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Breaking trade-offs between translucency and diffusion in particle-doped films

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Abstract: Particle-doped thin films that are translucent and diffusive have applications in cosmetics, coatings, and display technologies, but finding material combinations that produce these effects simultaneously is challenging: formulations tend to be either transparent or opaque. Using a combination of Mie scattering calculations and spectral transmission measurements on monodisperse colloidal suspensions, we demonstrate that the two characteristic optical properties of the films, total transmittance and haze, scale with the effective backscattering and forward scattering cross sections, both of which are properties of single particles. These scalings enable an efficient computational search for combinations of particle sizes, concentrations, and refractive indices that break the trade-off between translucency and diffusion. The optimum particle sizes and concentrations obey power-law dependences on the refractive index difference, a result of the interference condition for resonances in the scattering cross sections. The power laws serve as design equations for formulating particle-doped thin films.

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1. Introduction

Coatings and thin films of small particles suspended in a medium are important for many applications, including personal care products, paints, paper, display technologies, and polymer composites. Many of the most interesting applications require coatings that produce competing optical effects simultaneously. For instance, light diffuser plates in liquid crystal displays (LCD) [1] and 'soft focus' cosmetic products [2] require thin films that are both translucent and diffusive. That is, they must allow light to pass through, but that transmitted light should be scattered so as to appear diffuse. However, achieving translucency and diffusion simultaneously is challenging: as one increases the other tends to decrease. This trade-off, coupled with the wide variety of available ingredients, makes it difficult to formulate materials with the desired combination of translucency and diffusion by trial and error. Therefore, models and design rules able to predict bulk optical properties from single-particle attributes are needed.

A number of models describing the radiative transfer through particle-doped coatings have been developed over the past century [3]. However, all such models struggle to provide a connection between experimental parameters such as particle size, refractive index, and concentration, and their effects on the bulk optical properties of the composite film. On one hand, phenomenological models such as that of Kubelka and Munk [4, 5] can relate reflectance and transmittance of thin films to scattering and absorbing "constants," but the connection between these constants and single-particle scattering parameters is unclear. Moreover, the constants are not directly related to physical properties of the material and depend on external factors such as whether the illumination geometry is diffuse or collimated [6]. On the other hand, Monte Carlo-based models [7] that use Mie scattering theory [8] to explicitly calculate the trajectories of incident photons can predict the full angular and spatial light intensity distributions from single-particle attributes, but they are computationally expensive and obscure simple physical insight into the most relevant variables.

Here we take an intermediate approach that combines spectral transmission measurements

and Mie scattering calculations. With applications such as light diffuser plates and soft focus cosmetics in mind, we focus on coatings and thin films that maximize both total transmittance (translucency) and haze (diffusion). To systematically explore the relationship between transmittance and haze, we first measure the bulk optical properties of monodisperse colloidal suspensions, investigating the role of particle size, volume fraction, and refractive index. As we show, our measurements of transmittance and haze collapse when rescaled by two single-particle scattering quantities, the effective backscattering and forward scattering cross sections, showing that the film's appearance is primarily due to single-scattering processes. We also show that particle-size-dependent resonances in these two cross sections can be exploited to break the trade-off between translucency and diffusion, yielding a set of design rules for formulating particle-doped thin films.

2. Methods

2.1. Sample preparation

Monodisperse suspensions of polystyrene (PS) spheres with a variety of diameters are obtained from Life Technologies Corporation; poly(methyl methacrylate) (PMMA) particles are synthesized by surfactant-free emulsion polymerization (320-nanometer-diameter) or dispersion polymerization (2-micrometer-diameter)[9, 10]. All colloids are washed three times in Millipore water by centrifugation/resuspension and then resuspended in 10 mM NaCl/ Millipore water. Thin samples are then prepared by loading 20–30 microliters of suspension into a sample cell consisting of a precleaned glass slide and a No. 1 glass coverslip that are sealed on two sides with optical-grade, UV-curable epoxy (Norland Optical Adhesive 68, Norland Products, Inc.). The chamber thickness is controlled by Mylar® spacers (200 gauge, DuPont) epoxied between the slide and coverslip. Once fabricated, sample chambers are mounted onto the integrating sphere setup shown in Fig. 1.

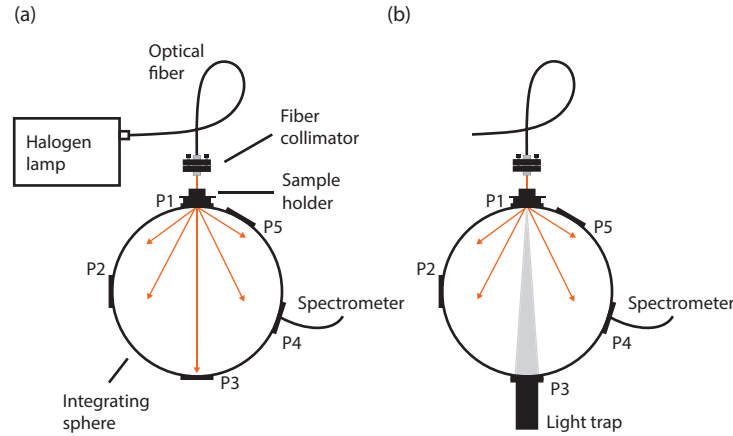


Fig. 1. Schematic of the experimental apparatus used to make spectral transmission measurements. (a) Total transmittance measurements are made with the sample at port-hole position P1, the light trap at P5 (not shown), and the reference chamber at P2 (not shown). (b) Diffuse transmittance measurements are made with the sample at P1, the light trap at P3, and the reference chamber at P2 (not shown). The reference spectrum is taken with the reference chamber at P1, the sample at P2, and the light trap at P5.

2.2. Spectral transmission measurements

The setup consists of a halogen lamp (DH-2000, Ocean Optics), an integrating sphere (RT-060-SF, Labsphere, Inc.), and a spectrometer (HR2000+, Ocean Optics). Unpolarized light from the halogen lamp is coupled to a multimode optical fiber (QP600-2-UV-Vis, Ocean Optics) and collimated by an achromatic fiber collimator (74-ACR, Ocean Optics) just upstream of the integrating sphere. After passing through the sample chamber, transmitted light is collected by the integrating sphere and sent to the spectrometer by an identical optical fiber.

Using the integrating sphere setup, we measure total transmittance T (the fraction of incident light that is transmitted through the sample) and diffuse transmittance T_{diffuse} (the fraction of incident light that is transmitted through the sample and scattered more than 4.75° from the direction of incident illumination) by changing the position of a light trap (Fig. 1). The recorded spectra are dark-count subtracted and normalized at each wavelength to a spectrum transmitted through a glass chamber filled with 10 mM NaCl/Millipore water. In an effort to minimize systematic errors due to variations in the average sphere reflectance, the sample, light trap, and reference chamber are all attached to the integrating sphere in each of three measurements taken per sample, only at different positions. For example, we place the light trap at the port hole opposite the sample chamber for measurements of diffuse transmittance, and at the port hole adjacent to the sample chamber for measurements of total transmittance. Removing the light trap from the integrating sphere entirely and replacing it with a port-hole plug for measurements of total transmittance would raise the average sphere reflectance, resulting in a systematic overestimation of T relative to T_{diffuse} . Using these measurements, we compute the haze, defined as the ratio of diffuse transmittance to total transmittance:

$$\frac{H}{100\%} = \frac{T_{\text{diffuse}}}{T}. \quad (1)$$

Although we measure the wavelength dependence of transmittance and haze, we report only the averages over the visible range, taken to be 450–750 nm.

3. Results and discussion

3.1. Relating bulk optical properties to single-particle scattering quantities

Our measurements of total transmittance and haze demonstrate a trade-off between translucency and diffusion. We measure T and H of aqueous suspensions of polystyrene or PMMA spheres of different diameters as a function of volume fraction ϕ (Figs. 2(a)-2(b)). For a given particle size, we find that both total transmittance and haze are monotonic functions of the particle concentration, with T decreasing and H increasing with increasing ϕ . This trend is consistent with our intuition: as the volume fraction (or number density) of particles increases, so does the likelihood of an incident photon being scattered by a particle.

Interestingly, however, we find that haze scales non-monotonically with particle size at fixed volume fraction: it first increases and then decreases with increasing particle diameter D (Fig. 2(b)). That is, there appear to be specific particle sizes for which haze is maximized (Fig. 2(b), inset). Total transmittance, in contrast, is only weakly dependent on particle size for the polystyrene samples studied here.

To quantify the relationship between particle size, volume fraction, and refractive index further, we construct a simple model that relates the observed bulk optical properties to single-particle scattering quantities. We first derive an expression for total transmittance, assuming that there are no structural correlations between particles and that effects due to multiple scattering are negligible. In the absence of absorption, attenuation of totally transmitted light is due to one of two processes: (1) scattering of light by more than 90° from the direction of incident illumination, or (2) total internal reflection of scattered light from the glass-air interface (Fig. 3).

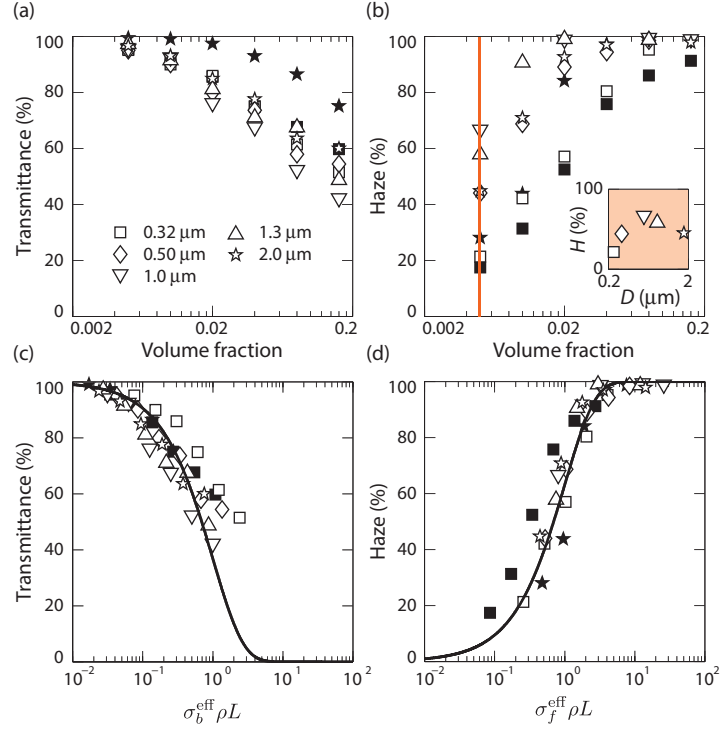


Fig. 2. Total transmittance (a) and haze (b) of colloidal films are monotonic functions of the particle volume fraction for differently sized polystyrene (open symbols) and PMMA (closed symbols) microspheres in 10 mM NaCl/ Millipore water (particle diameters indicated in (a)). The inset in (b) shows haze as a function of particle diameter D for polystyrene suspensions at a volume fraction of 0.005. All data collapse when plotted against two dimensionless groups, $\sigma_b^{\text{eff}} \rho L$ and $\sigma_f^{\text{eff}} \rho L$, and are captured quantitatively (curves) by Eqs. (3) and (5), respectively (c-d). Measurements are performed on samples with a thickness of 40 micrometers. The refractive index of polystyrene is taken from measurements of bulk samples [11]; the refractive index of PMMA is taken from direct measurements of single particles using digital holographic microscopy [12]. The effective backscattering cross section σ_b^{eff} and effective forward scattering cross section σ_f^{eff} are evaluated using the Mie module of the open-source software package HoloPy (<http://manoharan.seas.harvard.edu/holopy>) [13, 14]. The computed cross sections represent averages over the visible spectrum.

That is, no light scattered at an angle larger than the critical angle for total internal reflection $\theta_c = \sin^{-1}(n_{\text{air}}/n_m)$ is captured by the integrating sphere, where n_{air} is the refractive index of air and n_m is the refractive index of the medium [15]. We assume that contributions due to specular reflection are negligible since we normalize the measured transmission to that of an identical glass sample cell. Therefore, light of intensity I should be attenuated by an amount

$$dI = -\sigma_b^{\text{eff}} \rho I dx \quad (2)$$

when passing through a slab of differential thickness dx , where

$$\sigma_b^{\text{eff}} = 2\pi \int_{\theta_c}^{\pi} \frac{d\sigma_{\text{sca}}}{d\Omega} \sin \theta d\theta$$

is the effective backscattering cross section that includes both backscattering into the rear hemisphere ($\pi/2 < \theta < \pi$) and total internal reflection ($\theta_c < \theta < \pi/2$); ρ is the particle number density. Like the Beer-Lambert law, Eq. (2) comes from considering the scattering from a thin slab of thickness Δx with area A . In our case, we are concerned only with scattering at angles larger than the critical angle associated with total internal reflection. Therefore, the attenuation of intensity due to scattering is

$$A [I(x + \Delta x) - I(x)] = -\sigma_b^{\text{eff}} A \Delta x \rho I(x).$$

Rearranging and taking the limit as Δx goes to 0 yields

$$\lim_{\Delta x \rightarrow 0} \frac{I(x + \Delta x) - I(x)}{\Delta x} = \frac{dI(x)}{dx} = -\sigma_b^{\text{eff}} \rho I(x).$$

The differential scattering cross section $d\sigma_{\text{sca}}/d\Omega$ is proportional to the amount of light scattered into a unit solid angle about a given direction and can be evaluated exactly for scattering of electromagnetic radiation by a sphere, given by Mie's solution to Maxwell's equations [8]. Integrating Eq. (2) over the film thickness L yields an expression for the total transmittance

$$\frac{T}{100\%} = e^{-\sigma_b^{\text{eff}} \rho L}, \quad (3)$$

in which T scales exponentially with a dimensionless length scale $\sigma_b^{\text{eff}} \rho L$. The expression that we find is analogous to the Beer-Lambert law [16], except that the total scattering cross section has been replaced by the effective backscattering cross section.

We derive a similar expression for haze, relying again on the same assumptions. Our original definition of haze (given by Eq. (1)) can be rewritten as $H/100\% = 1 - T_{\text{direct}}/T$, where $T = T_{\text{diffuse}} + T_{\text{direct}}$ and T_{direct} is the fraction of incident light transmitted at $\theta = 0$. Determining H , then, reduces to calculating the fraction of transmitted light that is transmitted directly through the particle-doped film. In this case, in a slab of thickness dx , directly transmitted light of intensity I is attenuated by an amount

$$dI = -\sigma_{\text{sca}} \rho I dx, \quad (4)$$

where σ_{sca} is the scattering cross section, which is proportional to the total amount of scattered light. Integrating Eq. (4), we find that the fraction of light transmitted directly through the film is $T_{\text{direct}}/100\% = \exp(-\sigma_{\text{sca}} \rho L)$, recovering exactly the Beer-Lambert law and yielding the following expression for haze:

$$\frac{H}{100\%} = 1 - \frac{e^{-\sigma_{\text{sca}} \rho L}}{T}.$$

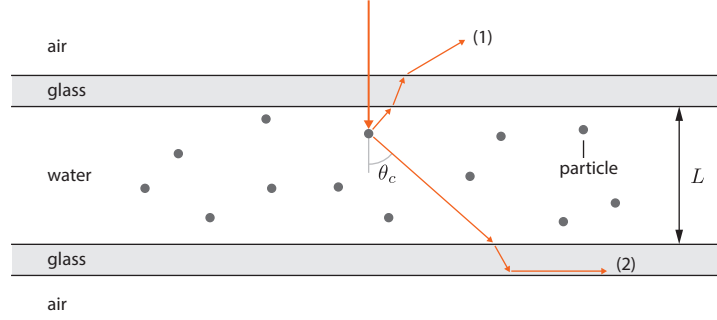


Fig. 3. Schematic of the sample chamber (not to scale). Totally transmitted light is attenuated by one of two processes: (1) scattering of light by more than 90° from the direction of incident illumination, or (2) total internal reflection of light scattered at angles exceeding the critical angle θ_c .

Plugging in our solution for transmittance, we find that haze should scale exponentially with a different dimensionless length scale $\sigma_f^{\text{eff}} \rho L$ according to

$$\frac{H}{100\%} = 1 - e^{-\sigma_f^{\text{eff}} \rho L}, \quad (5)$$

in which we define an effective forward scattering cross section

$$\sigma_f^{\text{eff}} = 2\pi \int_0^{\theta_c} \frac{d\sigma_{\text{sca}}}{d\Omega} \sin \theta d\theta$$

as the difference between the total scattering cross section and the effective backscattering cross section $\sigma_f^{\text{eff}} = \sigma_{\text{sca}} - \sigma_b^{\text{eff}}$. In the limit where σ_b^{eff} is much smaller than σ_{sca} , the effective forward scattering cross section is roughly equivalent to the total scattering cross section, and the dimensionless length scale $\sigma_f^{\text{eff}} \rho L \approx \sigma_{\text{sca}} \rho L$ represents the average number of scattering events experienced by a photon as it traverses the film. The length scale $1/(\sigma_{\text{sca}} \rho)$ is often called the scattering length or scattering mean free path and can again be calculated exactly for suspensions of spheres.

Remarkably, we find that all of our measurements of total transmittance and haze collapse onto two master curves when plotted against the two dimensionless length scales $\sigma_b^{\text{eff}} \rho L$ and $\sigma_f^{\text{eff}} \rho L$ (Figs. 2(c)-2(d)). The collapse demonstrates that T is a function of $\sigma_b^{\text{eff}} \rho L$ only, and H is a function of $\sigma_f^{\text{eff}} \rho L$ only. In other words, total transmittance is determined almost entirely by backscattering and total internal reflection, while haze is determined almost entirely by forward scattered light that is not totally internally reflected. Moreover, because our data are captured quantitatively by Eqs. (3) and (5) without any free parameters, we conclude that single scattering does indeed dominate to a first approximation, even for films with a white appearance. Only above $\sigma_b^{\text{eff}} \rho L \approx 1$ do our data of total transmittance begin to deviate from Eq. (3), likely because of multiple scattering. Indeed, calculations of the transport length, defined as $(\sigma_{\text{sca}} \rho)^{-1}/(1-g)$, where g is the asymmetry parameter [16], show that the transport length can be two to three times shorter than the sample thickness for the most concentrated suspensions. Models using the diffusion approximation have been developed to describe transmittance in the multiple scattering regime [17], but they are only applicable when the transport length is more than ten times shorter than the sample thickness, which is not the case in our experiments.

Ultimately, Eqs. (3) and (5) allow us to calculate the bulk optical properties of particle-doped films and evaluate their performance computationally. Because we hope to design films

that maximize total transmittance and haze simultaneously, we seek suspensions that maximize $\sigma_{\text{sca}}\rho L$ while minimizing $\sigma_b^{\text{eff}}\rho L$. That is, we seek combinations of particles and media that scatter strongly (maximize σ_{sca}), but do so primarily in the forward direction (minimize σ_b^{eff}). Breaking the trade-off between total transmittance and haze, then, requires not only maximizing the amount of scattered light, but also engineering the angular distribution of that scattered light.

3.2. Developing design rules

Following our experimental result that particle size is key to breaking the trade-off between translucency and diffusion, we use Eqs. (3) and (5), along with Mie scattering calculations to calculate the optical properties of thin films composed of different particle-medium combinations. Specifically, we seek to maximize the geometric mean of total transmittance and haze, $\sqrt{H \times T}$, by varying the volume fraction and particle size for particle-medium combinations with different refractive index contrasts. We choose the geometric mean as the figure of merit because it is more sensitive to extreme differences between T and H than the arithmetic mean. For example, a thin film characterized by a total transmittance of 0% could have an arithmetic mean of T and H as high as 50% even though it would be practically useless for many applications. The geometric mean, however, would be 0%, which is much more characteristic of the appearance of the film.

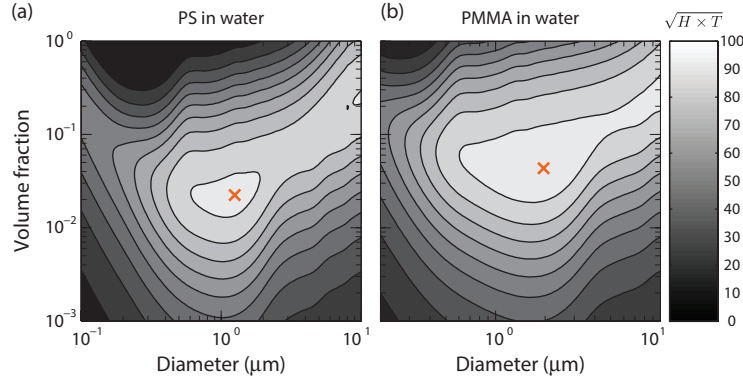


Fig. 4. Regions of parameter space corresponding to simultaneous translucency and diffusion (characterized by the geometric mean of T and H) are small. (a) shows $\sqrt{H \times T}$ for suspensions of polystyrene in water; (b) shows $\sqrt{H \times T}$ for suspensions of poly(methyl methacrylate) in water. Plots are computed using Eqs. (3) and (5) and Mie scattering calculations of σ_b^{eff} and σ_f^{eff} . From the plots, we define an optimum particle size D^* and volume fraction ϕ^* (orange symbols) that maximize the geometric mean of T and H . Calculations are for films of thickness $L = 40 \mu\text{m}$.

Representative calculations, shown in Fig. 4, highlight the challenge of designing particle-doped films that are both translucent and diffusive: $\sqrt{H \times T}$ is large only in a small region of parameter space. At fixed particle size, $\sqrt{H \times T}$ first increases and then decreases with increasing volume fraction. As one might expect, the film is transparent if there are too few particles, and opaque if there are too many. This competition gives rise to an optimum volume fraction, which we call ϕ^* . At fixed volume fraction, the geometric mean $\sqrt{H \times T}$ also displays a maximum with respect to particle size, reproducing the trend that we observe in experiment. This trend is less intuitive than the volume-fraction dependence, but still gives rise to an optimum particle diameter D^* . The (D^*, ϕ^*) coordinates are marked with an orange x in Fig. 4.

To explore the physical origin of the optimum particle size, we calculate D^* for particle-

medium combinations spanning a range of refractive index differences $\Delta n = n_p - n_m$ from 0.03 to 0.3, where n_p is the particle's refractive index; examples for polystyrene in water ($\Delta n = 0.26$) and PMMA in water ($\Delta n = 0.16$) are shown in Fig. 4. Comparing Fig. 4(a) to Fig. 4(b), we see immediately that the region of parameter space corresponding to high $\sqrt{H \times T}$, and thus the value of the optimum diameter, depends on the specific particle-medium combination: the best particle size for one particle-medium combination might differ from another. However, we find that the computed optimum diameters follow a master curve, scaling as a power law with the refractive index difference Δn for all particle-medium combinations (Fig. 5(a)). The scaling law that we find is fitted by

$$D^* = \frac{0.32 \mu\text{m}}{\Delta n}, \quad (6)$$

demonstrating that the optimum particle size is determined entirely by the refractive index difference regardless of the specific chemical composition of the particle-medium combination.

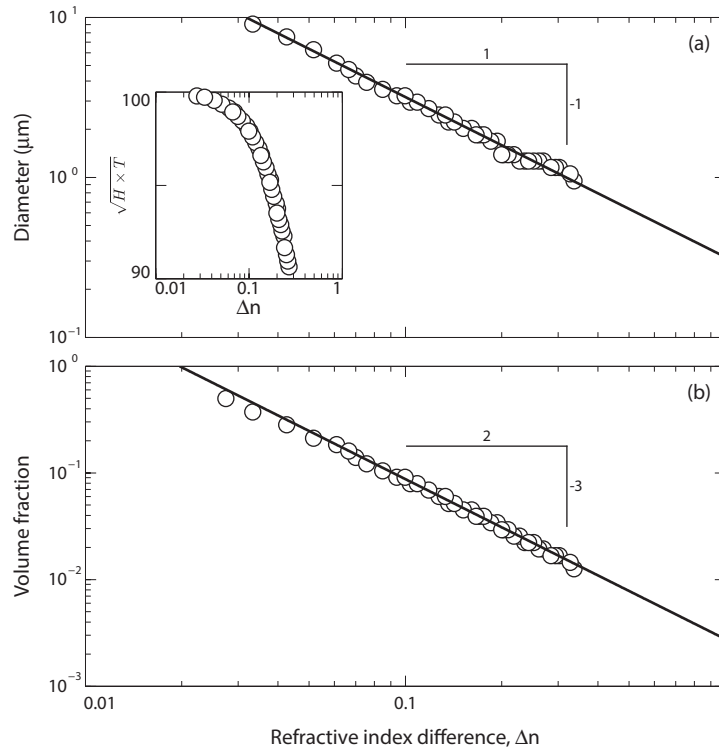


Fig. 5. The optimum particle size D^* (a) and volume fraction ϕ^* (b) of different particle-medium combinations (symbols) follow power law scalings (lines) with the absolute refractive index difference Δn and sample thickness L . The Δn^{-1} scaling of the optimum diameter results from the interference condition that gives rise to scattering resonances (Eq. (7)). The power-law relationships are fit well by Eqs. (6) and (8) and can be used to engineer the bulk optical properties of suspensions by controlling the single particle attributes (n_p, D, ϕ).

Although the scaling demonstrates that the optimum particle size is dominated by the refractive index difference, it does not provide a physical explanation. To understand the basis of the inverse relation between D^* and Δn , we return to our qualitative design criteria: to maximize total transmittance and haze simultaneously, we need suspensions that scatter strongly,

particularly in the forward direction. The scattering efficiency Q_{sca} , defined as $\sigma_{\text{sca}}/(\pi a^2)$, is enhanced for particles of particular sizes relative to the wavelength of light due to constructive interference between the incident and scattered light, where a is the particle radius. According to Mie scattering theory, these resonances occur when

$$x(m-1) = (2p+1)\pi/2, \quad (7)$$

where $m = n_p/n_m$ is the refractive index contrast, p is an integer, and $x = 2\pi a n_m/\lambda$ is the size parameter, which represents the size of the particle relative to the wavelength of light λ in the medium [16]. Rearranging Eq. (7), we see immediately that, for a fixed wavelength, the particle sizes corresponding to the resonances scale as $D \propto \Delta n^{-1}$, confirming that the non-monotonic dependence of haze on particle size is due to resonances in the scattering cross section. The effective backscattering cross section does not contribute significantly to the scaling since it is 1–2 orders of magnitude smaller than σ_{sca} for particle sizes near D^* .

We also find that the optimum volume fraction φ^* follows a power law scaling with the refractive index difference and is fit well by

$$\varphi^* = \frac{0.11 \mu\text{m}}{\Delta n^{3/2} L}. \quad (8)$$

While it is tempting to try to pin a physical explanation to the $-3/2$ exponent, we find that it depends sensitively on the figure of merit ($\sqrt{H \times T}$ in this case) and thus is unlikely to be universal. The optimum particle size scaling, in contrast, is insensitive to the figure of merit. The fact that the optimum volume fraction scales with the refractive index difference at all comes from the fact that the two dominant scattering cross sections, σ_{sca} and σ_b^{eff} , depend only on Δn . The total scattering cross section scales as Δn^{-2} , consistent with scattering from spheres with low refractive index contrast ($m < 2$) [18]. We also find that the effective backscattering cross section at D^* is constant and independent of Δn . As a result, to maintain balance between the two dimensionless length scales, $\sigma_b^{\text{eff}} \rho L$ and $\sigma_{\text{sca}} \rho L$, we would expect φ^* to scale with an exponent somewhere between -1 and -3 , which it does. The L^{-1} dependence of φ^* in Eq. (8) comes simply from the fact that the number of scatterers increases linearly with the sample thickness L .

Taken together, Eqs. (6) and (8) serve as convenient design equations for formulating thin, particle-doped films with both translucency and diffusion. For a particle-medium combination of known Δn , these equations can be used to select the optimum particle size and volume fraction needed for formulation. Instead, if it is desirable to minimize the particle loading, as is the case in many cosmetic applications, Eqs. (6) and (8) indicate that small particles with a higher refractive index difference are best.

4. Conclusions

We have shown that total transmittance and haze of colloidal suspensions depend only on two microscopic length scales under conditions where single scattering dominates. These length scales can be computed accurately using Mie scattering theory and controlled by varying the particle size, volume fraction, and refractive index, as well as the refractive index of the medium. Such quantitative relationships between the attributes of individual scatterers and the resulting bulk optical properties enable the rational design of particle-doped materials. For particular applications that simultaneously require high transmittance and high haze, seemingly contradictory requirements, we have shown that the optimum particle size and concentration follow power-law dependences on the refractive index difference between the particle and medium. These power-law scalings serve as simple design equations.

Although our analysis has considered scattering from spheres only, these concepts could also be extended to scattering from non-spherical particles [19, 20, 21]. Moreover, while we focused on designing suspensions that are both translucent and diffusive, a similar approach to deriving design criteria from Mie theory could also be used to choose particle specifications that maximize total transmittance while minimizing diffusion [22]. This might be desirable in composite materials where particles are added for their mechanical benefit, and light scattering is an unwanted side effect. More generally, having models that relate bulk optical properties to single-particle attributes should enable the rational design of other coatings whose appearance is dominated by light scattering.

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