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Transmission and diffraction by photonic colloidal crystals

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Abstract. We have performed optical transmission and synchrotron small-angle x-ray scattering (SAXS) experiments on colloidal crystals with optical refractive index ratios as large as possible over a wide range of volume fractions. These conditions push colloidal crystals into the regime where strong coupling of photonic crystals with light occurs. The optical transmission spectra reveal minima corresponding to stop gaps on the edges of the Brillouin zone of the photonic band structures. The positions of the optically measured stop gaps agree well with lattice spacings measured by SAXS. The stop gap in the 111 direction of crystals of polystyrene in water has a width of up to 5% of the gap frequency as a function of volume fraction, in agreement with theoretical band-structure calculations. A maximum of the relative width confirms the notion that the strength of the interaction between photonic crystals and light has an optimum as a function of volume fraction. The detailed structural information from SAXS data greatly assists in the interpretation of optical experiments on photonic crystals.

Advances in colloid science have made it possible to fabricate crystalline arrays with lattice parameters comparable to the wavelength of visible light [1]. Light travelling through such crystals experiences a periodic variation of the refractive index, analogous to the periodic potential energy of an electron in an atomic crystal [2]. Therefore, the dispersion relations may be described by photonic band structures in Brillouin zones in reciprocal space (figure 1), and the crystals are called ‘photonic’. The variation of the refractive index causes a splitting of the bands at the edges of the Brillouin zone (cf. figure 1). These stop gaps appear as minima in the transmission and give rise to Bragg scattering [3]. The coupling strength between light and a photonic crystal can be expressed by a parameter Ψ defined as the ratio of the optical volume per particle—the polarizability—to the physical volume per particle [4]. An exciting physical situation arises if the stop gaps overlap in all directions [5]: a complete photonic band gap appears [6], that may be used to localize light or inhibit spontaneous emission [7].

Several optical experiments have already been reported on weakly photonic colloidal crystals ($\Psi < 0.05$); see reference [8]. In particular, Tarhan and Watson [9] have resolved the stop bands and the dispersion curves in a colloidal single crystal. The strength of coupling Ψ between light and photonic crystals can be increased by using colloids with a higher refractive index and by raising the volume fraction ϕ of the particles. Colloidal particles with a high refractive index that are monodisperse enough to crystallize are currently being developed [10]. The effect of increased ϕ has been investigated in optical diffraction experiments on colloidal crystals with refractive index ratios m of the particles and the medium of up to 1.45, and $\Psi < 0.6$ [4]. It was found that the photonic band structures result in *apparent* Bragg spacings that strongly depend on the wavelength of

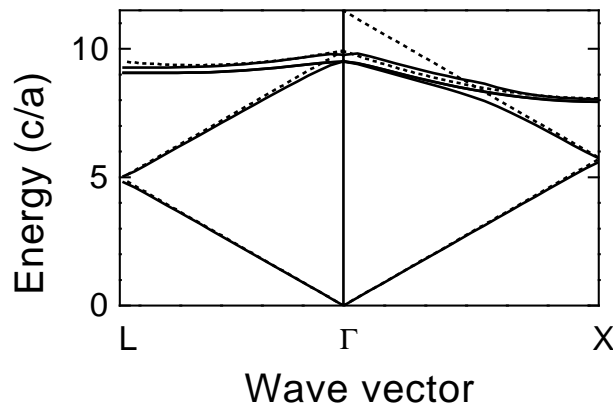


Figure 1. Photonic band structures calculated with the plane-wave method [17] in the X (100) and L ($\frac{1}{2}\frac{1}{2}\frac{1}{2}$) directions of an fcc crystal with about 50 vol% spheres (dots). The refractive index ratio $m = 1.20$ corresponds to $\Psi = 0.2$ and pertains to polystyrene in water or methanol. The full curves indicate the results for the first five bands. The dotted lines are the approximate bands that result when using the Maxwell-Garnett averaged refractive index.

light. It was found that the dynamical diffraction theory [11] breaks down because it only holds for low photonic strengths. Two improved simple models were presented [4]: first, Bragg's law combined with linear dispersion curves using an refractive index averaged by effective-medium theory, and second, a model of periodically stratified dielectric layers. In this contribution, we investigate the effects of volume fraction on the transmission of colloidal crystals, whose structure and orientation was determined by small-angle x-ray scattering (SAXS). To our knowledge, this is the first direct comparison between photonic band-structure calculations and experiments on photonic crystals in the optical regime.

We have grown colloidal crystals from polystyrene and silica particles with radii r between 100 and 220 nm, suspended in water, methanol, ethanol, or dimethylformamide [12]. Crystals with $\phi > 50$ vol% were made by sedimentation under gravity. Crystals with lower volume fractions were made by deionizing the particles with resin (BioRad AG501-X8) and adding resin to the capillaries. Optical transmission measurements were done with a BioRad FTS60 spectrometer using a Xe lamp. Knowledge of the crystal structure and orientations is essential to interpret the optical experiments. Therefore, we have also performed SAXS experiments because they probe a much wider range in reciprocal space than optical diffraction, which considerably facilitates structure identification. Moreover, the interpretation of SAXS is not hampered by multiple-scattering effects [4]. The use of a synchrotron beam [13] proves to be a key asset, because the beam can be focused to a small spot, while retaining enough flux to keep collection times reasonable [14].

A plot of optical transmission versus wavenumber is shown in figure 2 for a $\phi \approx 50$ vol% polycrystalline sample of $r = 99$ nm polystyrene spheres in methanol. With increasing frequency, the transmission decreases until a minimum appears at about $18\,200\text{ cm}^{-1}$. This minimum corresponds to a wavelength of 550 nm for Bragg diffraction in back scattering. It is associated with the stop gap in the L point of the Brillouin zone of fcc crystals (111 direction), that are oriented with the close-packed lattice planes parallel to the windows. The low transmission beyond the stop gap is caused by crystallites that have different orientations. With increasing height, the volume fraction is expected to decrease in sedimented samples [15]. Therefore, we have measured transmission spectra as a function

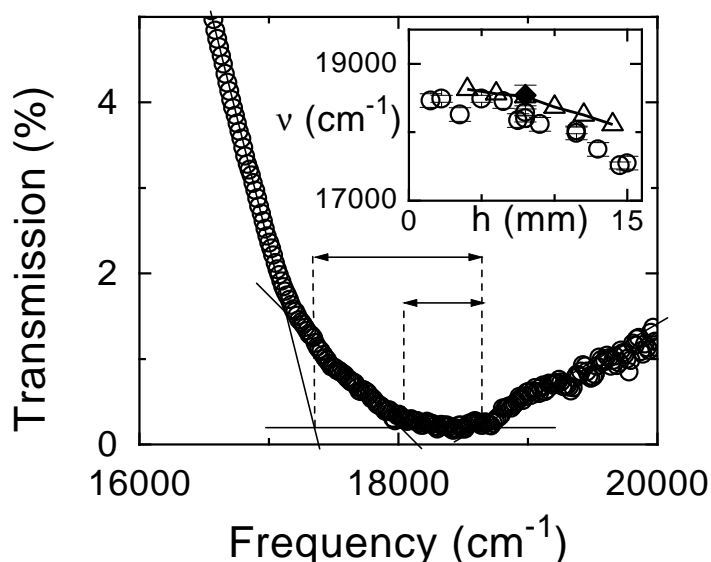


Figure 2. The optical transmission curve as a function of energy in a sedimented colloidal crystal of $r = 99$ nm spheres in methanol (circles). The spectra were referenced to the supernatant liquid or empty capillaries. The estimates for the width of the stop gap, using straight-line approximations for the transmission, are indicated. The inset shows the centre energy of the L gap versus height in this particular sample. The open circles are optical transmission measurements. The filled triangles indicate gap energies calculated from twice the 111 spacing (measured by SAXS) times the Maxwell-Garnett averaged refractive index. The full diamond with an error bar is a from similar calculation, but using the optically measured lattice spacing [4]. Note that the 111 lattice spacing is the only one that can be accessed optically. In contrast, synchrotron SAXS yields many more spacings, which demonstrates the power of this technique.

of height in the samples. Figure 2 (inset) shows indeed that the optical frequency decreases with increasing height. The L-gap frequencies are expected to be equal to 2 times the $hkl = 111$ lattice spacing, multiplied with the refractive index of the crystal. By using the SAXS data for the spacings and the Maxwell-Garnett effective-medium refractive index, we obtain good agreement. The good agreement between the two data sets confirms that the Maxwell-Garnett averaged refractive index is a good approximation for low-lying bands in the band structure (compare also figure 1).

We now turn to the width of the optical stop gaps. In figure 3, we have plotted the relative widths of the L gap versus ϕ for crystals of polystyrene particles in water (index ratio $m = 1.20$). The gap width increases because the photonic strength increases with the density of scatterers, to $\approx 5\%$ at $\phi \approx 40$ vol%. Beyond $\phi \approx 40$ vol%, the width is about constant or slightly decreasing. A decrease is expected for large ϕ , because in the limit where $\phi = 1$ there is no more scattering, and hence the width of the stop gaps is zero. The error bars of the experimental data are attributed to disorder in the colloidal crystals, which causes smearing of the band edges [16]. The full curve in figure 3 is the result of band-structure calculations [17]. The curve increases to 4.6% at $\phi = 35$ vol%, in agreement with the experimental data. As expected, the theoretical width decreases at higher volume fractions. The observation of a maximum width as a function of ϕ confirms earlier suggestions that a photonic strength parameter has an optimum as a function of ϕ

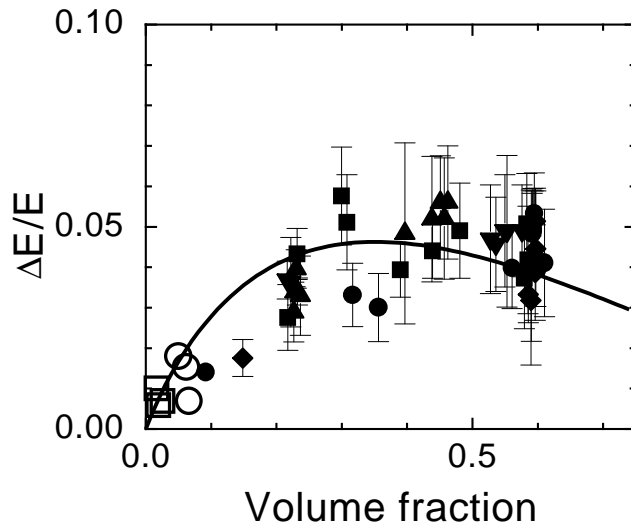


Figure 3. The width of the stop gaps divided by the energy of the L gap as a function of volume fraction for crystals of polystyrene spheres in water or methanol ($m = 1.20$). The open symbols at low volume fractions are taken from the literature [8, 9]. The filled symbols are our results for many different samples. The bars indicate the errors on the gap widths, estimated by taking different guesses for the widths as indicated in figure 2.

[18, 4]. A photonic strength parameter that incorporates this effect will be discussed in a future publication.

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