Absence of red structural color in photonic glasses, bird feathers, and certain beetles

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Colloidal glasses, bird feathers, and beetle scales can all show structural colors arising from short-ranged spatial correlations between scattering centers. Unlike the structural colors arising from Bragg diffraction in ordered materials like opals, the colors of these photonic glasses are independent of orientation, owing to their disordered, isotropic microstructures. However, there are few examples of photonic glasses with angle-independent red colors in nature, and colloidal glasses with particle sizes chosen to yield structural colors in the red show weak color saturation. Using scattering theory, we show that the absence of angle-independent red color can be explained by the tendency of individual particles to backscatter light more strongly in the blue. We discuss how the backscattering resonances of individual particles arise from cavity-like modes and how they interact with the structural resonances to prevent red. Finally, we use the model to develop design rules for colloidal glasses with red, angle-independent structural colors.

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I. INTRODUCTION

Structural color in materials arises from interference of light scattered from inhomogeneities spaced at scales comparable to optical wavelengths. Opals and most other familiar examples of structurally colored materials are ordered [1,2], and as a result, the color of these photonic crystals [3] depends on their orientation relative to the incident light: they are iridescent. There is another, less well-studied class of materials with angle-independent structural colors. These are called photonic glasses [4–7], because the inhomogeneities form a random, glassy arrangement with short-ranged order but no long-ranged order. As in crystals, the average spacing between neighboring scatterers in a photonic glass is narrowly distributed and determines the resonantly scattered wavelength [8,9]. But unlike crystals, photonic glasses are isotropic, so that the condition for constructive interference is independent of orientation. This coloration mechanism is common in the feathers of birds [9–11], whose colors are visually indistinguishable from those of conventional absorbing dyes. Photonic glasses with structural colors in the visible have also been produced in a variety of synthetic colloidal systems [8,12–20].

However, to our knowledge there are no photonic glasses with saturated yellow, orange, or red color. While systems with angle-independent structural red have been reported [12,15,17,18,21], the color saturation for long-wavelength hues is poor compared to that for blue. Interestingly, red angle-independent structural color also appears to be rare in nature. Birds use structural color only for blue and green; red colors in bird feathers come from absorbing pigments [11]. And while the scales of the longhorn beetle Anoplophora graafi have structural colors that span the visible spectrum, there are no saturated red colors—only a pale purple [22].

The absence of red photonic glasses does not appear to have been acknowledged, let alone explained. Previous work on photonic glasses [8,9,22–25] has focused on structures found in nature and their biomimetic analogues, nearly all of which are blue. Noh and coworkers [26,27] proposed a theoretical model based on single and double scattering to explain the optical properties of these blue samples, and Liew and coworkers [23] and Rojas-Ochoa and coworkers [5] showed that the interscatter correlations not only give rise to color but also suppress multiple scattering. However, if the color were entirely determined by correlations, one would expect that all colors could be made simply by linearly rescaling the structure. As we show below, this approach does not work (Fig. 1).

Here we present a model that explains the absence of long-wavelength structural colors in photonic glasses. Our model accounts for both interparticle correlations as well as the scattering behavior of individual particles. We show that short-wavelength resonances in the single-particle scattering cross-section near backscattering introduce a blue peak in the spectrum that changes the hue of a red structural color to purple. These resonances are not the traditional Mie resonances, which occur in the total scattering cross-section, but rather are akin to cavity resonances. The model, which agrees with measured spectra from synthetic photonic glasses, provides a framework for understanding the limitations of current photonic glasses and enables the design of new systems without those limitations.

II. EXPERIMENT

To demonstrate that resonant scattering from the interparticle correlations is not sufficient to explain the colors of photonic glasses, we prepare colloidal glasses from poly(methyl methacrylate) (PMMA) spheres of various diameters and study their colors with spectrometry. Figure 1 shows color photographs and reflection spectra of samples prepared in the same way using three different particle diameters $d = 170$, 240, and 330 nm. These samples were prepared by mixing one part of an aqueous suspension containing 1% w/w carbon black (Cabot) and 2% w/w Pluronic F108 (BASF) with two parts of a monodisperse suspension of PMMA particles at 20% w/w,
The vector difference $\mathbf{q} = \mathbf{k}_s - \mathbf{k}_\text{in}$ describes the momentum transferred in the scattering process. In our analysis, we assume elastic scattering, so that $|\mathbf{k}_\text{in}| = |\mathbf{k}_s| = k = 2\pi n_{\text{eff}}/\lambda$, and

$$q = 2k \sin(\theta/2).$$

Here $n_{\text{eff}}$ is the effective refractive index of the medium and $\lambda$ is the wavelength of light in vacuum. The effective index is a weighted average calculated using the Maxwell-Garnett mean-field approximation [29]:

$$n_{\text{eff}} = n_{\text{med}} \left[ \frac{2n_{\text{med}}^2 + n_p^2 + 2\phi(n_p^2 - n_{\text{med}}^2)}{2n_{\text{med}}^2 + n_p^2 - \phi(n_p^2 - n_{\text{med}}^2)} \right].$$

where $n_{\text{med}}$ is the refractive index of the material surrounding the particles (air, in our case), $n_p$ is the refractive index of the particles, and $\phi$ is the volume fraction occupied by the particles. We use the effective index because the particle packings are dense, so that the scattered fields “see” an index intermediate between the particle and medium index. Although

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1 See the bottom spectrum in Fig. 1(c) of Ref. [22].

2 See the pink curve in Fig. 1(b) of Ref. [20].
the Maxwell-Garnett approximation is typically used when the refractive index variations are much smaller than the wavelength, Vos and coworkers [30] showed that it is a good approximation even for photonic crystals, and Forster and coworkers [8] have shown the same for photonic glasses.

Assuming perfect monodispersity, we can express the differential scattering cross-section of a glassy ensemble of particles, \(d\sigma_{\text{glass}}/d\Omega\), as a product of the form factor \(F\) and the structure factor \(S\) [5,28]:

\[
d\sigma_{\text{glass}}/d\Omega = (1/k^2)FS.
\]

The form factor is related to the differential scattering cross-section of a single particle, \(d\sigma/d\Omega\), through \(F = (1/k^2)d\sigma/d\Omega\) [31]; we calculate \(F\) using Mie theory [31,32]. The structure factor is the Fourier transform of the pair correlation function of the particles [33]; we calculate it using a solution to the Ornstein-Zernike equation with the Percus-Yevick closure approximation [34]. In so doing, we are assuming that the structure of our particle glasses is close to that of a hard-sphere liquid. Figure 3 shows \(S\) calculated for a volume fraction \(\phi = 0.55\) as a function of a dimensionless wavevector \(x = qd\), where \(d\) is the diameter of the particles. We use this structure factor in all our calculations.

In the structure factor, the peak at \(x_o\) corresponds to the wavevector \(q_o = 2\pi/d_{\text{avg}}\), where \(d_{\text{avg}}\) is the average center-to-center spacing between nearest neighbors. The peak wavevector \(q_o\) gives rise to constructive interference and color, because it sets the relative phase difference between light waves scattered from neighboring particles. Resonant scattering occurs when this phase difference is an integer multiple of \(2\pi\). The wavelengths at which this happens can be determined from Eq. (1):

\[
\lambda = (4\pi n_o d/x_o)\sin(\theta/2).
\]

To describe the intensity of scattered light that reaches the detector, we integrate the differential scattering cross-section over the solid angle corresponding to the numerical aperture (NA) of our detector, taking into account transmission and refraction at the air-sample interface:

\[
s_{\text{detected}} = 1/k^2 \int_0^{2\pi} \int_{\theta_{\text{min}}}^{\theta_{\text{max}}} T_{\text{a-s}} FS \sin(\theta) d\theta d\phi,
\]

where \(T_{\text{a-s}}\) is the Fresnel coefficient for transmission at the sample-air interface, \(\theta_{\text{min}} = \pi - \arcsin(NA/n_o)\) is the minimum scattering angle that we detect, and \(\phi\) is the polar angle in the plane perpendicular to the scattering plane. There is no dependence on \(\phi\) because the particles are spherical and the structure is isotropic.

To compare our calculations to our measurements we now derive a relation between \(s_{\text{detected}}\) and the measured reflectivity, \(R\). To do this we must account for extinction of light as it propagates through the sample; the intensity of light scattered from layers close to the surface is higher than the intensity of light scattered deeper in the sample because of attenuation by scattering. Under the assumption of single scattering, this attenuation scales exponentially with depth following Beer’s Law, \(I(x) = I_0 e^{-\rho \sigma x}\), where \(\rho\) is the number density of particles, \(\sigma\) is the scattering cross-section for the full solid angle \((0 \leq \phi \leq 2\pi, 0 \leq \theta \leq \pi)\), and \(x\) is the distance light has propagated in the medium [31]. If the glass consists of slices of infinitesimal thickness \(\delta x\), the total reflected intensity \(I\) is the sum of the intensities \(\delta I\) reflected from each slice: \(\delta I = I(x)\delta \sigma_{\text{detected}}\delta x\), where \(\delta \sigma_{\text{detected}}\) is given by Eq. (5). After integrating both sides and including the Fresnel coefficients for transmission \((T_{\text{a-s}})\) and reflection \((R_{\text{a-s}})\) at the air-sample interface, we find

\[
R = T_{\text{a-s}} \frac{s_{\text{detected}}}{\sigma} (1 - e^{-\rho \sigma}) + R_{\text{a-s}}.
\]

where \(l\) is the optical thickness of the sample, or the maximum distance that light can propagate in it.

The reflectivity for a glass of PMMA spheres at a volume fraction \(\phi = 0.55\), as calculated according to Eq. (6), is shown in Fig. 4. We have omitted the Fresnel coefficient for reflection at the air-sample interface to better illustrate the features that arise from scattering from the bulk colloidal glass. The plot is shown as a function of the scaled particle size \(kd\), where \(k = 2\pi n_o/\lambda\). All terms in Eq. (6)—except for the Fresnel reflection coefficient, which adds an offset in amplitude—scale with \(kd\). Thus, this master curve describes reflectivity from a glass made of any particle size (of the same material and
FIG. 4. (Color online) Calculated reflectivity as a function of $kd$ for a photonic glass of spheres at a volume fraction $\phi = 0.55$, as calculated from Eq. (6) with the Fresnel reflection coefficient omitted. The vertical dashed lines denote the $kd$ values that correspond to the range of visible wavelengths we detect, 425 nm (blue line on the right) and 800 nm (red line on the left), when the particle size is $d = 334$ nm.

volume fraction), assuming dispersion is small. Depending on the particle sizes and refractive indices, different features of the curve will fall within the visible range; here we mark the edges of our detection range for $d = 334$ nm with the blue (425 nm, right) and red (800 nm, left) vertical dashed lines.

IV. RESULTS AND DISCUSSION

The calculated reflectivity reproduces the locations of all of the peaks in our data, as shown in Fig. 5. The only free parameters are the volume fraction $\phi = 0.55$ and the thickness $l = 16 \mu m$. The peaks predicted by the theory coincide with the peaks in the data for particle diameters $d = 238$ nm [Fig. 5(a)] and $d = 334$ nm [Fig. 5(b)]; these sizes are in good agreement with the sizes of the particles measured with scanning electron microscopy, 240 and 330 nm. The calculated reflectivity for the $d = 334$-nm system also reproduces the peak in the blue that we observe in the data.

The model underestimates the amount of light scattered off-resonance, especially at short wavelengths. We attribute this discrepancy to multiple scattering. Since the probability of multiple scattering increases with the scattering cross-section of individual particles, its contribution should be more pronounced at short wavelengths, which is consistent with what we see.

With this model and data at hand we can address our original question: why does the glass made of 330-nm spheres scatter so much blue light, when we expect the interparticle correlations to give rise only to a resonance in the red? To identify the source of the reflection peaks in this sample, we compare our data to the reflectivities predicted from the form factor alone and, in another comparison, the structure factor alone [Fig. 5(c)]. From the shapes of these two curves we immediately see that the blue peak comes from the form factor and the red peak from the structure factor, boosted by another peak in the form factor that occurs at a longer wavelength.

We conclude that the structural colors of our photonic glasses are determined not only by interference between waves scattered from correlated particles, but also by resonances in the single-particle scattering cross-section. This can also be seen by rescaling the measured reflectivities by $\sigma_F$,detected and plotting them as a function of the dimensionless wavevector...
FIG. 6. (Color online) (a) Reflection spectra from Fig. 1 plotted against the dimensionless lengths scale $k d$. Note the increased scattering at high $k d$ values (short wavelengths) for the $d = 330$-nm sample. (b) Same as (a) but normalized to the single-particle form factor integrated over the detected scattering angles, $\sigma_{F,\text{detected}}$, as defined in Eq. (7). The increased scattering at high $k d$ values disappears, indicating that it is due to the form factor. Differences in amplitude of the peaks are likely due to differences in the sample thickness $l$.

We see that after rescaling, the long-wavelength reflectivity peak of the $d = 330$-nm sample coincides with the reflectivity peak of the $d = 240$-nm sample at the same value of $k d$, showing that these peaks arise from structural resonances, while the short-wavelength (high $k d$) peak in the $d = 330$-nm sample disappears, showing that it arises from single-particle scattering.

We note that the single-particle resonances responsible for the high reflectivity at small wavelengths are not the so-called “Mie resonances.” Mie resonances are observed in the total single-particle scattering cross-section, obtained by integrating the differential scattering cross-section over all angles. 

The resonances that contribute to the high reflectivity at small wavelengths occur for scattering angles near backscattering.

We first consider the single-particle scattering cross-section for pure backscattering. This is proportional to the differential scattering cross-section for $\theta = \pi$. As shown in Fig. 7, the backscattering cross-section can have one or more resonances, and the wavelengths at which these occur increase linearly with the particle “optical diameter,” $n_p d$, following the relation

$$\lambda_{\text{resonant}} = 2n_p d/z,$$

where $z$ is an integer that corresponds to the order of the resonance. This suggests that these resonances are akin to those of a Fabry-Pérot cavity, where constructive interference occurs for wavelengths that fit an integer number of times within the round-trip optical pathlength enclosed by the cavity [35]. Similar resonances occur in the differential scattering cross-section for all angles, as shown in Fig. 8. Our calculations show that the resonant wavelength shifts toward the blue as the angle decreases. This blue-shift is consistent with the decrease in the round-trip optical pathlength inside the sphere with decreasing angle (see inset). When the differential scattering cross-section is integrated over the detected solid angle ($\theta = 150^\circ$–$180^\circ$ for our detection numerical aperture of 0.8, after refraction), these resonances, though broadened, persist [Fig. 5(c)]. We therefore conclude that constructive interference of light inside the particles contributes to enhanced reflection at short wavelengths.

Our results show that the absence of red structural color in photonic glasses can be attributed to the blue scattering resonances within the component particles. These resonances occur in addition to the resonances from interparticle correlations, meaning that structural color in photonic glasses arises from the combination of resonant scattering from the structure and from the individual particles. For blue and green
such as coatings, because all colors can be produced from absorbers makes structural color appealing for applications all other wavelengths. The absence of wavelength-dependent contrast, structural color must arise from resonances that allow particles that absorb the incident and scattered blue light. In consists of strongly scattering particles mixed with pigment introduce a dye that absorbs blue light. However, this is color.

Can this tradeoff be broken? One obvious way is to introduce a dye that absorbs blue light. However, this is how traditional colors are produced; red paint, for example, consists of strongly scattering particles mixed with pigment particles that absorb the incident and scattered blue light. In contrast, structural color must arise from resonances that allow scattering at certain wavelengths to dominate scattering at all other wavelengths. The absence of wavelength-dependent absorbers makes structural color appealing for applications such as coatings, because all colors can be produced from the same materials. Therefore, we pursue a different way to break the tradeoff between angular independence and long-wavelength structural color.

To create a red structural color, we would need to manipulate the resonances from two independent processes: single-particle scattering and coherent scattering from the particle assembly. The characteristic scale for the single-particle scattering resonances is the particle optical diameter \( n_p d \) [Eq. (8)], and for the structural resonances it is the effective interparticle spacing \( n_{\text{eff}} d_{\text{avg}} \) [Eq. (4)]. Our control parameters are therefore the particle diameter \( d \), its refractive index \( n_p \), the interparticle spacing \( d_{\text{avg}} \), and the index of the medium \( n_{\text{med}} \), which determines the effective index \( n_{\text{eff}} \).

Red photonic glasses could be made by tuning these control parameters to blue-shift the second resonance of the form factor into the UV while keeping the peak of the structure factor at long wavelengths. This can be achieved with particles that have a small optical diameter, as shown in Fig. 7. The simplest way to reduce the optical diameter is to use particles with a refractive index smaller than that of the medium. In these inverse glasses, the diameter of the particles is about the same as the spacing between their centers \( d_{\text{avg}} \sim \sqrt{6d}/3 \), but their lower refractive index makes the optical pathlength inside each particle shorter than the optical pathlength between two particles. As a result, the form factor resonances are blue-shifted compared to those of our PMMA colloids of similar size, while the structure factor resonances remain at about the same wavelength.

Another effective way to blue-shift the form factor resonance while not shifting the structural resonance is to decouple the particle size from the interparticle spacing and to use smaller particles as the scatterers. This can be done by packing core-shell particles with a strongly scattering core and a transparent shell. We have already demonstrated that this approach enables the creation of full-spectrum, angle-independent structural pigments [21]. Such pigments still suffer from poor color saturation in the red compared to the blue, but the short-wavelength reflectivity is substantially reduced relative to colloidal glasses made of homogeneous (that is, not core-shell) particles.

One can combine the core-shell and inverse-structure approaches to design a system with a single visible resonance at long wavelengths. In particular, the shell diameter could be chosen such that the interparticle spacing gives rise to a resonance in the red, and the core diameter chosen such that the first-order peak in the form factor boosts the peak from the structure factor, while the second-order form-factor peak is fully in the ultraviolet. Our calculations show that such a structure could be made from core-shell particles with air cores and silica shells, embedded in a silica matrix, as shown in Fig. 9.

Curiously, the photonic structures found in bird feathers resemble these inverse glasses: they often consist of air pockets in a matrix of \( \beta \)-keratin [9,11] that has a refractive index close to that of silica [36]. However, birds do not seem to have taken advantage of their inverse structures for colors other than blue. They rely instead on pigments to acquire yellow, orange, and red colors [11,37]. Whether this is due to a physical effect not accounted for in our model or is the result of evolution or chance remains to be seen.
are not sufficient to understand the reflectivity of photonic glasses. The scattering behavior of their constituent particles plays an equally important—and previously unrecognized—role. In particular, interference of light inside the particles can lead to enhanced scattering at wavelengths other than those related to the interparticle correlations. Our model describes our experimental observations well, and it can be used to guide the design of new photonic glasses with purely red structural color.

To this end, we have shown that it is possible to control the locations of both the single-particle scattering resonances and the structural resonances by tuning the refractive indices, particle sizes, and interparticle distances. Our model predicts that inverse glasses made of core-shell particles with a low-index core and a high-index shell that is index-matched to the medium might produce angle-independent structural red color. If future experiments show that such structures show poor color saturation in the red, these results would suggest that another mechanism, such as multiple scattering, should be accounted for. If successful, these structures would complete the palette of visible colors achievable with photonic glasses, opening the path to their use in practical applications such as long-lasting dyes or reflective displays.

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