



Characterization of internal order of colloidal crystals by optical diffraction

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Abstract. We report the results of the optical characterization of photonic crystals consisting of close-packed arrays of polymeric monodispersed microspheres. The excellent agreement of the diffraction peak wavelengths with Bragg's law enables a precise determination of the sphere diameter. Optical diffraction is used to assess the quality of the internal order of colloidal crystals and to identify optimum growth conditions. This work leads to an estimate of the average free propagation distance of light, which is limited by incoherent scattering due to lattice imperfections, of up to 30 lattice constants.

Key words: colloid, optical diffraction, oscillatory shear, photonic crystal

1. Introduction

A great deal of attention has recently been devoted to colloidal crystals made of monodispersed silica or polymer spheres for use as photonic crystals (Busch and John 1998; Blanco *et al.* 2000). In these materials, the photonic lattice composing the photonic crystal is realized by a close-packed ordered array of identical microspheres. By infiltrating the voids between the spheres with a high-index material, it is possible to obtain a full photonic band gap. Many potential applications have been proposed for photonic crystals, such as optical limiters and switches (Scalora *et al.* 1994; Pan *et al.* 1997).

The main advantage of colloidal crystals over other structures that are fabricated by photolithographic or similar techniques is their ease of fabrication, since the array of spheres is self-assembled. However, this brings a strong requirement for detailed characterization of the internal structure of these materials; furthermore, the impact of naturally occurring internal disorder on the optical properties of the photonic crystal must be studied and understood. This disorder comes either from anomalies of individual spheres or, more likely, from mispositioned spheres that break the perfect spatial periodicity of the photonic lattice. It is expected that the optical behavior of photonic crystals will depend strongly on the quality of internal order (Li *et al.* 1997; Koenderink *et al.* 2000).

Characterization can be accomplished in two ways: by direct observation using electron microscopy (Astratov *et al.* 1996; Míguez *et al.* 1997a) or confocal optical microscopy (Kalinina and Kumacheva 1999), or by observing optical or X-ray diffraction produced when the sample is illuminated by monochromatic radiation. This presents an interesting analogy with atomic crystals that can be characterized either by direct observation with transmission electron microscopy, or by X-ray or electron diffraction techniques.

Optical diffraction is simple, non-destructive and could be realized *in situ* during growth of the colloidal crystal. Ultra-small angle X-ray scattering (USAXS) is also a powerful technique (Vos *et al.* 1997), but is not as readily implemented. Most importantly, optical studies probe the properties that will lead directly to the realization of useful devices. Most of the work already published on the subject reports measurement of the optical transmission through a slab of photonic crystal (Astratov *et al.* 1996; Liu *et al.* 1997; Míguez *et al.* 1997b; Tarhan and Watson 1998; Wijnhoven *et al.* 1998; Park and Xia 1999; Vlasov *et al.* 2000); the results typically show important drops in the transmission for wavelengths corresponding to the stop bands. The reflection coefficient at normal incidence has also been measured, and found to complement well the transmission curves (Astratov *et al.* 1996). At the same time, the impact of disorder in colloidal crystals has been observed and quantified (Koenderink *et al.* 2000) using the enhanced backscattering method, permitting quantification the photon mean free path in the crystal.

In this report, we show that much critical information can be extracted from diffraction spectra, more than has been accomplished in the past. We have measured lattice constants of colloidal crystals with unprecedented accuracy and obtained information about the crystal surface geometry. Diffraction spectra, in conjunction with a simple model that considers the impact of lattice disorder on the reflectance, also provide an estimate of the photon mean free path, which constitutes a quantitative measure of the degree of internal disorder. Finally, we demonstrate how optical diffraction can be used to determine the optimum fabrication conditions for colloidal crystals.

2. Theory

In Bragg's theory of X-ray diffraction (Azároff 1968) light is diffracted by different crystallographic planes of atoms, each set of parallel planes bearing a set of Miller indices (hkl). The incident and diffracted beams form equal but opposite angles with the normal to the plane, even though the lattice plane is

not required to be parallel to the sample surface. In colloidal crystals, this situation is slightly modified: refraction of the beam at the surface of the sample must be taken into account. Combining Snell's law and Bragg's law, we obtain a relation between wavelength, λ , and the incidence angle, θ :

$$\lambda = \frac{2d_{hkl}}{m} \sqrt{n_{\text{eff}}^2 - \sin^2 \theta} \quad (1)$$

d_{hkl} is the distance between two diffracting (hkl) planes, m is the diffraction order, and θ is the angle between the incident beam and the normal to the plane, that is, the complement of the glancing angle. An effective refractive index is used (Yannopapas *et al.* 1997), given by

$$\frac{n_{\text{eff}}^2 - 1}{n_{\text{eff}}^2 + 2} = \varphi \frac{n_{\text{spheres}}^2 - 1}{n_{\text{spheres}}^2 + 2} \quad (2)$$

where φ is the volume filling fraction, which is 0.74 in a close-packed array of hard spheres. This treatment neglects the small corrections from the dynamical theory of diffraction (Liu *et al.* 1997).

We distinguish two classes of measurements, depicted in Figs. 1(b) and 2(b). In symmetric measurements, the planes probed are parallel to the sample surface; this situation corresponds to specular reflection from the sample. These measurements yield information on the distance separating the lattice planes normal to the surface, but not on the positions of the spheres within these planes. On the other hand, asymmetric measurements

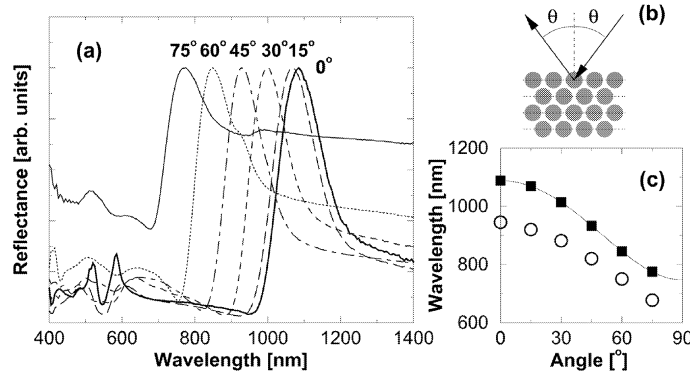


Fig. 1. Symmetric diffraction by colloidal crystals containing 500 nm diameter spheres. (a) Diffraction spectra for six different angles of incidence. The first- and second-order diffraction peaks are clearly seen. (b) Measurement configuration. (c) Angular dependence of the peak wavelengths on angle of incidence. The squares are the measured wavelengths while the solid line follows Bragg's law; the quality of the fit at every point is better than 1%. The circles are the measured wavelengths corresponding to reflectance minima.

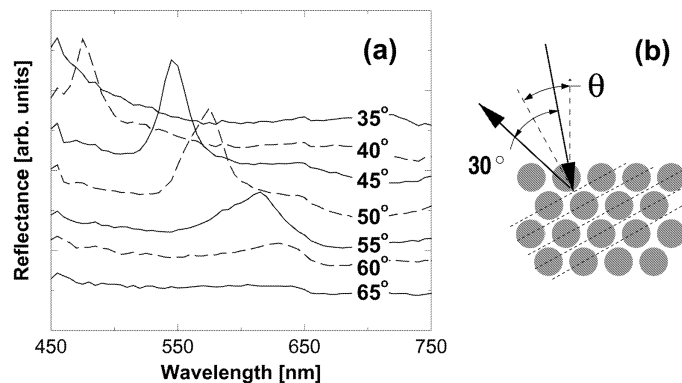


Fig. 2. Asymmetric diffraction by sample containing 400 nm spheres. (a) Diffraction spectra for seven different angles of incidence. (b) Measurement configuration; the incident and exit beams are kept 30° apart.

probe crystallographic planes not parallel to the surface and permit characterization of the lattice in directions along the crystal surface. Asymmetric measurements are commonly used to measure the presence of lattice strain in atomic crystals (Azároff 1968).

3. Experiment

The details of sample preparation are described by Kalinina and Kumacheva (1999). Poly(methyl methacrylate) latex particles with polydispersity index 1.03 were synthesized by emulsion polymerization and subsequently settled under controlled oscillatory shear to produce 3D close-packed arrays, which are then dried. Samples containing spheres of 300, 400 and 500 nm, as determined by electron microscopy, were fabricated. The 2 mm thick samples are not transparent to visible radiation, thus, optical diffraction experiments were carried out in a reflection mode.

Our setup consists of a tungsten–halogen lamp coupled to a monochromator. The light beam exiting the monochromator is collimated by a lens (less than 2° divergence) and passes through a polarizer and an aperture before reaching the sample, which is mounted vertically on a horizontal rotating stage. An optical detector collects the light that is transmitted, reflected or diffracted by the sample at any angle.

Scanning electron micrographs of our colloidal crystals (Vickreva *et al.* 2000) show several crystallographic planes of the {111} family, characteristic of a fcc lattice, one of them defining the crystal surface. This is consistent with what is generally observed in colloidal crystals (Míguez *et al.* 1997b). Thus, symmetric optical studies will always probe diffraction by (111) planes.

Fig. 1 show typical symmetric reflection spectra measured at various angles of incidence on samples containing 500 nm diameter spheres. The polarization of the incident light is perpendicular to the plane of incidence. The primary feature of the spectra is the 111 diffraction peak centered at 1085 nm for normal incidence; it is associated with the first-order stop bands in the L direction. The peak moves to shorter wavelengths as the incidence angle is increased. At normal incidence, the diffraction peaks have a full width at half maximum (FWHM) of approximately 157 nm (14%); this figure stays approximately constant as the incidence angle is changed. A similar analysis on samples containing 300 and 400 nm spheres yielded similar spectra, with peaks centered at 648 and 918 nm, with FWHM of 54 and 76 nm respectively (8% for both). The width of these diffraction peaks results from strong interaction between the light and the lattice, limiting the light penetration depth to relatively few lattice constants, relaxing the conditions for constructive interference of the diffracted beams. For comparison, the plane-wave expansion method (Busch and John 1998) predicts a stop band in the L direction with a width of 5.8% of the center frequency for a fcc close-packed lattice made of hard spheres ($n = 1.5$) surrounded by air. A zero of reflectivity is also found close on the short-wavelength side of this peak; this feature is associated with complete destructive interference by the waves reflected by both sides of a single layer of spheres and can be interpreted as a Mie resonance. The ratio of the peak to the minimum reflectance reaches 200 in the best case.

The second-order stop band manifests itself with another peak appearing at 522 nm at normal incidence, at close to half the wavelength of the primary peak. Its position also moves towards shorter wavelengths as the angle is increased. However, this diffraction exhibits a complex structure with a second peak present at a longer wavelength, at 583 nm, with a pronounced dip in between; this second peak moves towards longer wavelengths as the incidence angle is increased. This structure seems to be associated with Mie resonances and cannot be explained by Bragg diffraction alone.

Fig. 1c also shows the dependence of the wavelength corresponding to peak intensity on incidence angle for the 500 nm sample. The wavelength corresponding to the reflection minimum is also shown. Despite the breadth of the diffraction peaks, their regular shape permits an easy identification of the intensity maximum, corresponding to the center position of the peak. The experimental data were fit to Equation (1) to determine precisely the sphere diameter and the effective index. All measured peak wavelengths fall within 1% of the predicted values. The sphere diameter was found to be 485 nm, a value consistent with measurements performed using scanning electron microscopy that have a precision of about 10%. The effective refractive index obtained from the fit is 1.38. The refractive index of bulk PMMA, synthesized under identical conditions, was measured to be 1.491, which yields an

effective refractive index of 1.348. The small difference could be due to the fact that the field is mostly localized to the spheres at this resonance. A similar analysis on the other samples also yields a good agreement between theory and experiment and gives sphere diameters of 287 and 405 nm and the same index of 1.38. The measurements permit precise determination of both the sphere diameter and the effective refractive index within 1 nm and 1% respectively, considering the quality of the fit to Bragg's law.

The asymmetric diffraction produced by crystallographic planes not parallel to the surface was also studied. The measurements are conducted with the incident and exit beams fixed at 30° from each other and the bisector forming an angle ranging from $\theta = 35^\circ$ to 65° with the normal to the crystal surface. The 220 diffraction peak is expected to be seen at an angle of 45° (once refraction at the surface is considered) and only at that angle. In Fig. 2, however, diffraction peaks clearly appears at several angles. This can be explained by assuming that only a few layers of spheres contribute to the diffracted beam, so that there is incomplete destructive interference at other angles. Incoherent scattering is the likely cause of the low depth of penetration of light in the sample at the grazing angles considered here, and will be discussed in the following section. The wavelengths associated to the peaks here fit Bragg's law for a surface grating with a period of 375 nm, slightly in excess of the distance of 350 nm expected between rows of 405 nm close-packed spheres; this could be due to lattice deformation at the surface, where the spheres could not be as closely packed as in the bulk. The fact that the diffracted light originates only from the surface opens the interesting possibility that the surface structure could be studied in isolation, in a manner similar to what is accomplished by low-energy electron diffraction (LEED) for atomic crystals. The properties of photonic crystals surfaces are of great importance in many devices – photonic waveguides for example – as light often remains confined to the close vicinity of surfaces.

4. Impact of internal disorder

We have used symmetric optical probing to quantify the quality of internal ordering of a series of samples grown under different experimental conditions, that is, when different regimes of controlled oscillatory motion are applied during the settling stage of the latex dispersion. A dimensionless acceleration ratio $\Gamma = A \omega/g$ was used as a measure of the intensity of the lateral vibrations, where ω is the angular frequency, A is the amplitude of the displacement, and g is the acceleration due to gravity. The spectra measured on samples grown in five different regimes are shown in Fig. 3; the comparison requires that spectra be normalized to remove any effect of small optical misalignments. This was done by assuming that the diffracted in-

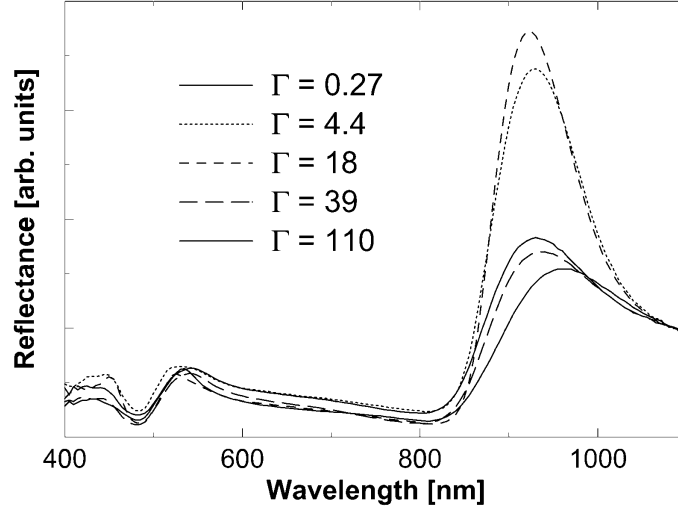


Fig. 3. Effect of oscillatory motion on the measured symmetric diffraction spectrum. Each curve denotes a sample grown with the acceleration ratio Γ given in the legend. The peak diffracted power quantifies the internal quality of the sample.

tensity is the same for all samples far from the diffraction peaks. This procedure is justified by the modeling work presented below. The sample grown at $\Gamma = 18$ exhibit the highest diffraction peaks. It is expected, and demonstrated below, that sharper and more intense diffraction peaks are associated with a higher quality of internal order. Thus, optical diffraction provides a simple way of identifying optimum conditions for the growth of colloidal crystals. We are currently investigating in depth the effect of oscillatory shear on colloidal crystal growth with this technique.

In order to interpret the diffraction data, most importantly of the impact of disorder, we have developed a simple model capable of explaining many of the features of diffraction spectra. The model computes the reflectance of a one-dimensional periodic stack of optical layers of alternating compositions. The refractive indices are taken to be those of air and the polymer (1 and 1.5 respectively), and the thicknesses were chosen to fit the position of the peak and the dip in the experimental spectra measured at normal incidence. The reflectivity of this stack can be solved analytically with the well-established transfer-matrix method (Yeh 1988). Fig. 4(a) shows the reflectivity of such a structure with various degrees of optical attenuation present in the stack.

At all frequencies lying inside the stop band of a photonic crystal, reflectance in the absence of attenuation should be very close to unity for thick samples. A flat top has never been reported, however, for peaks in measured reflectance spectra of colloidal crystals. This should be interpreted as a manifestation of the disorder inherent in these structures: because light no longer propagates in a perfectly periodic lattice, it will undergo incoherent

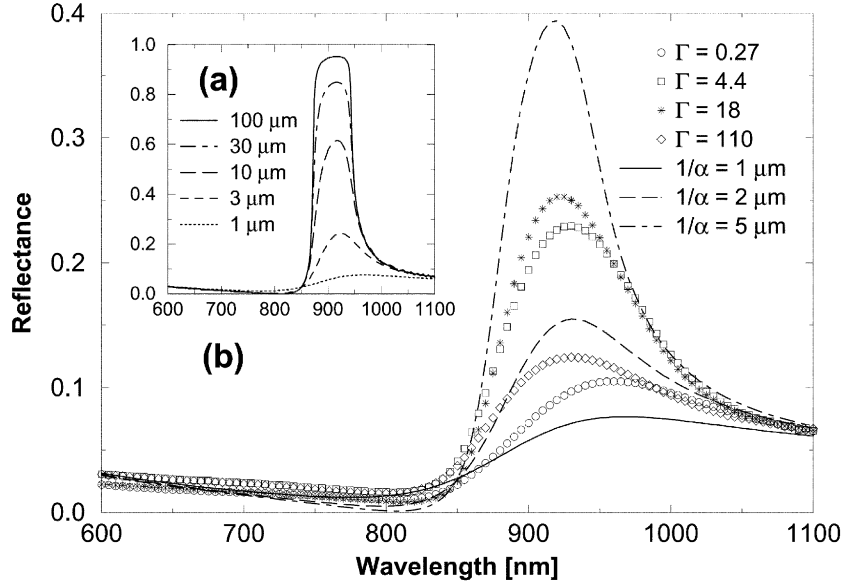


Fig. 4. Comparison of model and experimental data. (a) Reflectance computed with the model as a function of wavelength for different attenuation lengths. (b) The diffraction spectra measured on four samples grown under different conditions are compared to theoretical reflectance for three different attenuation lengths. The attenuation length is interpreted as a photon mean free path

scattering and be attenuated as it propagates inside the crystal. The scattered light is neither transmitted directly nor reflected back towards the detector; this is accounted as linear attenuation in the model. The attenuation length is then interpreted as a photon mean free path. Other ways of incorporating the effect of lattice disorder in the model, such as partially randomizing the thicknesses of the layers of the stack, yield results that are inconsistent with experimental results. As is seen in Fig. 4(a), when optical attenuation is introduced in the model, the reflectance peaks are rounded and the overall spectra resemble experimental results.

The experimental results and those obtained with the model are compared in Fig. 4(b). We must exercise caution in using a one-dimensional model to assess the diffraction spectra of a three-dimensional structure: physical quantities derived from this comparison are approximate and principally of heuristic value. This comparison nevertheless provides much insight into the optical properties of colloidal crystals. In Fig. 4, the experimental spectra are normalized to the reflected intensity away from the peak; at these wavelengths, the model shows that the reflectance is independent of the attenuation length. From this comparison, we obtain an estimate for the photon mean free path in the real samples varying between 1.5 and 4 μm , that is, between 3 and 12 lattice constants. Of all other samples analysed, the longest free propagation length was found to be 30 lattice constants. Koenderink

et al. (2000) used the backscattering method to find a photon mean free paths of 15- μm or about 35 lattice constants. This number is a critical figure: in any device based on colloidal crystals, it is imperative that photons be reflected by the photonic lattice before they undergo incoherent scattering by lattice imperfections. This establishes limits to the size of devices in which light propagates through a photonic crystal and may also provides design guidelines for the geometry of such devices.

5. Conclusion

In this work, we have used optical diffraction to obtain valuable information about internal photonic crystalline structure. Optical diffraction is first used to determine with a high degree of precision the particle diameter and the refractive index of colloidal crystals from measurement of the center position of the diffraction peaks. For the first time, asymmetric diffraction is studied and is shown to reveal details of colloidal crystal surface morphology; surface effects are expected to be of paramount importance in devices such as photonic crystal waveguides. Finally, and most importantly, optical diffraction provides a means to study the impact of lattice disorder on the optical properties of photonic crystals. In addition to enabling identification of optimum conditions for the growth of the colloidal crystals, it provided an estimate of the photon mean free path, in the range of 3–30 lattice constants. This figure, obtained with the help of a simple model, is confirmed by the low depth of penetration observed in asymmetric diffraction measurements realized at grazing angles. This parameter is very important as it will dictate guidelines for the design of photonic devices based on colloidal crystals. At this point, it is important to note that disorder will be present in some extent in any photonic crystal. It can either come from mispositioning of the elemental lattice units, as it is the case in colloidal crystals, but also from dissemblances from one unit to another, which, unlike in atomic crystals, are no longer guaranteed to be identical. In these circumstances, the impact of lattice disorder must be considered when envisaging the promising device applications of any type of photonic crystals. Optical diffraction, combined with advanced simulations, will play a key role in the design of these devices and in assessing, improving, and tailoring their optical characteristics.

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References

- Astratov, V., Yu.A. Vlasov, O. Karimov, A. Kaplyanskii, Y. Musikhin, N. Bert, V. Bogomolov and A. Prokofiev. *Phys. Lett. A* **222** 349, 1996.
- Azároff, L.V. *Elements of X-ray Crystallography*, McGraw-Hill, New York, 1968.
- Blanco, A., E. Chomski, S. Grachtak, M. Ibisate, S. John, S.W. Leonard, C. López, F. Meseguer, H. Míguez, J.P. Mondia, G.A. Ozin, O. Toader, et al. *Nature* **405** 437, 2000.
- Busch, K. and S. John. *Phys. Rev. E* **58** 3896, 1998.
- Kalinina, O. and E. Kumacheva. *Macromolecules* **32** 4122, 1999.
- Koenderink, A.F., M. Megens, G. van Soest, W.L. Vos and A. Lagendijk. *Phys. Lett. A* **268** 104, 2000.
- Li, H., B. Cheng and D. Zhang. *Phys. Rev. B* **56** 10734, 1997.
- Liu, L., P. Li and S. Asher. *J. Am. Chem. Soc.* **119** 2729, 1997.
- Míguez, H., F. Meseguer, C. López, A. Mifsud, J. Moya and L. Vázquez. *Langmuir* **13** 6009, 1997a.
- Míguez, H., C. López, F. Meseguer, A. Blanco, L. Vázquez and R. Mayoral. *Appl. Phys. Lett.* **71** 1148, 1997b.
- Pan, G., R. Kesavamoorthy and S. Asher. *Phys. Rev. Lett.* **78** 3860, 1997.
- Park, S. and Y. Xia. *Langmuir* **15** 266, 1999.
- Scalora, M., J.P. Dowling, C.M. Bowden and M.J. Bloemer. *Phys. Rev. Lett.* **73** 1368, 1994.
- Tarhan, I.I. and G. Watson. *Phys. Rev. Lett.* **76** 315, 1998.
- Vickreva, O., O. Kalinina and E. Kumacheva. *Adv. Mat.* **12** 110, 2000.
- Vlasov, Yu.A., M. Deutsch and D.J. Norris. *Appl. Phys. Lett.* **76** 1627, 2000.
- Vos, W.L., M. Megens, C.M. van Rats and P. Bosecke. *Langmuir* **13** 6004, 1997.
- Wijnhoven, J.E.G.J. and W.L. Vos. *Science* **281** 802, 1998.
- Yannopoulos, V., N. Stefanou and A. Modinos. *J. Phys.: Cond. Matt.* **9** 10260, 1997.
- Yeh, P. *Optical Waves in Layered Media*, Wiley, New York, 1988.