\pi\sqrt{2}/6 = 0.7405$.

The computed properties for the initial, undiluted dispersions are given in Table 1. Values for the other traverses were obtained by multiplying the concentration by the corresponding dilution factor.

RESULTS

The data were correlated in terms of the two-flux model which has been discussed by Chu and Churchill[5] and others, and successfully used by Larkin and Churchill[6] and others for multiple scattering. In this model the angular distribution of radiation scattered by a single sphere is represented by forward and backward components. The integro-differential equation describing the radiant intensity in a dispersion then reduced to two ordinary differential equations for the forward and backward components of the intensity.

The idealized experiment would have consisted of an infinite layer of dispersion with an infinite, collimated source at one face and a totally absorbing surface at the other. A finite source and dispersion of the same diameter with a perfect specular reflector at the circumference would produce the same transmission as the infinite system. The experimental transmission obtained in this investigation would be expected to be somewhat less than in the idealized case because of the finite dimensions of the source and dispersion, and the failure of the dispersion beyond the circumference of the source to act as a perfect reflector. A correction for the net sidewise loss of radiation was therefore incorporated in the two-flux model. The resulting equation describing the forward component I_1 and the backward component I_2 of the intensity are

$$- dI_1 = (BI_1 + SI_1 - BI_2)N\sigma_s dl \qquad (5)$$

and

$$dI_2 = (BI_2 + SI_2 - BI_1)N\sigma_s dl \qquad (6)$$

where B is the backward scattering coefficient for single scattering and S is the net sidewise scattering coefficient. The boundary conditions are $I_1 = 1.0$ at $l = 0$, and $I_2 = 0$ at $l = l_t$ where l_t is the thickness of the dispersion.

Solving these equations yields the following expression for the transmission:

$$T = \frac{I_1(l_t)}{I_1(0)} = \frac{1}{ch[p(l_m+l_o)] + q\ sh[p(l_m+l_o)]} \qquad (7)$$

where $p = N\sigma_s\sqrt{S(2B+S}$ and $q = (B+S)/\sqrt{S(2B+S)}$.

Values of the parameters p and q and the unknown reference distance l_o were determined by least squares on an IBM 650 computer using the method proposed by Scarborough(7) for non-linear equations. Values of BK_s and Sk_s were then computed from the previously determined values of N and the dilution factors. Although the computed values of BK_s were in all cases about 1000 times the values of SK_s, the inclusion of S in the model resulted in a distinctly better representation for the data.

The experimental transmissions and curves representing Eqn. (7) are plotted against l_t for the two particle diameters in Figures 3 and 4. The precision of the data and the excellent representation obtained with Eqn. (7) are apparent. The standard deviations for the 26 traverses averaged about 1.2%.

The experimental transmissions are replotted against $NK_s\pi d^2 l_t/4$ in Figures 5 and 6 using values of K_s for isolated spheres. For a dilute dispersion, this abscissa corresponds to the cell thickness in mean free paths for scattering; for concentrated dispersions K_s, and hence the mean free path, may be somewhat different. Due to compression of the data in this form, only data for selected concentrations and curves for the extreme transmissions are included. It should be noted that the data for different concentrations cover different ranges of the abscissa; for example, the data for the most dilute dispersion extend only over the lowest tenth of the abscissa. If there were no optical interference between particles, all data for a given particle size should lie along a single curve. Thus the spread for a given particle size should lie along a single curve. Thus the spread of the data and curves indicates the magnitude of the interference insofar as sidewise losses and other non-idealities in the experiment are negligible or the same from traverse to traverse. The transmission appears to increase and then to decrease as the particle separation distance is decreased, but the magnitude of the variation is less than $\pm$ 20% for both particle sizes.

A more critical test of interference is provided by Figure 7 in which the product of the coefficients B and K_s is plotted against δ/d for both particle sizes. This plot should be independent of sidewise losses from the cell. Insofar as the modified two-flux moded represents the physical situation, BK_s is the fraction of the geometrically obstructed light which is scattered into the backward hemisphere by a single particle. Since B, S and K_s occur in Eqn. (7) only as the products a BK_s and SK_s, the separate effects of particle separation on B and K_s cannot be deciphered from the data of this experiment. For both particle sizes BK_s appears to be essentially constant down to a δ/d of about 1.7, then to decrease to a minimum, to increase to a maximum and finally to decrease again. The magnitude of this variation is only about $\pm$ 10% and undoubtedly is due in part to experimental error. The uncertainty in the computed values of BK_s is greater than the uncertainty in the measurements of transmission and distance, but is difficult to estimate because of the non-linearity of the equations from which BK_s is derived.

Additional details concerning the equipment, procedures and data are given by Clark.[8]

TABLE I

Properties of Undiluted Dispersions

d, μ	N, particles/cm^3	x	δ/d
0.814	9.81×10^{11}	0.278	1.385
1.171	3.23×10^{11}	0.272	1.395

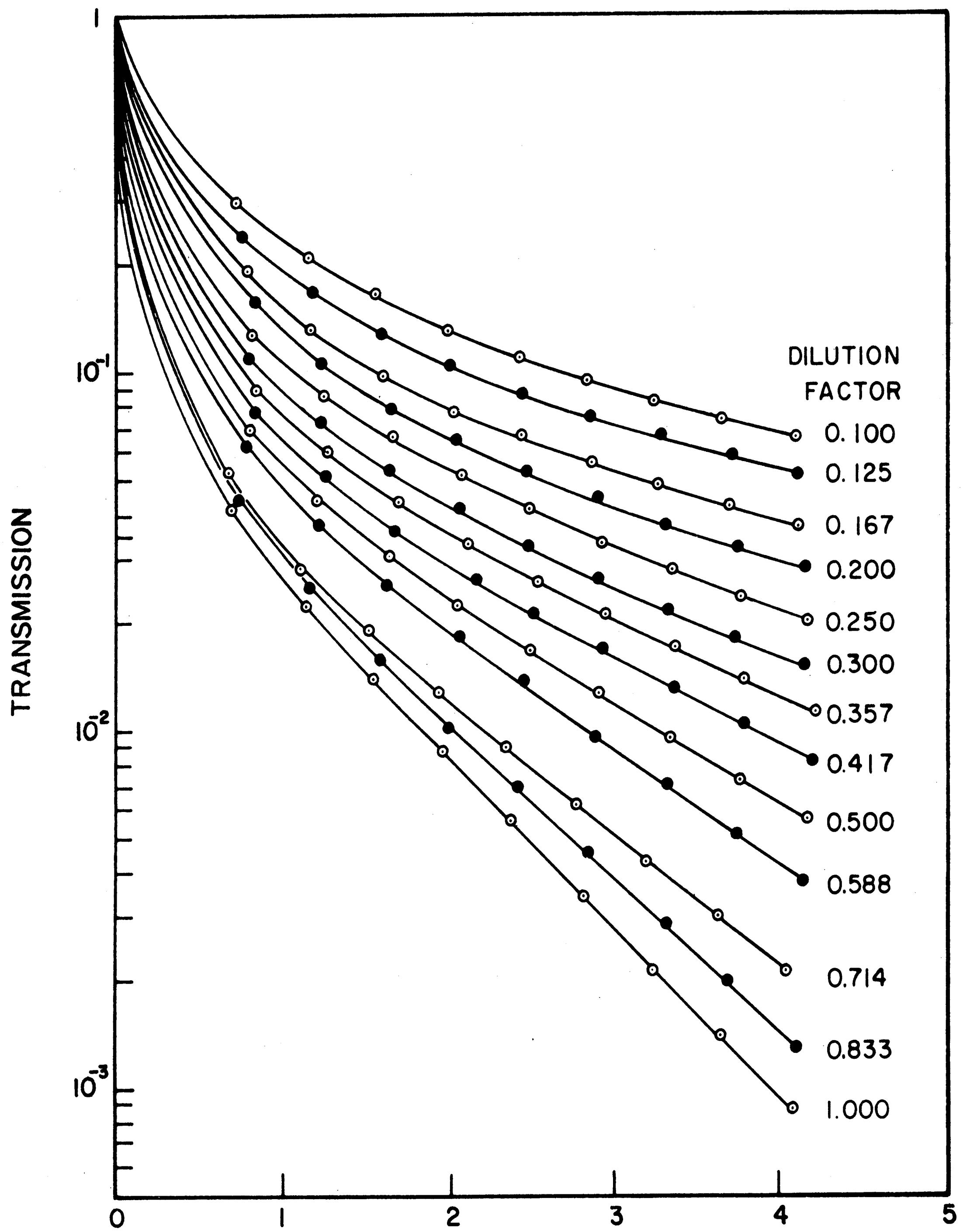

Figure 3. Experimental Transmissions, 0.814 μ Particles

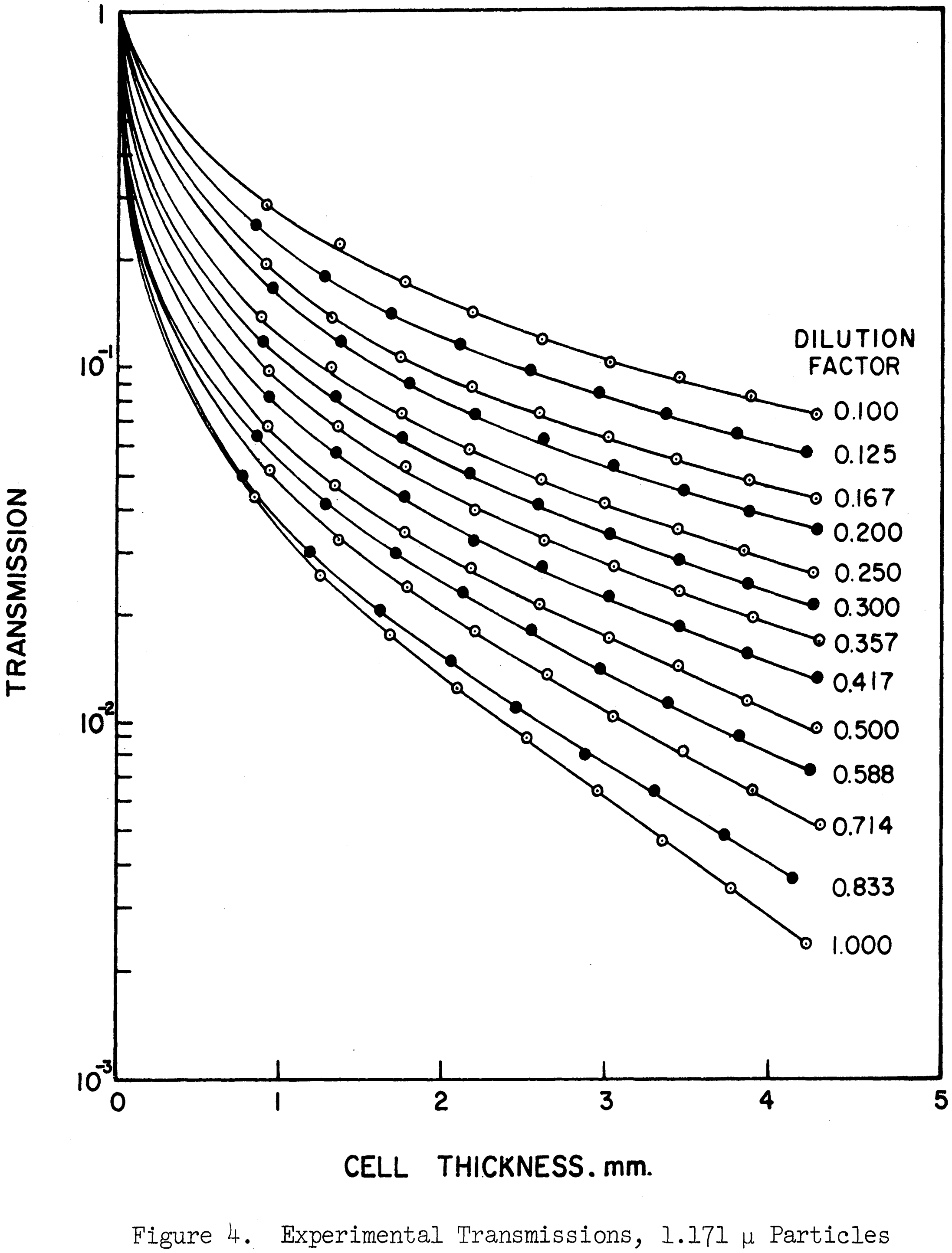

Figure 4. Experimental Transmissions, 1.171 μ Particles

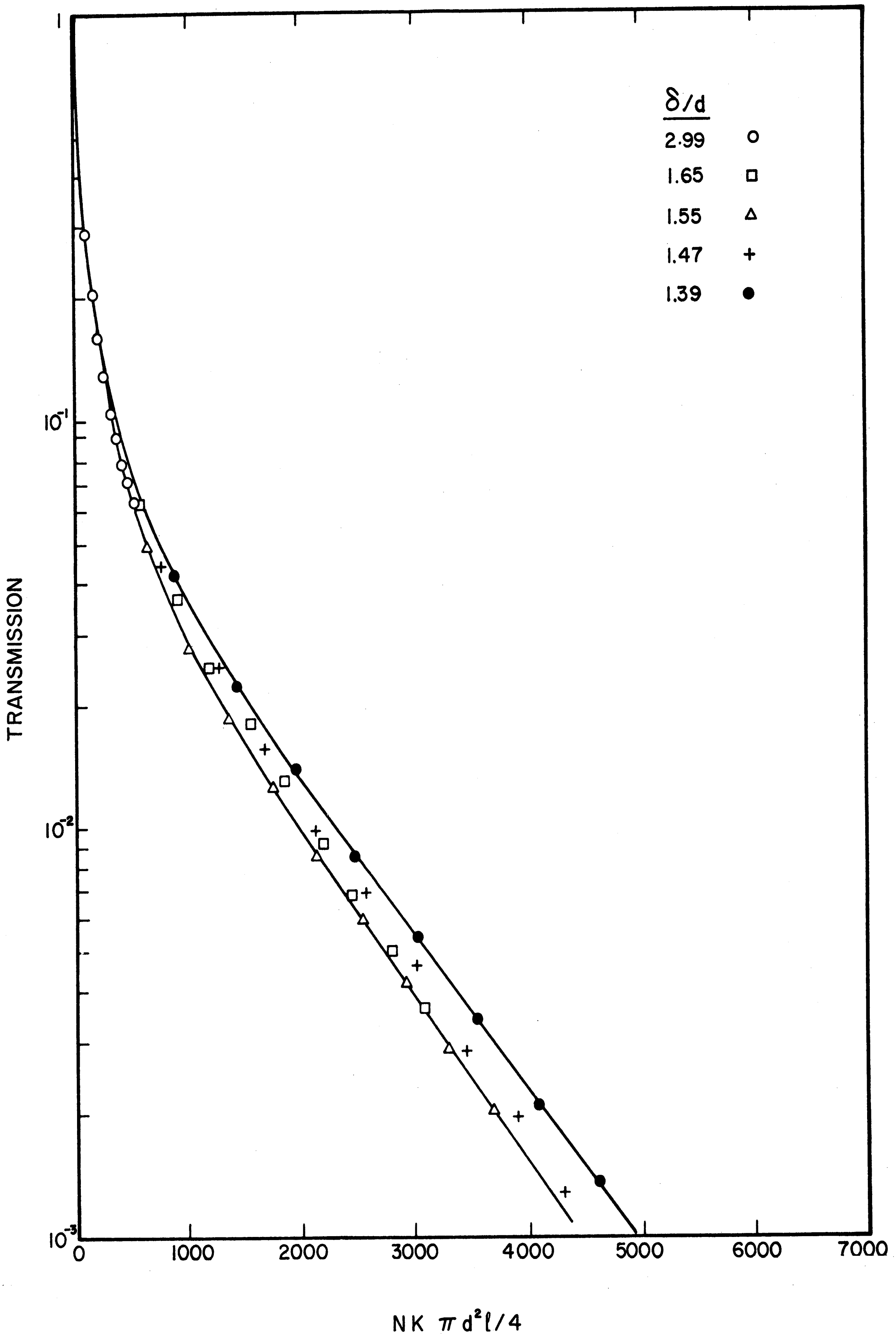

Figure 5. Effect of Particle Separation on Transmission, 0.814μ Particles

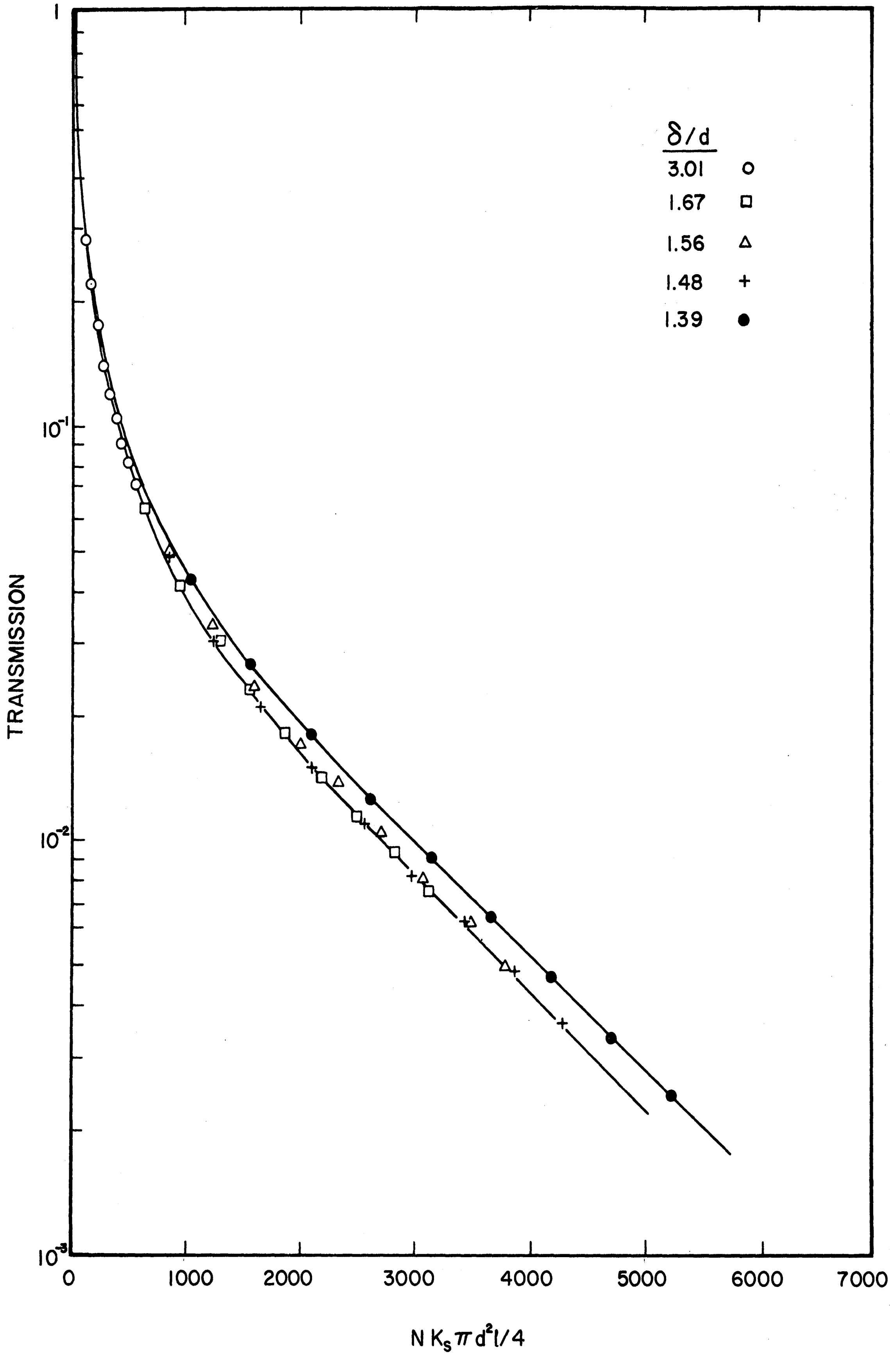

Figure 6. Effect of Particle Separation on Transmission, 1.171 μ Particles

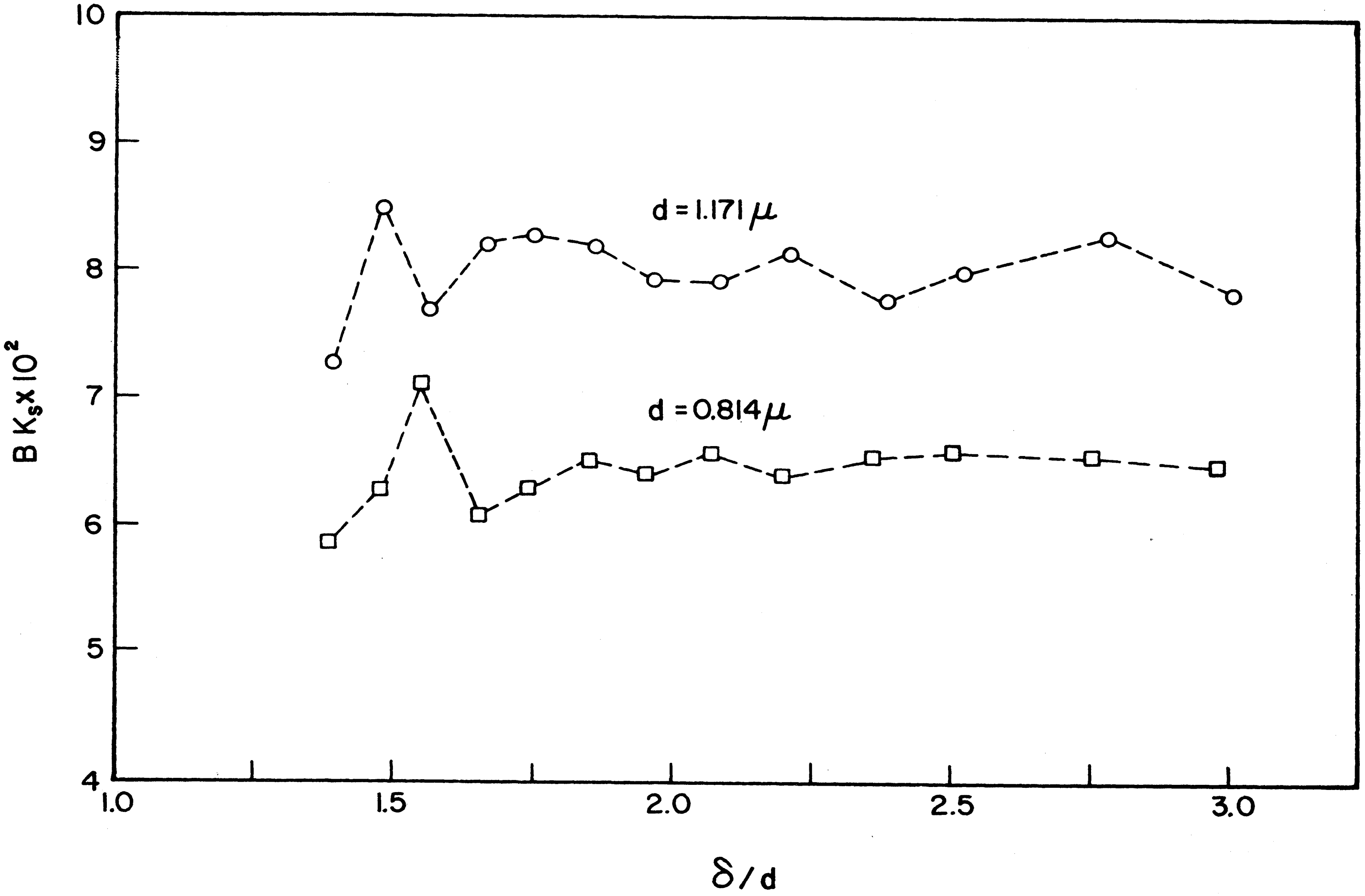

Figure 7. Effect of Particle Separation on Back Scattering Parameter

CONCLUSIONS

The modified two-flux model was found to provide an excellent representation for the data. The observed variations in BK_S and T with concentration are surprisingly small, considering the very small distances separating the particles. The limiting δ/d above which optical interference between particles can be neglected is apparently about 1.7 rather than 5 as postulated by Sinclair.(1) Therefore dispersions of spheres as concentrated as 15% solids can be used to simulate dilute dispersions without correction for interference between particles.

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