

Temperature-controlled random laser action in liquid crystal infiltrated systemsDiederik S. Wiersma^{1,*} and Stefano Cavaleri^{1,2}¹*European Laboratory for Non-Linear Spectroscopy and Istituto Nazionale per la Fisica della Materia, Via Nello Carrara 1, 50019 Sesto Fiorentino (Florence), Italy*[†]²*Department of Physics, University of Florence, Via Sansone 1, Sesto Fiorentino (Florence), Italy*

(Received 30 May 2002; published 26 November 2002)

We study an amplifying disordered dielectric material of which the scattering strength can be controlled externally via temperature. Such a system was realized by infiltrating liquid crystal and laser dye inside sintered glass powders. The random laser materials that were obtained this way can be brought below or above threshold by small changes in environment temperature, and the bandwidth of its emission can be tuned. We will go into the experimental details and the technical aspects of the realization of these systems, and show measurements on the diffusion constant and spectral properties of the emission.

DOI: 10.1103/PhysRevE.66.056612

PACS number(s): 42.25.Dd, 42.55.Ah, 42.70.Hj, 42.70.Df

I. INTRODUCTION

There exist fascinating analogies between the transport of light in complex disordered structures and electron transport in (semi)conductors [1]. An example of this is the diffusion of electrons in a resistor, which gives rise to Ohm's law of conductance. The optical analogy here is the diffusion of light in a disordered dielectric like a dense colloidal suspension of microspheres or a white powder, which obeys a conductance law that is similar to Ohm's law [1]. Other important examples of optical analogies of electron transport phenomena are Anderson localization of light [2], the photonic Hall effect [3], optical magnetoresistance [4], and universal conductance fluctuations of light [5].

We will concentrate here on disordered dielectric materials in which the transport of light can be described as a diffusion process. Of particular interest in that context are disordered dielectrics that are optically active in the sense that they not only scatter light but also amplify it via stimulated emission [6]. Such materials can be realized by powdering a laser crystal [7] or by introduction of laser dye in various random media [8]. If the total gain inside such amplifying random media becomes larger than the losses through the boundaries, the system goes above threshold and exhibits emission properties that are similar to those of a laser. It was shown, for instance, that the emission of an amplifying disordered dielectric above the threshold is narrow banded [8] and can exhibit laser spiking [7]. Such a system is now often referred to as a random laser [7–10]. Theoretical studies show that a random laser source has interesting photon statistics that are neither those of a regular laser nor those of a common light bulb [11]. Recent experiments on zinc-oxide powders aimed at combining random laser action with Anderson localization effects [12,13].

A crucial parameter in all multiple light scattering experiments is the scattering strength of the material expressed as the photon diffusion coefficient or scattering mean free path (average distance between successive scattering events). The

smaller the diffusion coefficient of a material, the stronger is its scattering strength. In many experimental studies, one would like to vary the scattering strength of a sample without modifying its other properties.

We have found a simple way to obtain external control over the diffusion constant of a random sample. Our technique is based upon an idea of Busch and John, who proposed to use a liquid crystal to influence the optical properties of photonic band gap materials [14]. Liquid crystals go through various partially ordered phases when heated and their index of refraction is different in every liquid crystal phase. Of special interest is the nematic phase due to its birefringence (the index of refraction depends on the direction of polarization), which disappears when the liquid crystal is heated into the isotropic phase [15]. By infiltrating a random sample with a liquid crystal, one can obtain a system in which the diffusion constant depends strongly on the temperature [16]. This is similar, for instance, to the concept of smart screens based on polymer dispersed liquid crystals that change their opacity with temperature [17]. For a random laser, having control over the diffusion constant has important consequences because the lasing threshold depends on the diffusion constant. This means that if we have a temperature-dependent diffusion constant, we are able to bring the system above and below threshold by changing its temperature. This concept was demonstrated experimentally in Ref. [18].

In this paper, we will describe the details of our experimental work on liquid crystal/laser dye infiltrated sintered glass systems that can be brought above threshold by optical pumping and that exhibit a tunable diffusion coefficient. We will go into the sample preparation process and describe time-resolved transmission experiments on two specific liquid crystal/glass combinations to determine the temperature dependence of the diffusion coefficient. Also, we provide the results of spectroscopic experiments to characterize the emission properties of these materials.

II. SAMPLE PREPARATION AND CHARACTERIZATION

Our samples were made in the following way. Various types of glasses were ground into fine powders by the use of

*Email address: wiersma@lens.unifi.it

[†]Web page: www.lightdiffusion.com; www.lens.unifi.it

a planetary micromill. Here we report on the results for two types of glasses: SK11 and F3 (Schott). The powders were then sintered into disks of 1 cm diameter under high pressure (1.2 GPa). The such obtained disks have a smooth but mat-white appearance and form a percolating porous structure that allows for infiltration by a liquid. The sample thickness could be chosen between 0.1 and 5.0 mm. The laser dye 4-dicyanmethylene 2-methyl 6-(*p*-dimethylaminostyryl) 4-H-pyran (DCM, lambdachrome 6500) was dissolved in liquid crystal 4-cyano-4'-*n*-heptylbiphenyl (7CB) in various concentrations. The sintered disks were then slowly infiltrated with the liquid crystal + dye solution at room temperature. The final volume fraction of the liquid crystal in the sample was determined from the sample weight before and after infiltration and we found it to be 0.26. The phase sequence of 7CB is crystalline-(15.0)-crystalline-(30.0)-nematic-(42.8)-isotropic, where the numbers between brackets denote the phase transition temperatures in degrees Celsius.

To characterize the scattering strength of our materials, we have measured the diffusion coefficient in time-resolved transmission experiments. A short laser pulse was incident on the front sample interface and the diffuse transmission was monitored by means of a streak camera. From the (exponential) decay of the diffuse transmission, one can obtain the diffusion constant D which, at long times, is inversely proportional to the characteristic decay time. For the details of this technique we refer to Ref. [16]. Our laser source was a 100-fs Ti:sapphire laser operating at 805 nm wavelength. The overall time resolution was determined by the streak camera (Hamamatsu model C5680) and laser jitter, and was better than 5 ps. The temperature of the sample was controlled with a relative accuracy of 0.2 °C and an absolute accuracy of 0.5 °C. The results for the infiltrated SK11 and F3 are shown in Fig. 1. We can see that the major change in D occurs, as expected, around the isotropic-nematic phase transition temperature of the liquid crystal. The diffusion constant depends on the refractive index contrast between the liquid crystal and the sintered glass. The refractive indices of SK11 and F3 in the 600–800 nm wavelength range are $n=1.56$ and $n=1.61$ respectively, and are hardly temperature dependent. Just above $T=42.8$ °C, the liquid crystal 7CB is isotropic (I) with a refractive index $n=1.56$, and this value gradually decreases with the rising temperature. Between $T=30.0$ °C and 42.8 °C, this liquid crystal is nematic (N) and locally birefringent with refractive index $n_o=1.52$ and $n_e=1.68$ at $T=36.0$ °C, and with increasing birefringence at decreasing temperature [19]. The observed strong decrease of D , when lowering the temperature into the nematic region is due to the enhanced refractive index contrast between the liquid crystal and sintered glass. In the case of infiltrated F3, we obtain an overall change in D of about a factor of 2, whereas in the case of SK11 the diffusion constant diverges above 42.5° (within our experimental resolution). This divergence is due to partial refractive index matching between SK11 and 7CB in the isotropic phase. By choosing different liquid crystal/glass combinations, one can obtain different tuning curves for the diffusion constant. Note that the phase behavior of a liquid crystal inside sin-

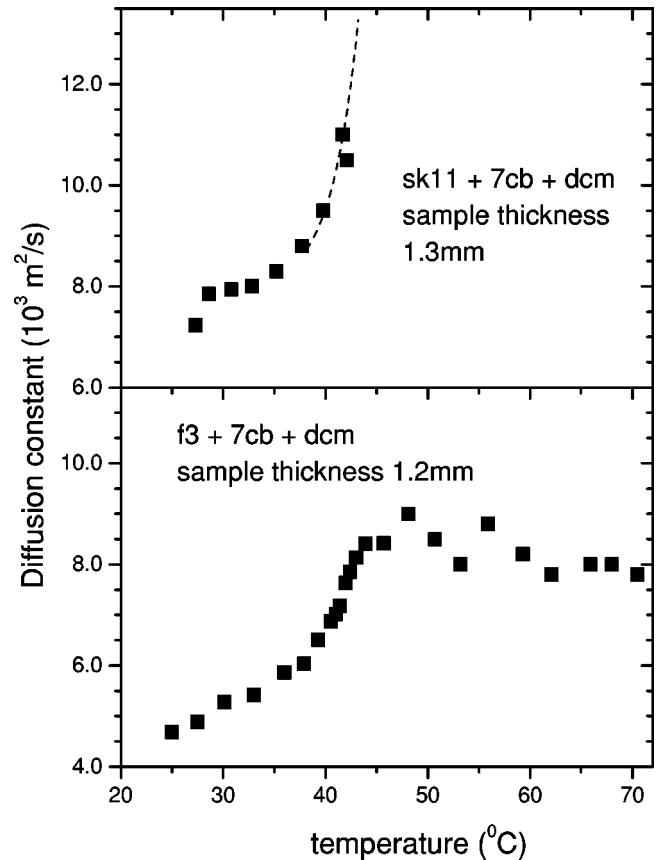


FIG. 1. Diffusion constant of two liquid crystal/sintered glass combinations versus temperature. Upper graph: sintered SK11 (Schott) infiltrated with liquid crystal 7CB and laser dye DCM (Lambdachrome 6500). (Concentration of DCM in liquid crystal: 4.1 mmol/l. Volume fraction liquid crystal in total sample $f=0.26$. The overall dye concentration in the sample is therefore 1.1 mmol/l. Sample thickness: 1.3 mm.) Above 42.5 °C, the diffusion constant diverges due to the partial refractive index matching between liquid crystal and sintered glass. Lower graph: same as above but sintered F3 (Schott) glass instead of SK11 and sample thickness 1.2 mm. The overall tunability of the diffusion constant is, in this case, about a factor of 2, with the major change occurring again at the nematic-isotropic phase transition temperature (42.8 °C).

tered glass is different from the typical phase behavior of the bulk liquid crystal. As one can see in Fig. 1, the nematic-isotropic phase transition is smeared out. This behavior is common for liquid crystals in confined geometries such as porous glasses, and is due to interaction between the liquid crystal molecules and the surface of the porous host [20].

III. EXPERIMENTS ON THE EMISSION SPECTRUM

The random laser emission from the liquid crystal/dye infiltrated sintered glass was characterized by exciting the samples from their front interface with a frequency double Q -switched Nd:YAG (neodimium doped yttrium aluminum garnet) laser, operating at 10-Hz repetition rate. The emission spectrum was recorded by imaging the diffuse emission from either the front or the rear sample surface on the input slit of a single grating spectrometer equipped with a cooled and

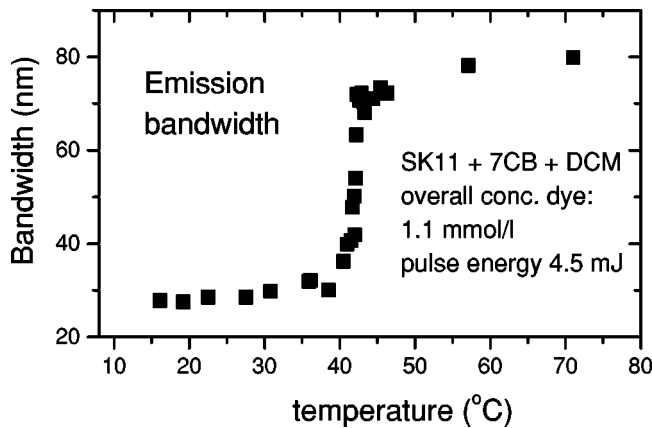


FIG. 2. Emission bandwidth versus temperature of sintered SK11 infiltrated with 7CB + DCM. Concentration of DCM in liquid crystal: 4.1 mmol/l, volume fraction liquid crystal in sintered glass is 0.26. The overall dye concentration in the sample is therefore 1.1 mmol/l. Sample thickness is 1.3 mm and excitation beam diameter on sample is 1.9 mm. Excitation pulse energy is 4.5 mJ and pulse duration is 14 ns. There is a strong decrease of bandwidth below 42.5 °C. Below this temperature the scattering strength of the material becomes large enough to bring the system above threshold.

gated optical multichannel analyzer to provide single shot spectra. At high powers the Q switch of the laser was operated in single shot mode to prevent cumulative heating (and consequent damage) of the sample. Filters were used to avoid exposure of the spectrometer to the intense scattered excitation light. The spectral response of the whole system was calibrated by a temperature controlled black body radiation source. Random laser action was observed in the nematic temperature range as a strong narrowing (factor of 2–5 in spectral width) of the emission spectrum and an abrupt increase of the emitted intensity occurring typically above a threshold of about 1 mJ pump pulse energy at room temperature. By heating the liquid crystal into the isotropic phase, the diffusion constant of the sample increases (the opacity decreases) and one would expect the random laser action to disappear.

This is indeed what we observe. In Fig. 2, we report on the width of the emission spectrum (full width at half maximum) of the SK11 / 7CB + DCM sample versus temperature. We see that indeed there is a strong effect of temperature on emission spectrum. The main feature is a strong decrease of the bandwidth of emission below 42.5 °C. The transition temperature corresponds, within the experimental error, with the nematic-isotropic phase transition temperature of 7CB (42.8 °C, see also Fig. 1). The onset of laser emission below 42.5 °C is nicely illustrated if we plot the observed intensity at the wavelength where the emission spectrum is maximal, as given in Fig. 3. We see an abrupt increase in intensity below 42.5 °C, which then saturates at lower temperatures. This strong abrupt increase in intensity, much greater than the inverse of the emission bandwidth narrowing, is commonly observed for random laser systems based on laser dye [8–10], and is most likely due to re-pumping of the laser dye above threshold.

The 7CB / SK11 combination was designed such that at

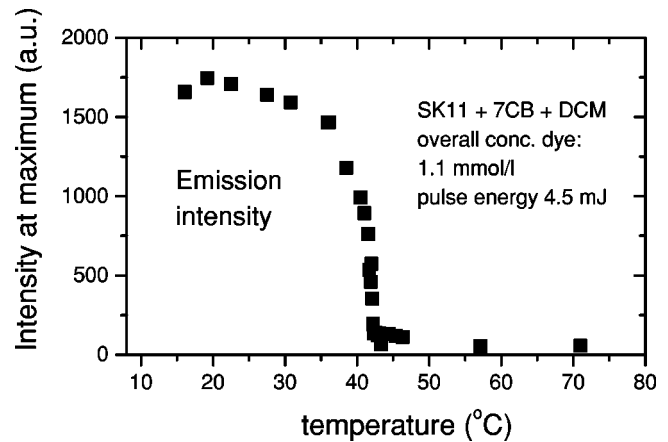


FIG. 3. Emission intensity versus temperature of the same sample as in Fig. 2. Excitation beam diameter on sample is 1.9 mm, excitation pulse energy is 4.5 mJ, and pulse duration is 14 ns. The emission intensity is taken at the wavelength where the emission is maximal. The strong increase of intensity below 42.5 °C is again due to the decrease of the diffusion constant, which brings the system in the condition that the total gain exceeds the losses.

high temperatures the diffusion constant increases so strongly that the random laser is far enough below threshold to recover the broadband fluorescence spectrum of DCM. By choosing different tuning curves for the diffusion constant, one can design the system with different spectral behavior. In the case of 7CB in sintered F3 glass, the reduction of the diffusion constant over the whole temperature range is only a factor of 2 (see Fig. 1). This leads to a smoother temperature dependence of the emission spectrum, as is shown in Fig. 4. Here the increase of the diffusion coefficient is not strong enough to bring the system far below the threshold at high temperatures, and some narrowing of the emission spectrum is maintained. This behavior could be useful for the realization of a source with temperature tunable emission band-

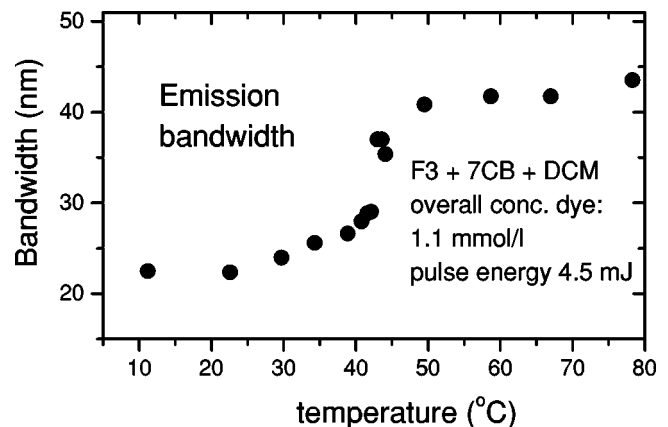


FIG. 4. Emission bandwidth versus temperature for a sample of sintered F3 glass infiltrated with liquid crystal 7CB and laser dye DCM. Overall dye concentration in the sample: 1.1 mmol/l. Sample thickness is 1.2 mm. Excitation pulse energy is 4.5 mJ and pulse duration is 14 ns. The tuning curve of the diffusion constant (Fig. 1) is less extreme for this sample, which yields a smoother dependence of bandwidth on temperature.

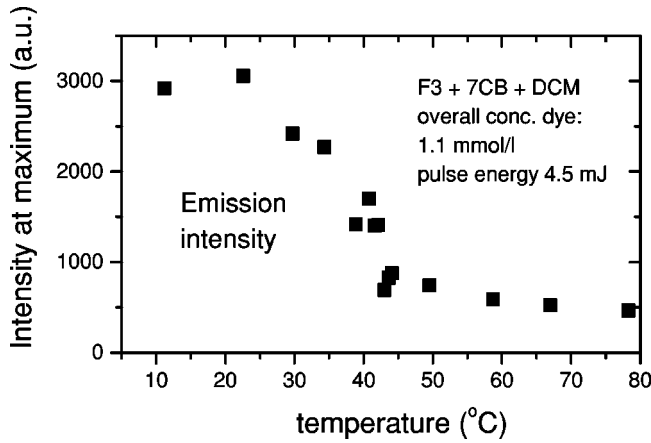


FIG. 5. Emission intensity at the wavelength where the emission is maximal versus temperature of the same sample and experimental conditions as in Fig. 4. Also the increase of the emission intensity is smoother in the case of the F3 + 7CB + DCM combination.

width. Also the increase of the intensity at the wavelength where the emission is maximal is smoother in that case, as can be seen from Fig. 5.

The threshold for random laser action is given by the condition that gain is larger than the loss in the system. Since the loss is proportional to the total sample surface and the gain is proportional to its volume, the threshold criterion can be expressed in terms of a critical volume V_{cr} above which the system lases [6]. For a slab geometry this translates in a critical thickness defined by [7,9]

$$L_{cr} = \pi \sqrt{\left(\frac{\ell \ell_g}{3}\right)}. \quad (1)$$

For our system reported in Fig. 2, we have at room temperature $D = 8000 \text{ m}^2/\text{s}$, which corresponds via $\ell = 3D/v$ (with $v = c_0/n_{av}$, where c_0 is the vacuum speed of light and $n_{av} \approx 1.56$ is the average refractive index of the sample) [1], to a mean free path of $\ell = 125 \mu\text{m}$. The gain length ℓ_g depends on the pump energy. Its minimum value (maximal gain) can be found assuming total inversion of the dye. The concentration of DCM in the 7CB is 4.1 mmol/l, and the volume fraction of liquid crystal in the sintered glass is 0.26. The overall concentration of DCM in the sample is therefore 1.1 mmol/l. This means that we have an overall dye concentration of $n = 6.4 \times 10^{23}$ dye molecules per m^3 , which at an

emission cross section of about $\sigma_{em} = 1.0 \times 10^{-20} \text{ m}^2$ leads to a minimum gain length of $\ell_g = 1/n\sigma_{em} = 0.16 \text{ mm}$ and a minimum critical thickness $L_{cr} = 0.25 \text{ mm}$. The excitation light will be distributed in a sample volume of $1.3 \text{ mm} \times 2.84 \text{ mm}^2 = 3.69 \text{ mm}^3$, so that we can excite at most $N = 2.4 \times 10^{15}$ dye molecules. Since the number of photons in our laser pulse (4.5 mJ pulse energy $\triangleq 1.2 \times 10^{16}$ photons) is almost five times larger than N , we expect our samples to be in the region of nearly complete inversion [7]. The critical thickness is therefore expected to be close to the minimum value $L_{cr} = 0.25 \text{ mm}$ and the threshold condition $L > L_{cr}$ is indeed satisfied confirming random laser action at room temperature. To obtain accurate predictions on the emission properties of the random laser, such as its exact spectral width and temporal behavior, it is essential to do a full calculation that includes the spatial distribution of the excitation light inside the sample and the dynamics of the excitation and the emission.

IV. CONCLUSION

We have demonstrated that by infiltrating a random medium with a liquid crystal/laser dye combination, it is possible to obtain random laser action that can be externally controlled via environment temperature. This results in a light source of which the emission bandwidth and intensity can be temperature controlled, and that can be brought above and below threshold by small changes in temperature. The fact that random laser sources can be made extremely small (tens of microns) and the possibility to work with different spectral tuning curves allows for interesting application as sources in photonic devices, as active displays, and as temperature sensitive screens. The tunable random laser can be designed to have its threshold behavior at very specific temperatures, which opens up applications in remote temperature sensing especially in the temperature regime of biological processes.

ACKNOWLEDGMENTS

We wish to thank Roberto Righini, Marcello Colocci, and Ad Lagendijk for continuous support and discussions and Anna Vinattieri and Daniele Alderighi for help with the time-resolved experiments. This work was financially supported by the European community (Contract No. HPRI-CT1999-00111) and by section E of the Istituto Nazionale di Fisica della Materia (PAIS project RANDS).

- [1] See, for instance, P. Sheng, *Introduction to Wave Scattering, Localization, and Mesoscopic Phenomena* (Academic Press, San Diego, 1995).
- [2] R. Dalichaouch, J.P. Armstrong, S. Schultz, P.M. Platzman, and S.L. McCall, *Nature (London)* **354**, 53 (1991); A.Z. Genack and N. Garcia, *Phys. Rev. Lett.* **66**, 2064 (1991); D.S. Wiersma, P. Bartolini, A. Lagendijk, and R. Righini, *Nature (London)* **390**, 671 (1997).
- [3] G.L.J.A. Rikken and B.A. van Tiggelen, *Nature (London)* **381**, 54 (1996).

- [4] A. Sparenberg, G.L.J.A. Rikken, and B.A. van Tiggelen, *Phys. Rev. Lett.* **79**, 757 (1997).
- [5] F. Scheffold and G. Maret, *Phys. Rev. Lett.* **81**, 5800 (1998).
- [6] V.S. Letokhov, *Zh. Éksp. Teor. Fiz.* **53** 1442 (1967) [*Sov. Phys. JETP* **26**, 835 (1968)].
- [7] C. Guedard, D. Husson, C. Sauteret, F. Auzel, and A.J. Migus, *J. Opt. Soc. Am. B* **10**, 2358 (1993); D.S. Wiersma and A. Lagendijk, *Phys. Rev. E* **54**, 4256 (1996).
- [8] N.M. Lawandy, R.M. Balachandran, A.S.L. Gomes, and E. Sauvin, *Nature (London)* **368**, 436 (1994).

- [9] R.Y. Chiao and J. Boyce, *Phys. Rev. Lett.* **73**, 3383 (1994); A.Y. Zyuzin, *Phys. Rev. E* **51**, 5274 (1995); S. John and G. Pang, *Phys. Rev. A* **54**, 3642 (1996); Xunya Jiang and C.M. Soukoulis, *Phys. Rev. Lett.* **85**, 70 (2000).
- [10] M.A. Noginov, N.E. Noginova, H.J. Caulfield, P. Venkateswarlu, T. Thompson, M. Mahdi, and V.J. Ostroumov, *J. Opt. Soc. Am. B* **13**, 2024 (1996); G.A. Berger, M. Kempe, and A.Z. Genack, *Phys. Rev. E* **56**, 6118 (1997); G. van Soest, F.J. Poelwijk, R. Sprik, and A. Lagendijk, *Phys. Rev. Lett.* **86**, 1522 (2001).
- [11] C.W.J. Beenakker, *Phys. Rev. Lett.* **81**, 1829 (1998).
- [12] H. Cao, Y.G. Zhao, S.T. Ho, E.W. Seelig, Q.H. Wang, and R.P.H. Chang, *Phys. Rev. Lett.* **82**, 2278 (1999); H. Cao, Y. Ling, J.Y. Xu, C.Q. Cao, and Prem Kumar, *ibid.* **86**, 4524 (2001).
- [13] Y. Sun, J.B. Ketterson, and G.K.L. Wong, *Appl. Phys. Lett.* **77**, 2322 (2000).
- [14] K. Busch and S. John, *Phys. Rev. Lett.* **83**, 967 (1999).
- [15] P. G. de Gennes and J. Prost, *The Physics of Liquid Crystals*, 2nd ed. (Oxford, New York, 1993); S. Chandrasekhar, *Liquid Crystals* (Cambridge University Press, Cambridge, 1977).
- [16] D.S. Wiersma, M. Colocci, R. Righini, and F. Aliev, *Phys. Rev. B* **64**, 1442208 (2001).
- [17] See, for instance, P. S. Drzaic, *Liquid Crystal Dispersions* (World Scientific, Singapore, 1995).
- [18] D.S. Wiersma and S. Cavaleri, *Nature (London)* **414**, 708 (2001).
- [19] Refractive index values at $\lambda = 632.8$ nm. See D.A. Dunmur, M.R. Manterfield, W.H. Miller, and J.K. Dunleavy, *Mol. Cryst. Liq. Cryst.* **45**, 127 (1978).
- [20] *Liquid Crystals in Complex Geometries Formed by Polymer and Porous Networks*, edited by G.P. Crawford and S. Zumer (Taylor & Francis, London, 1996).