

## Structure-Factor Scaling at the Isotropic-to-Nematic Transition of Cesium Perfluoro-Octanoate

Apollo P. Y. Wong, Pierre Wiltzius, and Bernard Yurke

*AT&T Bell Laboratories, Murray Hill, New Jersey 07974*

(Received 2 March 1992)

The structure factor of the lyotropic liquid-crystal cesium perfluoro-octanoate-water after the material has been quenched from the isotropic phase to the nematic phase was found to display non-Porod power-law behavior in the limit of large wave vectors. Our measurements were consistent with the scaling law  $S(q,t) \sim t^{-3/2} q^{-6}$  for bulk samples and  $S(q,t) \sim t^{-1} q^{-4}$  for thin samples exhibiting two-dimensional behavior. Dimensional crossover was also observed.

PACS numbers: 64.70.Md, 64.60.Cn

When a system is quenched into its ordered phase, "domains" of ordered phase will grow as a function of time. The dynamics of the ordering process are believed to depend on the dimensionality of the system ( $d$ ) as well as the number of components in the order parameter field ( $n$ ). In addition, there is increasing theoretical and experimental evidence that the dynamical structure factor  $S(q,t)$  obeys asymptotic scaling laws. Here  $q$  denotes the length of the wave vector, and  $t$  is the time since the quench. In particular, as the system enters its late stage of growth, a regime emerges in which there is a single characteristic length scale  $L(t)$ . In such a scaling regime, if the system is rescaled with the proper length scale, the pattern of the ordered phase at later times would look similar to that at earlier times. Such scaling phenomena have attracted much interest lately [1]. Probably the most studied case of phase separation is the spinodal decomposition in binary mixtures (e.g., metal alloys, fluid mixtures, polymer and glass blends). Here the order parameter is a scalar, the composition, and the symmetry is discrete. There is ample experimental and theoretical evidence that the structure factor assumes the form  $S(q,t) \sim L(t)^3 g(qL(t))$  in three dimensions. For large  $q$ , the scaling function  $g$  approaches the Porod form  $q^{-4}$ . The question arises whether there is similar scaling behavior in dimensions other than three and in systems with more complicated order parameters. Recent theories [2-4] suggest that the asymptotic behavior of the structure factor in the scaling regime obeys a surprisingly simple scaling law of  $S(q,t) \sim L(t)^d g(qL(t))$ . The scaling function approaches asymptotically  $g(x) \sim x^{-(d+n)}$ , where  $d$  is the dimension of the system and  $n$  is the number of components of the order parameter. The above-mentioned Porod law  $S(q) \sim q^{-4}$  is recovered as the special case for  $d=3$  and  $n=1$ . In addition, the characteristic length scale is expected to grow with time according to  $L(t) \sim t^{1/2}$ . Although these predictions have been made for  $n$ -component vector models, one expects that they should be applicable to systems with more complicated internal symmetries like liquid crystals. For thin films of nematic liquid crystals in which boundary conditions constrain the director to behave like a spin vector of a 2D  $XY$  model,  $n=2$  and  $d=2$ . The situation is more complicated

in three dimensions. For a uniaxial nematic, the order parameter is a traceless second-rank tensor. If one takes  $n$  to be the number of independent components of the order parameter, this would imply  $n=5$ . On the other hand, if one considers the relevant part of the order parameter to be the director field, one would expect  $n=3$ . Alternatively, the fact that the dominant defects in a nematic liquid crystal are stringlike, such as those exhibited by a 3D  $XY$  model, would suggest  $n=2$ . At present, a consensus on the value of  $n$  for a three-dimensional nematic liquid crystal has not been established. Addressing this interesting theoretical issue should be very revealing.

In this Letter we report the measurements of the structure factor for a lyotropic liquid-crystal system quenched into the nematic phase. We studied the optical scattering of the isotropic-nematic transition of cesium perfluoro-octanoate (CSPFO) in both two and three dimensions. CSPFO was chosen because of the ease of preparation compared to other lyotropics [5] and the slow ordering time scale involved. The difference in index of refraction between the two optical axes is much smaller than that of the thermotropic liquid crystals. The latter are very strong scatterers of visible light in the nematic phase and thus unsuitable for quantitative light scattering experiments due to multiple scattering problems. Solutions of CSPFO are weak scatterers and do not cause these problems. Furthermore, the CSPFO system was very well studied and the complete phase diagram was readily available [6].

The sample used in this experiment was prepared by reacting cesium carbonate ( $\text{CsCO}_3$ ) and perfluoro-octanoic acid [ $\text{CF}_3(\text{CF}_2)_6\text{COOH}$ ] in a bath of hexane. The precipitate was then dried and recrystallized from a mixture of hexane and ethanol (1:1 by volume). Finally, the CSPFO crystal was dissolved in heavy water ( $\text{D}_2\text{O}$ ) with a mass ratio of 1:1.857 and then filtered by a 0.5- $\mu\text{m}$  Teflon filter into the sample cells. Because the phase boundary is very sensitive to the composition, care had to be taken to have air-tight sample cells. The isotropic-nematic transition temperature of the solution was at 28 °C.

The experimental setup to measure  $S(q,t)$  has been

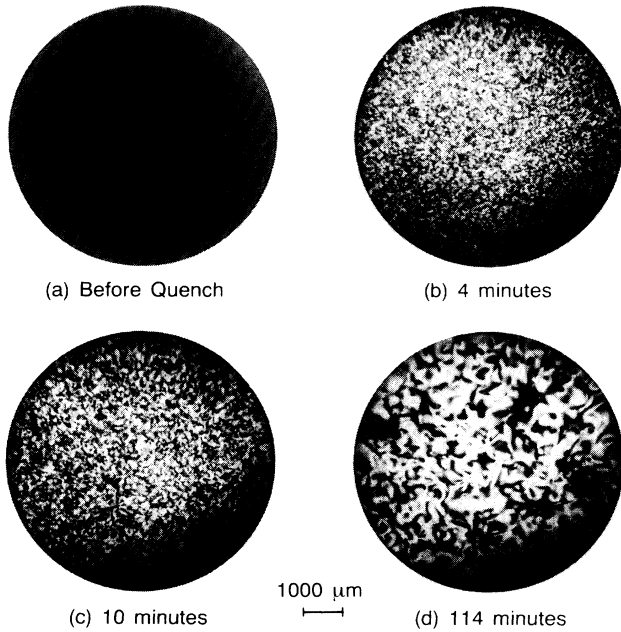


FIG. 1. The pattern of nematic domains under cross polarizers for 3D sample (a) before the quench and (b) 4 min, (c) 10 min, and (d) 114 min after the quench.

described elsewhere [7] in detail. The sample in the form of a thin slab was placed right at the focal point of a paraboloidal mirror which collected a wide range (approximately 0° to 40° scattering angle) of scattered light and converted it into a bundle of parallel beams. The bundle was then fed through a lens system for collimation so that the whole bundle could fit onto a square charge-coupled-device (CCD) chip of 10.25×10.25 mm size. The CCD had an active area of 512×512 pixels. This system offered an advantage of measuring a wide range of  $S(q)$  simultaneously which is crucial in order to study  $S(q,t)$  in real time.

Two sample cells were used in this study. For the study of the three-dimensional behavior, the cell was a 1-mm-thick cuvette sealed by a Teflon stopper with rubber O rings. For the dimensional crossover study, the cell was made of two pieces of 2.1-cm-diam glass windows with a small 0.5-mm Teflon spacer placed in between near the rim. The windows were glued with epoxy and formed a wedgelike cavity where the liquid was sealed. The thickness of the accessible portions of the wedge varied from 95 to 400 μm. During the experiment, the samples were first annealed at 2° above  $T_c$ , then quenched to 1° below  $T_c$  into the nematic phase. For completeness reasons we want to point out that the sample, like those studied by other researchers, had a 0.5° region of coexistence between the isotropic and nematic phases as characterized by forward light scattering. The quench procedure described above thus took the sample from the isotropic phase to 0.5° into the nematic phase. The quench rate was 1.7°C per min. Since the measure-

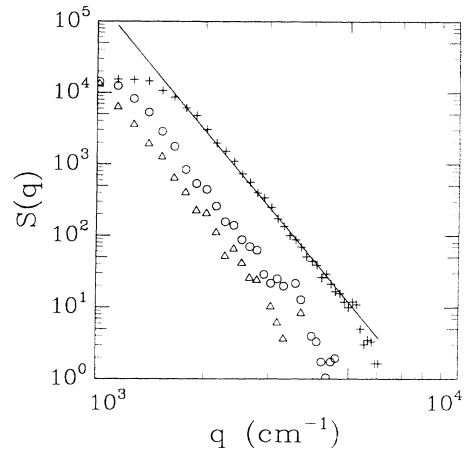


FIG. 2.  $S(q)$  vs  $q$  for 3D sample at 300 (crosses), 870 (circles), and 1650 sec (triangles) after the quench.

measurements were done in the one-phase nematic region, and since the time scales of interest ( $\sim 10^3$  sec) were much longer than the time the sample spent in the coexistence region (18 sec), we do not believe that the presence of a coexistence region is relevant to our observations.

A series of microphotographs taken with the sealed cuvette sandwiched between a pair of crossed polarizers is shown in Fig. 1. The sample was quenched from 30 to 27°C. A scale bar shown is 1000 μm long. When the sample was in the isotropic phase, it was optically inactive and appeared dark in the photograph. After the temperature quench, the characteristic nematic Schlieren patterns due to the optical activity were observed. It can clearly be seen that the patterns were coarsening with time.

The  $S(q)$  for the sealed cuvette is plotted as a function of  $q$  at 300, 870, and 1650 sec after the quench in log-log scale in Fig. 2. The solid line is a fit to the scaling region of the 300-sec data. The slope of the line is  $-6.0 \pm 0.3$ . This is consistent with the scaling form  $S(q,t) \sim L(t)^d \times [qL(t)]^{-(d+n)}$  with  $d=3$  and  $n=3$ . The deviation from the power-law behavior in the small- $q$  region reflects that at such early times as 300 sec the characteristic length scale  $L(t)$  has not grown large enough to bring the product  $qL(t)$  into the asymptotic regime yet. When the length scale grew to larger values at later times, the scaling regime extended to regions of lower  $q$  values as shown in Fig. 2. The scaling regime at a different time could be fitted with the same functional form:

$$S(q,t) = A^* q^{-6}. \tag{1}$$

The amplitude  $A^*$ , arbitrarily normalized to 1 at  $t=210$  sec, is shown in Fig. 3 as a function of time after quench in log-log scale. The data are fitted well with a straight line of slope  $-1.50 \pm 0.15$ .

Consider the following relationship:

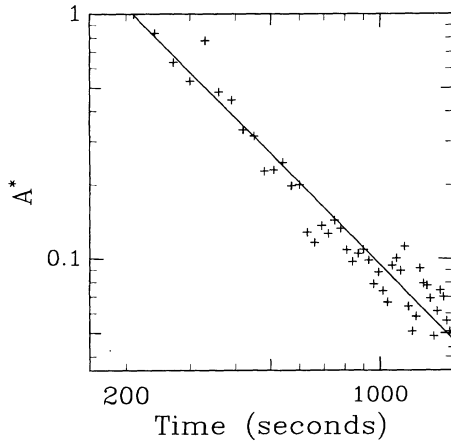


FIG. 3. Amplitude of the power law ( $A^*$ ) vs time after quench for 3D sample.

$$S(q,t) \sim L(t)^{-3} q^{-6} \sim A^*(t) q^{-6}. \quad (2)$$

$A^*(t) \sim t^{-3/2}$  would thus imply that the characteristic length scale was growing with time in a  $t^{1/2}$  fashion. This growth of the scaling length is consistent with previous observations of Chuang, Turok, and Yurke [8], Mondello and Goldenfeld, and Toyoki and Honda [9] and recent computer simulation results of Mondello and Goldenfeld [10]. We have also quenched the sample to  $2^\circ$  below  $T_c$  to study the quench depth dependence of the dynamics. We did not observe any quench depth dependence for the range studied.

When the experiment was repeated on the wedge cell, strikingly enough, the system displayed two-dimensional behavior when the thickness was thinner than  $100 \mu\text{m}$ . In two dimensions with both  $d$  and  $n$  equal to 2, the theoretical prediction would become  $S(q) \sim q^{-4}$ . Indeed, as shown in Fig. 4, the slope of the scaling regime did become  $-4$  in this case. The results for 200, 600, and 1400 sec after the quench are shown in the figure. The solid line is a fit to the linear regime of the set at 600 sec. The fitted slope yields a value of  $-4.1 \pm 0.3$  which is in good agreement with theories. As a matter of fact, under closer inspection of Fig. 4, the first trace at 200 sec would yield a slope steeper than  $-4$  for the scaling regime. This could be understood in terms of dimensional crossover. At early times (e.g., 200 sec after the quench), the length scale of the system is still shorter than the thickness of the sample ( $100 \mu\text{m}$  in this case) and the system is not fully two dimensional. Indeed, when the measurements were repeated on thicker regions, the slope actually started out at about  $-5$ . Only after about 1000 sec did it gradually drop to a value of  $-4$ . For sample thicknesses larger than  $250 \mu\text{m}$ , the system recovered pure 3D behavior.

In analogy to the previous case, we fitted the  $S(q)$  results at different times to  $A^* q^{-4}$  and found the time dependence of  $A^*(t)$  as shown in Fig. 5. The solid line in

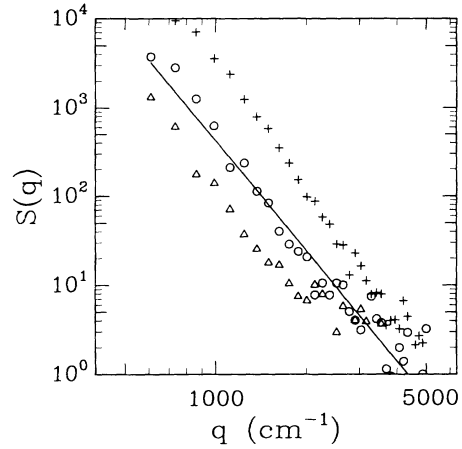


FIG. 4.  $S(q)$  vs  $q$  for 2D sample at 200 (crosses), 600 (circles), and 1400 sec (triangles) after the quench.

the figure is a fitted line of slope  $-1.05 \pm 0.2$ . Consider the following relationship in 2D similar to Eq. (2):

$$S(q,t) \sim L(t)^{-2} q^{-4} \sim A^*(t) q^{-4}. \quad (3)$$

$A^*(t) \sim t^{-1}$  would imply that the characteristic length was growing with time as  $t^{1/2}$  also [3]. The essential reason for the same square root of time dependence of the length scale is that the order parameter is governed by the same differential equation in both 3D and 2D, where the dimensionality has no effect on the time dependence [11]. Previous studies of the annealing of two-dimensional polymer nematic liquid crystals [12] have reported a characteristic length growth as  $t^{0.35}$ .

In conclusion, we have observed a novel power-law and scaling behavior of the structure factor for a system with a nonscalar order parameter in both two and three dimensions. Unfortunately our experiments do not allow us to determine the absolute value of  $L(t)$ . An independent experiment measuring the magnitude of the length scale

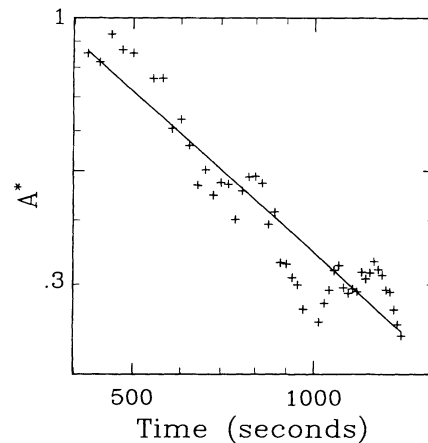


FIG. 5. Amplitude of the power law ( $A^*$ ) vs time after quench for 2D sample.

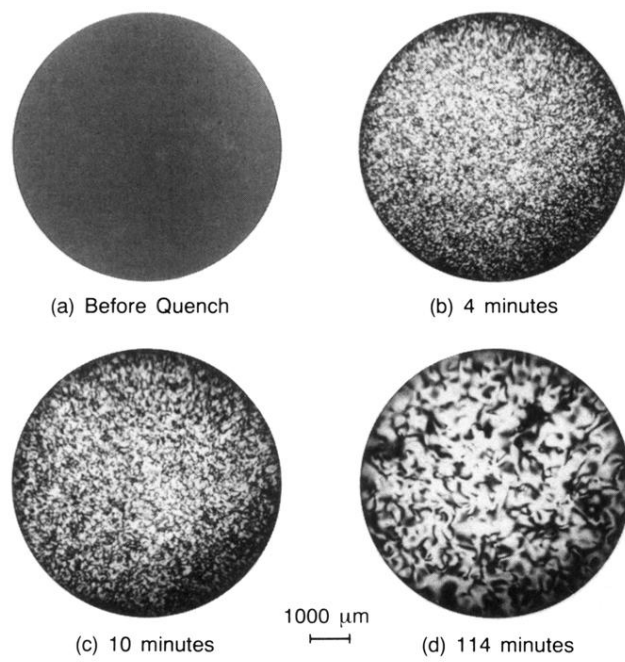
involved should be revealing. In the simple case of  $d=3$  and  $n=1$ ,  $L(t)$  has the very intuitive and physical meaning of a domain size. In the cases ( $d=3, n=3$ ) and ( $d=2, n=2$ ), however, a physical picture for  $L(t)$  is not obvious. Our results are in excellent agreement with theoretical predictions for the case ( $d=2, n=2$ ). The three-dimensional data also obey the scaling form  $S(q,t) \sim L(t)^d [qL(t)]^{-(d+n)}$  for  $d=3$  provided  $n=3$ . These are the first observations of such power-law behavior for systems with a nonscalar order parameter.

We would like to thank A. J. Bray, N. Goldenfeld, D. Huse, F. Liu, and G. F. Mazenko for very constructive discussions. We would also like to thank M. Marcus for his valuable assistance in the preparation of the samples.

---

[1] See, e.g., J. D. Gunton, M. S. Miguel, and P. S. Sahni, in *Phase Transitions and Critical Phenomena*, edited by C. Domb and J. L. Lebowitz (Academic, New York, 1983), Vol. 8, p. 267.

- [2] A. J. Bray and S. Puri, Phys. Rev. Lett. **67**, 2670 (1991).
- [3] F. Liu and G. F. Mazenko (to be published).
- [4] H. Toyoki, Phys. Rev. A **42**, 911 (1990).
- [5] N. Boden, S. A. Corne, and K. W. Jolley, J. Phys. Chem. **91**, 4092 (1987).
- [6] N. Boden, P. H. Jackson, M. McMullen, and M. C. Holmes, Chem. Phys. Lett. **65**, 476 (1979).
- [7] A. Cumming, P. Wiltzius, F. S. Bates, and J. H. Rose-dale, Phys. Rev. A **45**, 885 (1992).
- [8] I. Chuang, N. Turok, and B. Yurke, Phys. Rev. Lett. **66**, 2472 (1991).
- [9] See M. Mondello and N. Goldenfeld, Phys. Rev. A **42**, 5865 (1990); H. Toyoki and K. Honda, Prog. Theor. Phys. **78**, 237 (1987), for the theoretical works on defect growth in 3D.
- [10] M. Mondello and N. Goldenfeld, Phys. Rev. A **45**, 657 (1992).
- [11] P. C. Hohenberg and B. I. Halperin, Rev. Mod. Phys. **49**, 435 (1977).
- [12] T. Shiwaku, A. Nakai, H. Hasegawa, and T. Hashimoto, Polymer Commun. **28**, 174 (1987); Macromolecules **23**, 1590 (1990).



**FIG. 1.** The pattern of nematic domains under cross polarizers for 3D sample (a) before the quench and (b) 4 min, (c) 10 min, and (d) 114 min after the quench.