Holographic characterization of individual colloidal spheres’ porosities

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Holograms of colloidal spheres recorded through holographic video microscopy can be analyzed with the theory of light scattering to measure individual spheres’ sizes and refractive indexes with part-per-thousand resolution. This information, in turn, can be interpreted to estimate each sphere’s porosity.

INTRODUCTION

Synthetic colloidal spheres play a central role in applications as diverse as catalysis, medical diagnostics, and photonics. Even as many applications advance toward single-sphere implementations, methods for characterizing colloidal spheres typically offer only sample-averaged overviews of such properties as spheres’ sizes and porosities. Moreover, such characterization methods as mercury adsorption porosimetry, nitrogen isotherm porosimetry, transmission electron microscopy and x-ray tomography require preparatory steps that may affect particles’ properties. Here, we demonstrate that holographic video microscopy can meet this need for particle-resolved in situ characterization, and that results of these optical measurements can be interpreted to measure individual spheres’ porosities.

HOLOGRAPHIC PARTICLE CHARACTERIZATION

Our measurements are based on in-line holographic video microscopy [1, 2] in which individual colloidal spheres are illuminated by the collimated beam from a fiber-coupled laser (iFlex Viper) on the stage of an otherwise conventional light microscope (Nikon TE 2000U). Light scattered by a sphere interferes with the unscattered portion of the beam in the focal plane of the microscope’s objective lens (Nikon Plan-Apo, 100×, numerical aperture 1.4, oil immersion). The interference pattern is magnified by the microscope, and its intensity is recorded with a video camera (NEC TI-324AII) at 30 frames/s with a resolution of 135 nm/pixel. The example in Fig. 1(a) shows the hologram of a polystyrene sphere dispersed in water obtained at a vacuum wavelength of \( \lambda = 640 \text{ nm} \).

Each sphere’s image is digitized with a nominal intensity resolution of 8 bits/pixel and analyzed [3, 4] using predictions of the Lorenz-Mie theory of light scattering [5] to obtain the particle’s position in three dimensions [6], its radius, and its complex refractive index [3, 4]. Fig. 1(b) shows the pixel-by-pixel fit to the measured hologram in Fig. 1(a). The microscope is defocused for these measurements so that each sphere’s interference pattern subtends a 100 × 100 pixel field of view. Fits then reliably yield estimates for the adjustable parameters with part-per-thousand resolution [3, 4].

Each data point in Fig. 1(c) represents the result for one sphere and is colored by the relative probability density \( \rho(a_p, n_p) \) for finding spheres of radius \( a_p \) and refractive index \( n_p \). These data were obtained by flowing the aqueous dispersion through a microfluidic channel past the observation volume at a peak speed of 100 \( \mu \text{m/s} \). This is slow enough that motion blurring has no measurable influence on the characterization results [4, 8]. The suspension was diluted with deionized water to the point
that no more than 10 spheres were in the field of view at any time, thereby minimizing overlap between neighboring spheres' scattering patterns. The entire data set was acquired in 5 min.

The spheres’ average radius $a_p = 0.786 \pm 0.015 \, \mu m$ is consistent with the manufacturer’s specification. By contrast, the mean refractive index $n_p = 1.444 \pm 0.007$ is significantly smaller than the value of $n_{PS} = 1.4568$ for fused silica at the imaging wavelength [9]. Similar discrepancies have been reported in previous measurements on dispersions of colloidal silica spheres [10].

The data in Fig. 1(c) also reveal a distinct anticorrelation between radius and refractive index. Such a relationship could not have been detected with bulk probes, such as dynamic light scattering. It suggests that the larger particles in a sample are less optically dense than those on the smaller end of the size distribution.

The data in Fig. 2 further demonstrate that this anticorrelation is not an artifact of the technique, but rather is a common feature of colloidal samples synthesized by emulsion polymerization. Figure 2(a) shows results for a very polydisperse sample of silicone oil droplets (Dow Corning 200 fluid) stabilized with Pluronic L92 surfactant in water. Although the range of particle radii is large, the droplets’ measured refractive indexes all are consistent with the bulk value of $n_p = 1.404 \pm 0.002$ to within the part-per-thousand resolution of the single-particle fits [3, 4]. This is reasonable because the droplets all should be composed of fluid at bulk density. Results for smaller droplets are more strongly influenced by the surfactant [11], which has a bulk refractive index of 1.38. Variation in surfactant coverage thus causes variation in the apparent refractive index. The peak of the probability distribution nevertheless falls within error estimates of the refractive index of bulk silicone oil for all sizes. The lack of covariance between measured radii and refractive indexes in this sample therefore demonstrates the absence of instrumental or analytical bias.

The data in Fig. 2(b) and Fig. 2(c) show additional results for monodisperse aqueous dispersions of colloidal polystyrene spheres (Duke Scientific, catalog number 5153) and colloidal polymethylmethacrylate (PMMA, Bangs Laboratory, catalog number PP04N) spheres, respectively, both synthesized by emulsion polymerization. Like the silica spheres in Fig. 1, both of these samples yield mean refractive indexes significantly lower than bulk values at the imaging wavelength and also display anticorrelations between size and refractive index.

**HOLOGRAPHIC POROSIMETRY**

Chemically synthesized colloidal spheres are known to be less dense than the bulk material from which they are formed [12, 13]. The difference may take the form of voids that can be filled with other media, such as the fluid in which the spheres are dispersed [10]. A sphere’s porosity $p$ is the fraction of its volume comprised of such pores. If the pores are distributed uniformly throughout the sphere on lengthscales smaller than the wavelength of light, their influence on the sphere’s refractive index may be estimated with effective medium theory [14]. Specifically, if the bulk material has refractive index $n_1$ and the pores have refractive index $n_2$ then the sphere’s porosity is related to its effective refractive index $n_p$ by the Lorentz-Lorenz relation [14, 15].

$$p = \frac{f(n_p) - f(n_2)}{f(n_1) - f(n_2)},$$

where $f(n) = (n^2 - 1)/(n^2 + 2)$. Provided that $n_2$ can be determined, Eq. (1) provides a basis for measuring the porosity of individual colloidal spheres in situ.

The value of $n_2$ is readily obtained in two limiting cases. If the suspending medium wets the particle, then it also is likely to fill its pores. In that case, we expect $n_2 = n_m$, where $n_m$ is refractive index of the medium. If, at the other extreme, the particle repels the solvent, then the pores might better be treated as voids with $n_2 = 1$.

An idealized model for single-particle porosity offers a way to distinguish these cases, and thereby to obtain information on the nature of the medium in the sphere’s pores. We model a colloidal sphere as an aggregate of $N$ monomers of specific volume $v$. Assuming a typical sphere to be comprised of a large number of monomers, and further assuming that all of the spheres in a dispersion grow under similar conditions, the probability distribution for the number of monomers in a sphere is given

![Figure 2](image-url)

FIG. 2: (a) Distribution of droplet sizes and refractive indexes for emulsified silicone oil in water. (b) Anticorrelated properties of a monodisperse sample of emulsion polymerized polystyrene spheres in water. (c) Equivalent results for a monodisperse sample of PMMA spheres in water.
by the central limit theorem:

\[ P_N(N) = \frac{1}{\sigma_N} \sqrt{\frac{2}{\pi}} \exp\left(-\frac{(N-N_0)^2}{2\sigma_N^2}\right), \tag{2} \]

where \(N_0\) is the mean number of monomers in a sphere and \(\sigma_N^2\) is the variance in that number.

Were each sphere to grow at its bulk density, its volume would be \(N_v\). Development of porosity \(p\) during the growth process increases the growing sphere’s volume to

\[ V_p = \frac{4}{3} \pi \sigma_p^3 = \frac{vN}{1-p}. \tag{3} \]

The probability distribution for finding a sphere of volume \(V_p\) therefore depends on the porosity:

\[ P_V(V_p|p) = \frac{1-p}{\sigma_V} \sqrt{\frac{2}{\pi}} \exp\left(-\frac{(V_p(1-p) - N_0v)^2}{2\sigma_V^2}\right), \tag{4} \]

where \(\sigma_V = v\sigma_N\).

If the porosity develops uniformly as a particle grows, then the probability distribution \(P_p(p)\) of particle porosities will be independent of size. In that case, the joint probability

\[ P(V_p, p) = P_V(V_p|p) P_p(p) \tag{5} \]

may be factored into a term that depends only on porosity \(p\) and another that depends only on the rescaled volume \(V_p(1-p)\).

Within the assumptions of this model, the correct choice for \(n_2\) should decorrelate the rescaled volume \(V_p(1-p)\) and the porosity \(p\). We therefore select the value of \(n_2\) for which the Pearson’s correlation coefficient between \(p\) and \(V_p(1-p)\) vanishes. The scatter plots in Fig. 3 show the distribution of particle volumes and porosities obtained with these optimal values of \(n_2\). The upper plots show estimates for \(P(V_p|p)\) obtained by integration over \(p\), together with fits to the anticipated Gaussian form. Agreement is good enough in all three cases to justify the use of Eq. (4) to interpret the experimental data.

The results for the silica sample in Fig. 3(a) were obtained using \(n_1 = 1.4568\) for fused silica [9]. The estimated value of \(n_2 = 1.31 \pm 0.03\) is consistent with the value of 1.3324 for water at the imaging wavelength [16]. This suggests that pores in the hydrophilic silica spheres are filled with water. The associated mean porosity, \(p = 0.092 \pm 0.004\), is comparable to the 8 percent porosity determined by low-temperature nitrogen adsorption for similar samples [17].

The equivalent results for the polystyrene sample in Fig. 3(b) were obtained using \(n_1 = 1.5866\) for bulk polystyrene [18–20]. In this case, the estimated value of \(n_2 = 1.13 \pm 0.05\) is substantially smaller than the refractive index of either water or styrene. Rather than solvent-filled voids, the pores in the spheres seem rather to represent density fluctuations in the cross-linked polymer matrix. The failure of water to invade these pores is consistent with the hydrophobicity of polystyrene. With these choices for \(n_1\) and \(n_2\), the sample-averaged porosity is estimated to be \(p = 0.054 \pm 0.008\).

More surprisingly, the results for water-borne PMMA spheres plotted in Fig. 3(c) yield \(n_2 = 1.33 \pm 0.01\), and therefore suggest that the spheres’ pores are filled with water, even though PMMA is hydrophobic. The porosity, \(p = 0.02 \pm 0.01\), estimated using \(n_1 = 1.4887\) for bulk PMMA, is comparable to previously reported values for similar spheres [21]. Whereas the polystyrene spheres appear to exclude water, the substantially less porous PMMA spheres seem to imbibe it. These observations suggest either that the two samples have substantially different pore morphologies, or else that hydrophilic groups are present within the pores of the PMMA sample.

Values obtained for single-particle porosities should be interpreted with care. Our model assumes that a particles’ pores are distributed uniformly and have uniform optical properties. Departures from these assumptions will have little effect on the precision of the porosity estimates, which is governed by the precision of the measurement for \(n_p\). Rather, they give rise to systematic errors. Similarly, uncertainty in the values for \(n_1\) and \(n_2\) contribute to systematic offsets in \(p\) through Eq. (1). The precision of the porosity distributions in Fig. 3 therefore need not guarantee their accuracy.

**CONCLUSIONS**

We have shown that correlations in the radii and refractive indexes of colloidal spheres measured through holographic particle characterization [3, 4] can be ascribed to porosity. Holographic characterization, therefore, can be used to assess the porosity of individual colloidal spheres and to gain insight into the medium filling their pores.

The present implementation uses sample averages to infer the refractive index of the medium filling the individual spheres’ pores. Given this parameter, the porosity can be estimated for each sphere individually. The need to aggregate data from multiple particles could be eliminated by performing holographic characterization measurements in multiple wavelengths simultaneously. The resulting spectroscopic information, in principle, could be used to characterize both the porosity of a single sphere and also the medium filling its pores in a single snapshot.

Particle-resolved porosimetry probes the mechanisms by which porosity develops in samples of emulsion-polymerized colloidal spheres. For the samples we have studied, porosity appears to have developed uniformly as the particles grew, both within individual spheres, and
throughout the sample as a whole. Differences between results for polystyrene and PMMA samples point to possible differences in the shapes or properties of their pores. These observations, in turn, have ramifications for possible uses of emulsion polymerized colloidal particles in such applications as catalysis, bead-based medical diagnostics and colloidal photonics.

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