Quantitative diffuse reflectance spectroscopy of large powders: the Melamed model revisited

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The popular statistical theory of absolute diffuse reflectance of powders put forth by Melamed [J. Appl. Phys. **34**, 560–570 (1963)] a quarter century ago has been re-examined thoroughly. Substantial errors in the physical formulation of the theory have been found and a corrected version is being presented. Some of Melamed's data fits to the theory are also re-examined in the light of the corrected theoretical model.

I. Introduction

In the past quarter century the Melamed model[1] has been used by many investigators wishing to perform quantitative diffuse reflectance spectroscopy of powdered specimens. The success of that theory lies in the fact that, unlike earlier discontinuum theories,[2,3] Melamed was the first author to use statistical summations over discrete particles reflecting light diffusely according to the laws of geometrical optics. Therefore, the realism of the Melamed statistical approach prevailed over theories treating particles as discrete plane parallel layers,[2,3] although its validity is limited only to the geometric optics limit, i.e., for particle sizes much larger than the exciting optical wavelength. Kortüm has reviewed the salient features of the layer discontinuum theories and those of Melamed's model.[4]

A review of the literature built on the Melamed model revealed that warnings about numerous typographical errors encountered in the original paper[1] have been voiced previously.[5,6] These errors include the final analytical expression for the absolute diffuse reflectance R, given by Melamed [Ref. 1, Eq. (6)]. A great deal of confusion exists even in ascertaining whether a given author has used the erroneous formula[7] for R, or the typographically correct one.[5] In our own effort to obtain quantitative optical absorption coefficient spectra of large size powders using diffuse reflectance IR Fourier transform spectroscopy (DRIFTS) we thoroughly re-examined the Melamed model due to its direct applicability to the interpretation of compensated (i.e., relative) spectra in terms of the optical properties of powders. In addition to the numerous, but easily corrigible typographical errors, we found several physical inconsistencies of the model. We also encountered great difficulties in the use and application of numerical formulas for the pertinent internal and external reflection coefficients, integral parts of the calculation for R given by Melamed.

In this paper a corrected version of Melamed's theory is given in agreement with fundamental physical principles of energy conservation. New fits to some original data by Melamed are worked out and discussed. Finally, correct analytical expressions for the average external reflection coefficient, $\bar{m}_e$, and the internal reflection coefficient, $\bar{m}_i$, themselves a subject of inexact numerical approximations in the past, are given in the Appendix.

II. Physically Corrected Melamed Theory

The pertinent diffuse reflectance geometry utilized by Melamed is shown in Fig. 1. Application of Lambert's cosine law over the volume of an idealized spherical particle[1,4] yields the following expression for the radiation fraction reaching the particle surface after absorption in bulk:

$$M = \frac{2}{(kd)^2}\,[1 - (kd + 1)\exp(-kd)], \tag{1}$$

where $k = k(\lambda)$ is the particle optical absorption coefficient at the wavelength λ, and d is the particle diameter. The total transmitted fraction through a single particle layer T was found to be[1]

$$T = \frac{(1 - \bar{m}_i)M}{1 - \bar{m}_i M}, \tag{2}$$

where $\bar{m}_i$ is the averaged internal reflection coefficient

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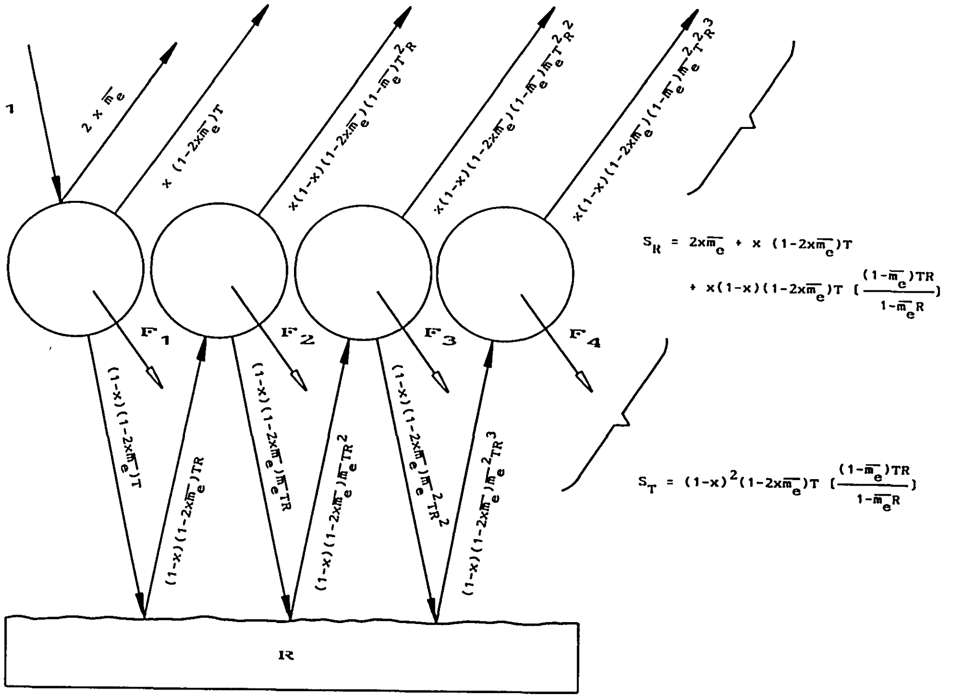

Fig. 1. Idealized geometry used by Melamed to represent light scattering, absorption, and diffuse reflectance processes in powders. [Ref. (1), Fig. 1].

of the particle, integrated over all angles up to the critical angle $\alpha_c = \sin^{-1}(1/n)$, n being the refractive index of the powdered material relative to that of the surrounding gas (air). Equation (2) includes both downward and upward transmission, i.e., all escaping optical energy. This is one of the shortcomings of the model, as only the downward component can be associated with actual transmission, while the upward fraction contributes to reflection. In this case, the sum of all transmitted fractions of an original ray impinging on the surface particle from above after an infinite number of interreflections is given by:

$$F_T(M) = (1-\bar{m}_i)M + (1-\bar{m}_i)\bar{m}_i^2M^3 + (1-\bar{m}_i)\bar{m}_i^4M^5 + \dots = \frac{(1-\bar{m}_i)M}{1-(\bar{m}_iM)^2}, \quad (3)$$

where

$$F_R(M) = (1-\bar{m}_i)\bar{m}_iM^2 + (1-\bar{m}_i)\bar{m}_i^3M^4 + (1-\bar{m}_i)\bar{m}_i^5M^6 + \dots = \frac{(1-\bar{m}_i)\bar{m}_iM^2}{1-(\bar{m}_iM)^2} \quad (4)$$

is the sum of all upward fractions contributing to the reflected energy. The choice of the T value, of course, does not affect the functional dependence of the expression for the absolute diffuse reflectance R on T. Figure 2 shows the corrected version of Fig. 1. The most crucial correction appears in the value of the fraction of light that emerges from the upper surface of the surface layer particle after a single internal reflection at the lower surface: Assuming unit input intensity of radiation, the initial contribution to R is taken to be[1] $2x\bar{m}_e$, where x is the fraction of radiation scattered in the upward direction, expressed as a fraction of 4π steradians. Therefore, the fraction of downward scattered radiation of a ray impinging on the upper surface of a particle from the inside (i.e., being internally reflected/scattered downward) is given by $(1-x)$ (as a fraction of 4π steradians). In practice x and $(1-x)$ are probabilities of upward and downward diffuse scattering of the incident radiation. The remaining intensity $(1-2x\bar{m}_e)$ enters the particle. Out of that, a fraction $x(1-2x\bar{m}_e)$ is reflected upward at the lower surface. Once it reaches the upper surface, a fraction $(1-x)[x(1-2x\bar{m}_e)]$ is internally reflected downward, while the remainder exits the particle in the upward direction, thus contributing to R. This remainder is $x(1-2x\bar{m}_e) - (1-x)[x(1-2x\bar{m}_e)] = x^2(1-2x\bar{m}_e)$, so that the emerging (transmitted) fraction is $x^2(1-2x\bar{m}_e)T$ as shown in Fig. 2. This is at variance with Melamed's calculation of a fraction equal to $x(1-2x\bar{m}_e)T$. With this correction the sum S of all rays emerging from inside the particle, following internal reflections, is

$$S(T) = 2x\bar{m}_e + (1-x)(1-2x\bar{m}_e)T + x(1-x)(1-2x\bar{m}_e) + x^2(1-2x\bar{m}_e)T. \quad (5)$$

In the limit of $k = 0, M = T = 1$ and Eq. (5) gives

$$S(1) = 1, \quad (6)$$

as expected from conservation of optical energy for unit input intensity and a totally nonabsorbing particle. It should be noted that energy conservation cannot be attained with the expressions derived by Melamed in Fig. 1. The uncorrected absolute diffuse reflectance from the surface layer alone is given by the upward fraction of Eq. (5), i.e., $S_U(T) = 2x\bar{m}_e + x^2(1-2x\bar{m}_e)T$. At $kd = 0$, $T = 1$ and $S_U(1) = 2x\bar{m}_e(1-x^2) + x^2 > 0$, so that, in this limit, $S_U(T) + T$ results in the nonphysical situation of nonconservation of optical

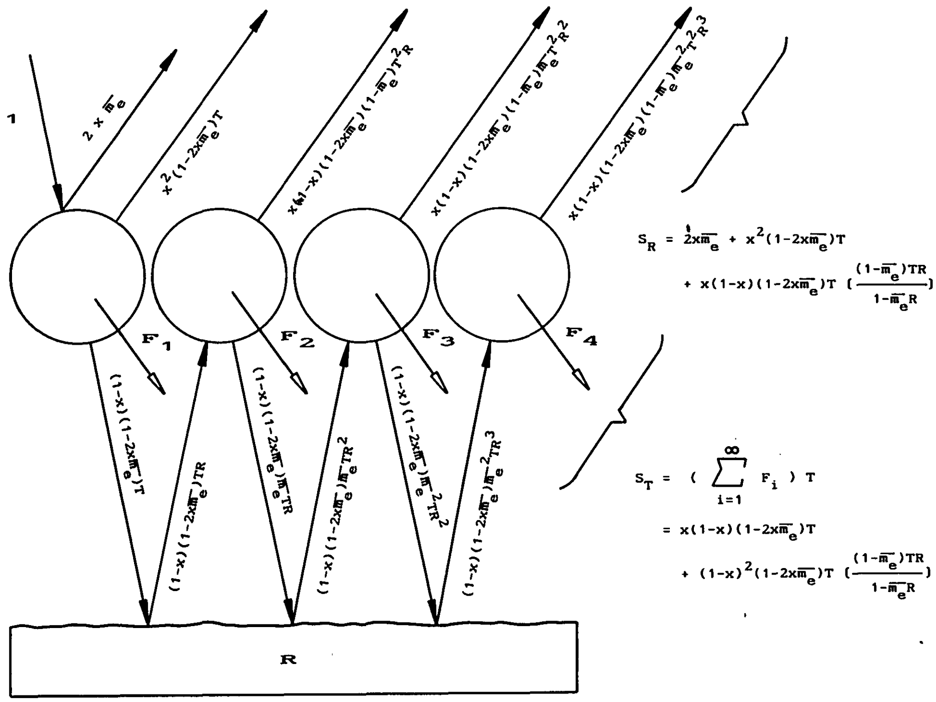

Fig. 2. The physically corrected idealized Melamed geometry. The successive values of F_i are: $F_1 = x(1-x)(1-2x\bar{m}_e)$, $F_2 = (1-x)^2(1-\bar{m}_e)(1-2x\bar{m}_e)TR$, $F_3 = (1-x)^2(1-\bar{m}_e)(1-2x\bar{m}_e)\bar{m}_eTR^2$, $F_4 = (1-x^2)(1-\bar{m}_e)(1-2x\bar{m}_e)\cdot\bar{m}_e^2TR^3$, etc.

energy. Physically, in the limit of no absorption, upward and downward emission should be equally probable, so that R will be determined by the scattering process. When the proper upward and downward fractions of T are taken into account, Eqs. (3) and (4) yield at $k = 0$:

$$F_T(1) = \frac{1}{1+\bar{m}_i}; \qquad F_R(1) = \frac{\bar{m}_i}{1+\bar{m}_i} \tag{19}$$

so that $F_T(1) + F_R(1) = 1$, as expected. This inadequacy of Melamed's theory will be addressed in a separation publication.[8]

Figures 1 and 2 show that the remaining fractions of upward and downward transmitted light, after reflection from the underlying bulk, have been calculated correctly by Melamed. However, the summations for each transmitted component are different: The contribution of the initial ray to the upward transmission (i.e., to the observed reflectance) after infinite interreflections is

$$S_R = 2x\bar{m}_e + x^2(1-2x\bar{m}_e)T + x(1-x)(1-\bar{m}_e)(1-2x\bar{m}_e)\left(\frac{T^2R}{1-\bar{m}_eR}\right). \tag{7}$$

The contribution of the initial ray to the downward transmission (i.e., to the observed transmittance from a single layer of particles) after infinite interreflections is

$$S_T = x(1-x)(1-2x\bar{m}_e)T + (1-x)^2(1-2x\bar{m}_e)(1-\bar{m}_e)\left(\frac{T^2R}{1-\bar{m}_eR}\right). \tag{8}$$

A consideration of Fig. 2 and Eqs. (7) and (8) shows why the correction of a single term in the summations carries so much weight in the final result: The correction term $x^2(1-2x\bar{m}_e)T$ is responsible for the second largest contribution to diffuse reflectance. It is also the most important term carrying optical absorption coefficient information from the particle, as it results from the first upward emerging ray after a single pass through the body of the surface particle. The importance of this term will become apparent in computer simulations later on.

The expression:

$$r(I_0) = xRT\left(\frac{1-\bar{m}_e}{1-\bar{m}_eR}\right)I_0 \tag{9}$$

represents the fraction of light of intensity I_0 which emerges upward (away from the bulk of the powder) after an infinite number of interreflections between the lower surface of the upper layer particles and the bulk matter of reflection R. This was first presented without proof by Melamed and is easy to derive as the summation of a series of the rays F_j emerging between particle and bulk in Fig. 2. Furthermore, the fraction of the light which emerges downward (into the bulk of the powder) and thus contributes to transmittance is the remainder of Eq. (9):

$$t(I_0) = (1-x)RT\left(\frac{1-\bar{m}_e}{1-\bar{m}_eR}\right)I_0. \tag{10}$$

If I_0 is now replaced by the total fraction transmitted into the bulk in Fig. 2, we obtain

$$r\left[\left(\sum_{i=1}^{\infty} F_i\right)T\right] = T(1-2x\bar{m}_e)[x^2(1-x)Q + x(1-x)^2Q^2], \tag{11}$$

where

$$Q \equiv \frac{(1-\bar{m}_e)RT}{1-\bar{m}_e R}. \tag{12}$$

Eq. (11) is there entirely due to the fact that the, otherwise nondescript, bulk reflects upward a fraction R of the downward transmitted ray fraction

$$T\left(\sum_{i=1}^{\infty} F_i\right).$$

It should be noticed that this is an oversimplification (and perhaps an inconsistency) of the Melamed model, as the diffuse reflectance of the semi-infinite bulk is that of a continuous plane interface with no particulate characteristics, which is not the same as the statistically averaged (summed up) quantity above the free surface of the distinctly discrete surface powder. In any event, we uphold this assumption for the sake of retaining the main features of the Melamed theory.

The fraction of $(\sum_{i=1}^{\infty} F_i)T$ which returns to the bulk is:

$$t\left[\left(\sum_{i=1}^{\infty} F_i\right)T\right] = T(1-2x\bar{m}_e)[x(1-x)^2Q + (1-x)^3Q^2] \tag{13}$$

and, out of this amount, the fraction:

$$r\{T(1-2x\bar{m}_e)[x(1-x)^2Q + (1-x)^3Q^2]\} = T(1-2x\bar{m}_e)[x^2(1-x)^2Q^2 + x(1-x)^3Q^3] \tag{14}$$

returns to the upper particle surface, exits the powder and contributes to R. A straightforward repetition of this process *ad infinitum* results in the final expression for R, using Eqs. (7), (13), (14):

$$R = 2x\bar{m}_e + x^2(1-2x\bar{m}_e)T[1 + (1-x)Q + (1-x)^2Q^2 + (1-x)^3Q^3 + \ldots] + x(1-x)(1-2x\bar{m}_e)TQ[1 + (1-x)Q + (1-x)^2Q^2 + (1-x)^3Q^3 + \ldots]$$

or

$$R = 2x\bar{m}_e + x(1-2x\bar{m}_e)T\left\{\frac{(1-\bar{m}_e)(1-x)TR + (1-\bar{m}_eR)x}{(1-\bar{m}_eR) - (1-x)(1-\bar{m}_e)TR}\right\}. \tag{15}$$

Eq. (15) is quite different from Melamed's final Eq. (6), the typographically corrected form of which is repeated here for comparison purposes.

$$R_M = 2x\bar{m}_e + x(1-2x\bar{m}_e)T\left\{\frac{1-\bar{m}_eR_M}{(1-\bar{m}_eR_M) - (1-x)(1-\bar{m}_e)TR_M}\right\}. \tag{16}$$

The solution of Eq. (15) requires retaining the negative root only, for physically meaningful values ($R \leq 1$):

$$R = [1 + AC - BD - \sqrt{(1 + AC - BD)^2 - 4C(A + xB)}]/2C, \tag{17}$$

where

$$A \equiv 2x\bar{m}_e \tag{18a}$$

$$B \equiv x(1-2x\bar{m}_e)T \tag{18b}$$

$$C \equiv \bar{m}_e + (1-x)(1-\bar{m}_e)T \tag{18c}$$

$$D \equiv (1-x)(1-\bar{m}_e)T - \bar{m}_e x. \tag{18d}$$

III. Computer Simulations of the Corrected Theory

The corrected Melamed formalism has been used for simulating large size powder behavior and best-fitting some of the originally published data by Melamed.[1] The calculations require evaluation of the coefficients $\bar{m}_e(n)$ and $\bar{m}_i(n)$. Details on the evaluation are shown in the Appendix. Figure 3 shows the absolute diffuse reflectance as a function of kd for $n = 1.55$ corresponding to didymium glass.[1] As expected $R(0) < 1$, while $R_M(0) = 1$. Figure 4 shows the diffuse reflectance with the refractive index as a parameter. All curves have been normalized by the $R(0)$ values.

In the usual experimental range $kd < 1$, Fig. 5 indicates the differences between the original Melamed model, Eq. (16) and the corrected version, Eq. (17): For small values of n, there is substantial disagreement in the $kd < 0.1$ range. Large values of n, however, exhibit disagreement throughout the entire kd range of Fig. 5 except for $kd < 0.02$. In Fig. 6 we show the best fit of the physically corrected normalized quantity $R(kd)/R(0)$ to data for didymium glass presented by Melamed. Eq. (17) was normalized by its value at $kd = 0$ and the best fits were obtained using an expression for x taking into account the anisotropic emission from the particles due to absorption[6]:

$$x = \frac{x_u}{1 - (1 - x_u[1 + \exp(-kd)])T}. \tag{20}$$

In Eq. (20) x_u represents the probability for diffuse scattering in the upward direction, thus contributing to the diffuse reflectance. Curve 1 was obtained with $x_u = 0.284$, the same value as that used by Melamed for close-packed spheres, corresponding to a solid angle of $(4 - \sqrt{3}/2)\pi$ steradians. Melamed's fit, though, was obtained[1] for radiation emerging isotropically from a particle by means of the simplified expression

$$x = \frac{x_u}{1 - (1 - 2x_u)T}. \tag{21}$$

When Eq. (21) was used in our fit to the data on Fig. 6, a best fit was obtained for $x_u = 0.321$. The resulting curve was essentially identical to Curve 1 and is not shown here. Curve 2 indicates the effect of varying x_u in Eq. (20) from its optimum value 0.284 to the value 0.321, the optmum value when Eq. (21) is used. It is important to notice that both fits in Fig. 6 are quite good in the $kd > 0.08$ region and poor in the region below that. Melamed's original fit (Ref. 1, Fig. 6) also showed some deviation at very low values of kd, less than the one observed in Fig. 6 (ca. 10%). Figure 7 shows the sensitivity of Eq. (17) to the value x_u: It turns out that both the original and the corrected Melamed model are most sensitive to this value, which can only be estimated upon fitting the model to the data for nonhomogeneous, nonspherical particles. This sensitivity has been noticed previously: Companion[5] had to use $x_u = 0.1$ with Eq. (21) for a best fit of Eq. (16) to V_2O_5 spectra, assuming $n = 2.4$. A comparison between Figs. 7(a) and 7(b) shows that the actual functional form of $x = x(kd)$, Eq. (20) or Eq. (21), has little effect on powders of loose packing (low x_u). The

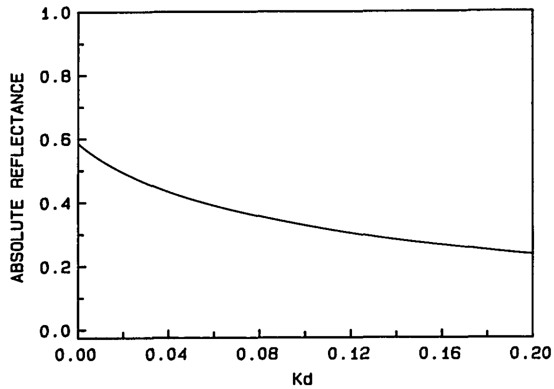

Fig. 3. Corrected Melamed theory for a material of $n = 1.55$. The diffuse reflectance curve shown is unnormalized (absolute).

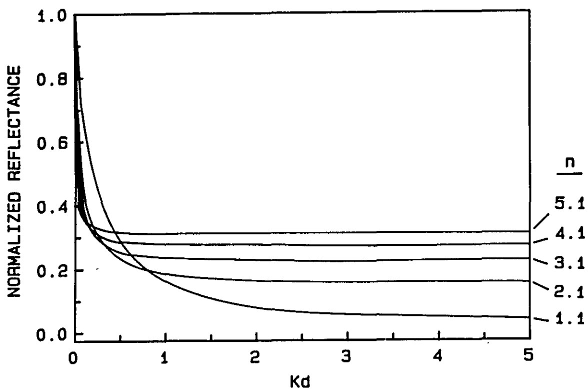

Fig. 4. Diffuse reflectance $R(kd)$ dependence on kd with n as a parameter: $1.1 \le n \le 5.1$. All values are normalized by the $R(0)$ value for each n.

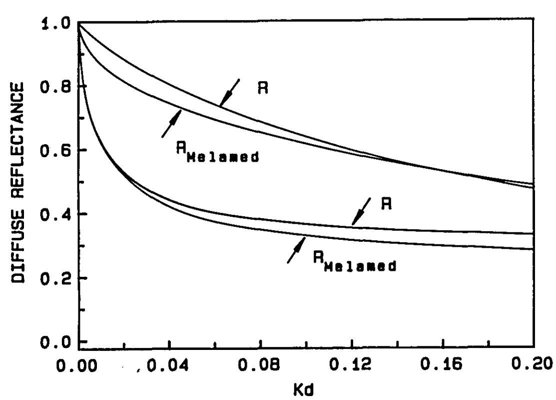

Fig. 5. Comparison between the $R_M(kd)$ (absolute) and $R(kd)$ (normalized by $R(0)$) for the two values of n; Upper curves: $n = 1.2$; Lower curves: $n = 5$.

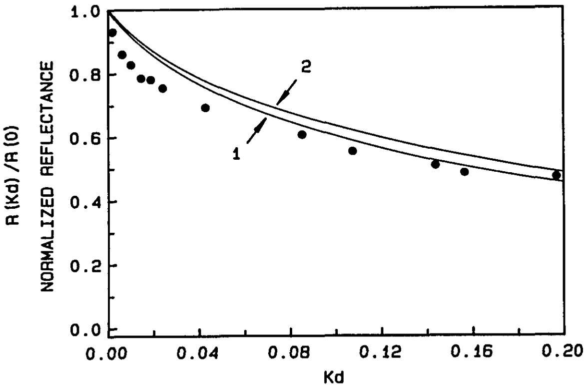

Fig. 6. Best fits of theoretical $R(kd)/R(0)$ curves for didymium glass ($n = 1.55$) to data from 128-μm diam particles presented by Melamed.[1] The fitting parameter was $x = x(x_u)$ with $x_u = 0.284$ [optimum fit with Eq. (20), Curve 1]; and with $x_u = 0.321$ [optimum fit with Eq. (21), Curve 2]. Both fits used Eq. (20).

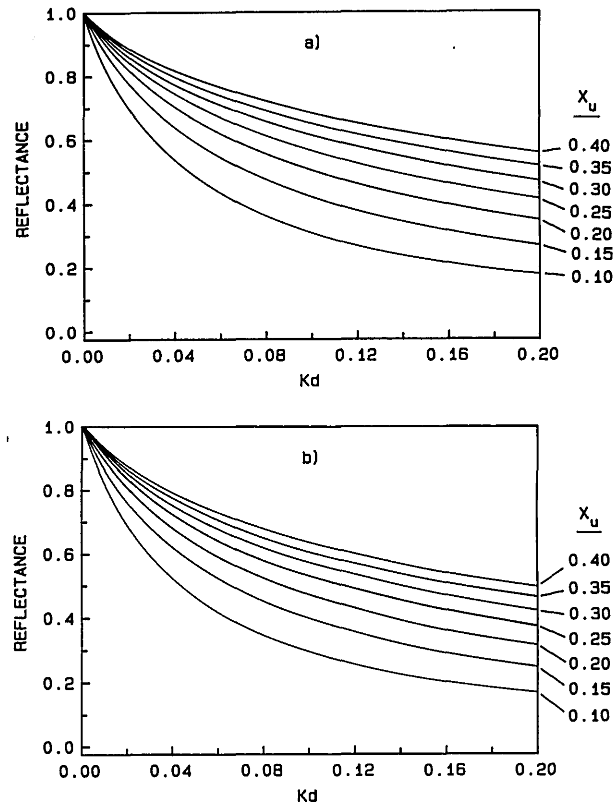

Fig. 7. Computer simulations of Eq. (17) with $n = 1.55$ and x_u as a parameter; (a) $x = x(x_u)$, Eq. (20); (b) $x = x(x_u)$, Eq. (21).

effect becomes much more pronounced at high x_u, with the $x_u = 0.35$, Eq. (21), curve in Fig. 7(b), virtually coinciding with the $x_u = 0.30$, Eq. (20), curve in Fig. 7(a). These considerations clearly indicate that little physical significance can be given to the actual x_u value that determines a best fit, and that x_u may only be significant as a characteristic indicator of the reproducibility of average packing conditions in powdered specimens. Figure 8 shows that the model is much less sensitive to the refractive index value than to the x_u value. The greatest variation with n occurs at very low kd values (See also Fig. 4). In view of the steeper decrease in R with increasing n at low kd, an improved fit to the data in Fig. 6 could have been obtained in the $kd < 0.1$ range, if allowance for the variation of n with k had been made in the model. A similar remark with

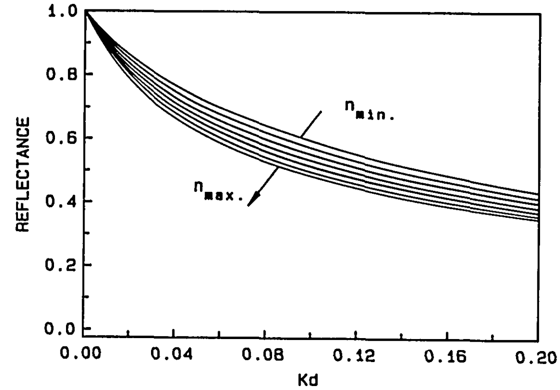

Fig. 8. Computer simulations of Eq. (17) with $x_u = 0.284$, Eq. (21), and n as a parameter $n_{\min} = 1.4$, $n_{\max} = 2.0$, $\Delta n = 0.1$.

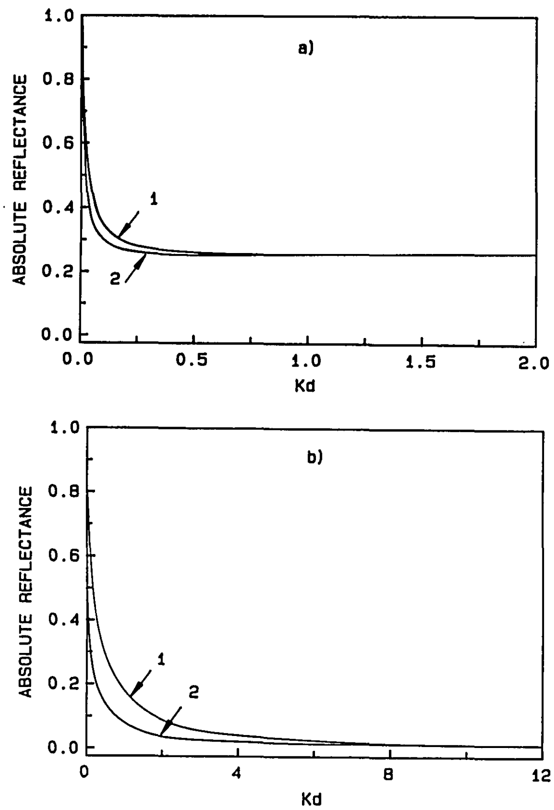

Fig. 9. Range of convergence of the corrected model (Curve 1) and the original Melamed theory (Curve 2); (a) $n = 5$, and (b) $n = 1.2$. All reflectance curves shown are absolute (unnormalized).

respect to both Johnson[3] and Melamed[1] models has previously been made by Companion.[5]

The original and corrected Melamed models converge in the limit of very high kd to the same value [Eqs. (16), (17)]:

$$R_M(kd \gg 1) \approx R(kd \gg 1) \to 2x\bar{m}_e(n). \tag{22}$$

For very opaque powders only the first ray reflected from the surface particle will contribute to the diffuse reflectance. Any other ray entering the particle will be extinguished due to absorption, before it can perform the requisite double traversal through the bulk of the particle, including an internal reflection at the lower surface. Figure 9 shows that for high n the two models converge at $kd > 0.5$, whereas for low n substantial differences remain up to $kd \approx 8$. It thus appears that the present model should be used in lieu of the original theory for practically all quantitative analysis of powder spectroscopy.

IV. Conclusion

The present physically corrected Melamed model has been compared with the original theory. The most substantial differences were found to occur at low kd, with the goodness of fit of the corrected model to the didymium glass spectroscopic data of Melamed being ~5–10% worse than the original uncorrected model. The variation of n with k was found to be a possible cause of the discrepancy. As a side result, a corrected analytical expression for $\bar{m}_e(n)$, and an analytical expression for $\bar{m}_i(n)$ for the first time, have been presented. The corrected Melamed model should be used in most cases of practical experimental interest (low n, low kd ranges semi-infinite powder layer). A more realistic discontinuum model for layers of finite thickness has recently been developed.[8]

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Appendix: Analytical Expressions for the Reflection Coefficients $\bar{m}_e(n)$ and $\bar{m}_i(n)$

The Fresnel relations for specular, unpolarized reflection yield the refractive index dependence of the average external and internal reflection coefficients, $\bar{m}_e$ and $\bar{m}_i$, for uniformly diffuse radiation. It can be shown that[4]

$$\bar{m}_e(n) = \int_0^{\pi/2} f(\alpha,n) \sin\alpha \cos\alpha \, d\alpha \tag{A1}$$

$$\bar{m}_i(n) = 1 - \sin^2\alpha_c + \int_0^{\alpha_c} f(\alpha,n) \sin\alpha \cos\alpha \, d\alpha, \tag{A2}$$

where

$$f(\alpha,n) = \frac{\sin^2(\alpha - \beta)}{\sin^2(\alpha + \beta)} + \frac{\tan^2(\alpha - \beta)}{\tan^2(\alpha + \beta)}, \tag{A3}$$

where α and β are angles of incidence and refraction, respectively. Walsh[9] carried out the integration for Eq. (A1) over 50 years ago; however, the expression as perpetuated by Kortüm,[10] at least, is wrong and gives negative values for $\bar{m}_e(n)$ in some n ranges. Furthermore, no easy access to the original paper by Walsh can be had, in our experience, due to the obscurity of the publication. Numerical techniques have been also used to carry out the integrations, Eqs. (A1) and (A2). The results vary somewhat from one author to the next, owing to the nature of the approximation(s) used.[11,12] Melamed (in Ref. 1, Appendix I) used numerical integrations for both coefficients. For small values of α_c he also gave an explicit formula for $\bar{m}_i(n)$, which is, however, erroneous. As there is a lack of analytical expressions for $\bar{m}_i(n)$ and no easy access to a (correct) $\bar{m}_e(n)$, we carried out the analytical calculations in this Appendix. The resulting expressions can henceforth be used without recourse to numerical procedures.

A. External Reflection Coefficient $\bar{m}_e(n)$

Snell's law can be written as

$$\sin\beta = \frac{1}{n}\sin\alpha \tag{A4}$$

for incidence from a medium of unit refractive index into a medium of refractive index n. Combination of Eqs. (A1) and (A3) and transformation of variables from trigonometric to algebraic yields

$$\bar{m}_e(n) = \int_0^1 \left[\frac{(1-y^2/n^2)^{1/2} - \frac{1}{n}(1-y^2)^{1/2}}{(1-y^2/n^2)^{1/2} + \frac{1}{n}(1-y^2)^{1/2}}\right]^2 ydy + \int_0^1 \left[\frac{(1-y^2)^{1/2} - \frac{1}{n}(1-y^2/n^2)^{1/2}}{(1-y^2)^{1/2} + \frac{1}{n}(1-y^2/n^2)^{1/2}}\right]^2 ydy \tag{A5}$$

Rationalizing the fractions involved in both integrands and performing the resulting algebra gives

$$\bar{m}_e(n) = \frac{1}{(n^2-1)^2}(J_1 - 4J_2 + J_3 - 4n^2J_4) \tag{A6}$$

where

$$J_1 \equiv \int_0^1 [n^4 + 6n^2 + 1 + 8x^4 - 8(n^2+1)x^2]xdx = \frac{1}{2}\left(n^4 + 2n^2 - \frac{1}{3}\right); \tag{A7}$$

$$J_2 \equiv \int_0^1 (n^2 + 1 - 2x^2)[x^4 - (n^2+1)x^2 + n^2]^{1/2}xdx = \frac{1}{3}n^3 \text{ [Ref. 13, entries 2.262.1 and 2.262.2]}; \tag{A8}$$

$$J_3 \equiv \int_0^1 \{[n^4(n^2+1)^2 + 4n^6] - 2n^2(n^2+1)^3x^2 + [(n^4+1)^2 + 4n^4]x^4)/[n^2 - (1+n^2)x^2]^2\}xdx = \frac{1}{2(n^2+1)^2}[n^8 - 8n^6 + 6n^4 + 1 + 16n^4(n^4+1)\ln(n)/(n^2+1)]; \tag{A9}$$

$$J_4 \equiv \int_0^1 \{[n^2(n^2+1) - (n^4+1)x^2] \times [x^4 - (n^2+1)x^2 + n^2]^{1/2}[n^2 - (1+n^2)x^2]^2\}xdx = \frac{1}{2(n^2+1)^2}\left[2n(n^2-1)^2 + \frac{(n^2-1)^4}{2(n^2+1)}\ln\left(\frac{n+1}{n-1}\right)\right] \tag{A10}$$

(Ref. 13, entries 2.267.1 and 2.267.2; also 2.261 and 2.266). Finally, Eqs. (A7–A10) give

$$\bar{m}_e(n) = \frac{n^4 - \frac{8}{3}n^3 + 2n^2 - \frac{1}{3}}{2(n^2-1)^2} + \frac{n^8 - 8n^6 + 6n^4 + 1}{2(n^2+1)^2(n^2-1)^2} - \frac{2n^3}{(n^2+1)^2} + \left[\frac{8n^4(n^4+1)}{(n^2+1)(n^2-1)^4}\right]\ln(n) - \left[\frac{n^2(n^2-1)^2}{(n^2+1)^3}\right]\ln\left(\frac{n+1}{n-1}\right) \tag{A11}$$

B. Internal Reflection Coefficient $\bar{m}_i(n)$

Snell's law from an optically thick to an optically thin medium of unit refractive index gives:

$$\sin\beta = n\sin\alpha \tag{A12}$$

with the critical angle $\alpha_c = \sin^{-1}(1/n)$. Eq. (A2) may be expressed as:

$$\bar{m}_i(n) = 1 - n^{-2} + F(n) \tag{A13}$$

where, when treated as in case (a) above, the function $F(n)$ can be written as:

$$F(n) = \int_0^{1/n}\left[\frac{(1-n^2y^2)^{1/2} - n(1-y^2)^{1/2}}{(1-n^2y^2)^{1/2} + n(1-y^2)^{1/2}}\right]^2 ydy + \int_0^{1/n}\left[\frac{(1-y^2)^{1/2} - n(1-n^2y^2)^{1/2}}{(1-y^2)^{1/2} + n(1-n^2y^2)^{1/2}}\right]^2 ydy \tag{A14}$$

The functional dependence of $\bar{m}_i(n)$ can be written in the form

$$\bar{m}_i(n) = 1 - n^{-2} + \frac{1}{(n^2-1)^2}(J_5 - 4nJ_6 + J_7 - 4nJ_8) \tag{A15}$$

where

$$J_5 \equiv \int_0^{1/n}[n^4 + 6n^2 + 1 - 8n^2(n^2+1)x^2 + 8n^4x^4]xdx = \frac{1}{2}\left(n^2 + 2 - \frac{1}{3n^2}\right), \tag{A16}$$

$$J_6 \equiv \int_0^{1/n}(n^2 + 1 - 2n^2x^2)[n^2x^4 - (n^2+1)x^2 + 1]^{1/2}xdx = \frac{1}{3} \text{ [Ref. 13, entries 2.262.1 and 2.262.2]}, \tag{A17}$$

$$J_7 \equiv \int_0^{1/n}\{([(n^2+1)^2 + 4n^2] - 2(n^2+1)^3x^2 + [(n^4+1)^2 + 4n^4]x^4)/[(n^2+1)x^2 - 1]^2\}xdx = \frac{1}{2(n^2+1)^2}[n^6 - 8n^4 + 6n^2 + n^{-2} + 16n^2(n^4+1)\ln(n)/(n^2+1)], \tag{A18}$$

$$J_8 \equiv \int_0^{1/n}\{[(n^2+1) - (n^4+1)x^2][n^2x^4 - (n^2+1)x^2 + 1]^{1/2} \times [(n^2+1)x^2 - 1]^2\}xdx = \frac{1}{2(n^2+1)^2}\left[(n^2-1)^2 + \frac{(n^2-1)^4}{2n(n^2+1)}\ln\left(\frac{n+1}{n-1}\right)\right] \tag{A19}$$

(Ref. 13, entries 2.267.1 and 2.267.2; also 2.261 and 2.266). Collecting terms in Eqs. (A15–A19) gives the following explicit expression for the internal reflection coefficient.

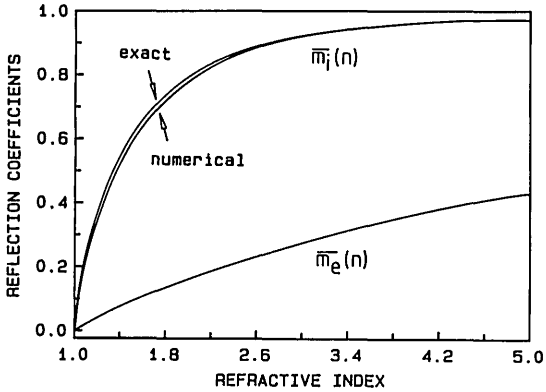

Fig. 10. Refractive index dependence of the reflection coefficients $\bar{m}_e(n)$ and $\bar{m}_i(n)$. Analytical results [Eqs. (A11) and (A20)] and numerical integration are shown for comparison. See the Appendix for details.

$$\bar{m}_i(n) = 1 - \frac{1}{n^2} + \frac{1}{2(n^2-1)^2}\left(n^2 - \frac{8}{3}n + 2 - \frac{1}{3n^2}\right) - \frac{2n}{(n^2+1)^2} + \frac{n^6 - 8n^4 + 6n^2 + n^{-2}}{2(n^2+1)^2(n^2-1)^2} + \left[\frac{8n^2(n^4+1)}{(n^2+1)(n^2-1)^4}\right]\ln(n) - \left[\frac{(n^2-1)^2}{(n^2+1)^3}\right]\ln\left(\frac{n+1}{n-1}\right) \quad \text{(A20)}$$

Eqs. (A11) and (A20) have been plotted in Fig. 10. Along with the explicit forms, we have plotted the results of a numerical integration using the trapezoidal rule and an increment $\Delta\alpha = \pi/400$.

There is no difference between numerical and exact formulas for $\bar{m}_e(n)$ up to the third significant digit and both curves coincide entirely in the $1 \leq n \leq 5$ range. Some deviation of the numerical integration from the exact formula for $\bar{m}_i(n)$ appears in the region $1.2 < n < 2.6$, i.e., where the increase of $\bar{m}_i$ is steepest. Consequently, the exact formulas for $\bar{m}_e$ and $\bar{m}_i$ were used in all plots of the physically corrected Melamed model.

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