Critical Behavior of the Structure Factor for Higher Harmonics in Density Wave Systems

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The structure factor $S_n(\mathbf{q}) = \langle \psi_n(\mathbf{q})\psi_n^*(\mathbf{q})\rangle$ associated with fluctuations in the nth harmonic density wave (DW) order parameter ψ_n of a uniaxial system is affected by its bare $\mathbf{q}$ dependence, and by the coupling $\mathrm{Re}(\psi_n^*\psi_1^n)$. The latter involves correlations in the secondary order parameter ψ_1^n, characterized by a correlation length $\xi_n = \xi_{n0}[(T - T_c)/T_c]^{-\nu}$, with *the same XY* model exponent ν for all n, and decaying as $q^{-(2-\eta_n)}$ for large q. For $n > 1$, η_n is large. The ratio $X_n = (\xi_{n0}/\xi_{10})^2$ is universal, and $X_2 = \epsilon/20 - \epsilon^2/100 + O(\epsilon^3)$ in $d = 4 - \epsilon$. This naturally explains previously puzzling experimental results for S_2 at a nematic–smectic-A_2 transition. Similar predictions apply for other secondary order parameter correlations.

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The order parameter of density waves (DW) in a uniaxial system is characterized by the complex amplitude $\psi_1 = x + iy$, determined by the contribution $\mathrm{Re}(\psi_1 e^{iq_0 z})$ to the density modulation. Therefore, the critical behavior associated with the order parameter is described by the XY model universality class [1]. A simple example of such behavior is provided by the smectic-A phase of thermotropic liquid crystals [2]. Other examples include charge density wave systems, spin density wave systems, and rare earth magnets. Recently, there has been considerable interest in the critical behavior of higher harmonics, associated with the contributions $\mathrm{Re}(\psi_n e^{inq_0 z})$ to the density modulation. Theoretically, the exponents describing correlation functions of the order parameters ψ_n were derived from the XY model which describes the leading order parameter ψ_1 [3], and the results were nicely confirmed by measurements of the bond orientational order harmonics in hexatic liquid crystals [4]. More recently, experiments on the nematic–smectic-A_2 (N–Sm-A_2) transition in the polar thermotropic liquid crystal material 4′-n-heptyloxycarbonylphenyl-4′-(4″-cyanobenzoyloxy) benzoate (7APCBB) succeeded in observing the critical fluctuations associated with the second harmonic of the DW order parameter [5]. Although these experiments confirmed the theoretical predictions for the second harmonic susceptibility, χ_2, fits of the second harmonic structure factor $S_2(\mathbf{q})$ by a single Lorentzian shape yielded correlation lengths $\xi_{\|2}$ and $\xi_{\perp 2}$ which seemed to scale very differently from their first harmonic counterparts. Very close to the transition, the former were at least an order of magnitude smaller than the latter at the same temperatures. Attempts to modify the Lorentzian shape failed to change these conclusions.

These results were very surprising: A different scaling of the correlation lengths ξ_n's for the different harmonics would imply that the N–Sm-A_2 transition involves more than one critical length scale and that it cannot be simply described by the XY model. Furthermore, the fitted exponents $\nu_{\|2}$ and $\nu_{\perp 2}$ severely violated the hyperscaling relation $2\nu_{\perp 2} + \nu_{\|2} = 2 - \alpha$, with no explanation. In the present Letter we present several new theoretical results, which clarify the critical behavior of higher harmonics in DW and similar systems. Specifically, we predict that all the harmonics are still dominated by the critical behavior of the XY model, and therefore that $\xi_n^2 = X_n \xi_1^2$, where X_n is a universal number. However, since X_n may be quite small, the structure factor of the nth harmonic, $S_n(\mathbf{q})$, may be strongly influenced by its bare (noncritical) value. Furthermore, since at the transition $S_n \sim q^{-\eta_n}$, with large values of η_n, deviations from the Lorentzian shape are also important. These new theoretical results describe the experimental results of Ref. [5], as well as some new measurements [6].

We define the "local" nth harmonic order parameters as the slowly varying complex functions $\psi_n(\mathbf{r})$ determining the density

$$\rho(\mathbf{r}) = \rho_0 + \mathrm{Re} \sum_{n=1}^{\infty} \psi_n(\mathbf{r}) \exp(iq_0 nz). \tag{1}$$

In the most general case, one should treat all the ψ_n's as competing order parameters. In the absence of couplings, each ψ_n would undergo a separate XY-like phase transition, at a temperature T_n, described by a free energy

$$\mathcal{H}_n = \int d^d\mathbf{r} \Big\{ \frac{1}{2} r_{n0}[|\psi_n|^2 + \xi_{\|nb}^2 |\nabla_\| \psi_n|^2 + \xi_{\perp nb}^2 |\nabla_\perp \psi_n|^2] + u_n |\psi_n|^4 \Big\}. \tag{2}$$

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We must also take into account the coupling terms

$$\mathcal{H}_{n,\mathrm{int}} = \mu_n \int d^d\mathbf{r}(\psi_1^n\psi_n^* + \psi_1^{*n}\psi_n). \quad (3)$$

The correlation functions of the secondary order parameters, ψ_n's with $n > 1$, can, in principle, be derived from Eqs. (2) and (3).

Assuming T_n to be far enough below T_1, one has a transition at $T_c = T_1$, with the leading two component order parameter ψ_1. Near this transition, we can neglect the self-interaction of the ψ_n's and set $u_n = 0$ in Eq. (2). Thus the ψ_n's for $n > 1$ can be treated in the harmonic approximation and we can solve the partition function for ψ_n exactly in terms of the correlation functions of ψ_1. For example, the average density modulation with the wave vector $nq_0\hat{\mathbf{z}}$ is determined by

$$\Psi_n = \langle\psi_n\rangle = \mu_n\chi_{nb}\langle\psi_1^n\rangle, \quad (4)$$

where $\chi_{nb} = 1/r_{n0}$ is the bare susceptibility for the nth harmonic. Since χ_{nb} is not singular at T_1, the singularity comes only from $\langle\psi_1^n\rangle \propto |t|^{\beta_n}$, where $t = (T - T_c)/T_c$, $\beta_n = 2 - \alpha - \phi_n$ and ϕ_n is the crossover exponent associated with nth order anisotropy near the rotationally invariant XY model fixed point [3]. Specifically, ϕ_2 is the crossover exponent for a uniaxial anisotropy term, proportional to $\mathrm{Re}(\psi_1^2) = x^2 - y^2$. Indeed, the experiments on bond orientational harmonics confirmed these predictions [4].

The above theory can now be extended to the structure factor [7,8]

$$S_n(\mathbf{q}) = \langle\psi_n(\mathbf{q})\psi_n^*(\mathbf{q})\rangle = S_{nb}(\mathbf{q}) + \mu_n^2 S_{nb}(\mathbf{q})^2\tilde{S}_n, \quad (5)$$

where $\psi_n(\mathbf{q})$ is the Fourier transform of $\psi_n(\mathbf{r})$, and

$$S_{nb}(\mathbf{q}) = \frac{k_BT\chi_{nb}}{1 + \xi_{\|nb}^2 q_\|^2 + \xi_{\perp nb}^2\mathbf{q}_\perp^2} \quad (6)$$

is the bare nth harmonic structure factor. Here, $\tilde{S}_n = \langle\psi_1^n(\mathbf{q})\psi_1^{*n}(\mathbf{q})\rangle$ has to be calculated with the XY model Hamiltonian $\mathcal{H}_1$ [9,10]. Asymptotically close to T_1, and for very small $\mathbf{q}$, $S_{nb}(\mathbf{q})$ is practically temperature independent, and the divergent part of S_n is proportional to $\tilde{S}_n$, which we calculate next. However, the experimental data usually extend over a range of momenta $\mathbf{q}$ in which the $\mathbf{q}$ dependence of S_{nb} cannot be ignored, as we show in our discussion of these data below. This fact may be associated with the physical nature of the polar material, where the smectic-A_2 phase may be close to the transition into the smectic-A_1 phase.

We next discuss the correlation function $\tilde{S}_n(\mathbf{q})$. Since this function is dominated by the critical behavior of the XY model represented by $\mathcal{H}_1$, we expect it to have the asymptotic scaling form $\tilde{S}_n(\mathbf{q}) = \chi_n f_n(q\xi_1)$, where $\chi_n \sim |t|^{-\gamma_n}$, with $-\gamma_n = 2 - \alpha - 2\phi_n$ [3,5], and f_n is a universal scaling function [11]. For $x \ll 1$, $f_n(x)$ may be expanded in powers of x, and thus be approximated by a Lorentzian that is $f_n(x) = 1/[1 + X_n x^2 + O(x^4)]$, and X_n is a universal amplitude ratio [11]. Rewriting $\tilde{S}_n = \chi_n/[1 + \xi_n^2 q^2 + \cdots]$, this yields $\xi_n^2 = X_n\xi_1^2 = X_n\xi_{10}^2|t|^{-2\nu}$, that is, *all* the harmonic correlation lengths scale with the *same* XY model correlation length exponent ν, but with *different amplitudes*. The ratios of these amplitudes, X_n, are universal. Indeed, our ϵ-expansion calculations described below confirm these expectations. In addition, these expansions show that X_n can be small compared to unity, causing the $\mathbf{q}$ dependence of $\tilde{S}_n$ to become dominant only very close to T_c. For $x \gg 1$, $f_n(x) \sim x^{-(2-\eta_n)}$, with $2 - \eta_n = \gamma_n/\nu$. For $n > 1$, η_n is quite large, and we expect significant deviations from the Lorentzian shape at large x. To approximate the crossover between these limits, we shall follow Fisher and Burford [12] and write

$$f_n(x) = \frac{(1 + A_n x^2)^{\eta_n/2}}{1 + (X_n + A_n\eta_n/2)x^2}. \quad (7)$$

Our last theoretical step is the explicit calculation of $\tilde{S}_2$, in $d = 4 - \epsilon$ dimensions. This part is somewhat technical, and the unmotivated reader can easily skip this paragraph and move on to Eq. (10). It is easy to check that $\tilde{S}_2$ is proportional to $\langle(x^2 - y^2)(\mathbf{q})(x^2 - y^2)(-\mathbf{q})\rangle$ [13]. Technically, it is convenient to shift the bare parameter r_{10} in Eq. (2), and replace it by the true inverse susceptibility $r = 1/\chi_1 \sim |t|^{\gamma_1}$ [14]. Also, it is convenient to do the calculations for the isotropic case ($\xi_{\|nb} = \xi_{\perp nb}$) and to replace the sharp Brillouin zone cutoff Λ by a smooth one, replacing the propagator $1/(r + q^2)$ by $G(r,\mathbf{q}) = 1/(r + q^2) - 1/(\Lambda^2 + q^2)$. Expanding now in powers of u_1, this yields $\tilde{S}_2 \sim \Omega - 8u_1\Omega^2 + O(u_1^2)$, where $\Omega = (2\pi)^{-d}\int d^d p\, G(r,p)G(r,\mathbf{p} + \mathbf{q})$. An explicit calculation at small q (with $\Lambda = 1$) now gives (to all orders in ϵ)

$$\Omega = C(\epsilon)\{r^{-\epsilon/2}(1 - \epsilon/2) - (1 + \epsilon/2) + O(r) + \epsilon q^2[(\epsilon - 2/24)r^{-1-\epsilon/2} + O(r^0)] + O(q^4)\}, \quad (8)$$

where the factor C is $C(\epsilon) = K_d\pi/2\sin(\pi\epsilon/2) = 1/2^d\pi^{d/2-1}\Gamma(d/2)\sin(\pi\epsilon/2)$. Expanding in powers of ϵ, and setting u_1 at its fixed point value $K_d^{-1}\epsilon/40$, we end up with

$$\tilde{S}_2 \sim 1 + \frac{1}{2}(1 - z\epsilon)\ln r - \frac{1}{4}z\epsilon\ln^2 r + \frac{q^2}{12r}(1 - z\epsilon - z\epsilon\ln r), \quad (9)$$

where $z = 3/10$. Exponentiating in ϵ (and taking out a constant of order $1/\epsilon$), this can be matched with $\tilde{S}_2 \sim r^{-\gamma_2/\gamma_1}/(1 + bq^2/r^{2\nu/\gamma_1})$, where $\gamma_2/\gamma_1 = z\epsilon - 6\epsilon^2/100 + O(\epsilon^3)$, $2\nu/\gamma_1 = 1 + O(\epsilon^2)$, and $b = z\epsilon(1 - \epsilon/5)/6 + O(\epsilon^3)$. Since to order ϵ we have $\xi_1^2 = 1/r$, this confirms our prediction that ξ_2 scales with the same exponent as ξ_1, and we identify $X_2 = b = \epsilon/20 - \epsilon^2/100 + O(\epsilon^3) \approx 0.04$ for $\epsilon = 1$. We have also calculated the ϵ expansion for the universal coefficients of higher powers of $\xi_1 q$, and they all turn out to be very small [15]. In summary of this part, we can now write

$$\tilde{S}_2(\mathbf{q}) = \frac{k_BT\chi_2[1 + A_2(\xi_{\|1}^2 q_\|^2 + \xi_{\perp 1}^2 q_\perp^2)]^{\eta_2/2}}{1 + (X_2 + A_2\eta_2/2)(\xi_{\|1}^2 q_\|^2 + \xi_{\perp 1}^2\mathbf{q}_\perp^2)}, \quad (10)$$

with $\chi_2 \sim |t|^{-\gamma_2}$. Equations (5), (6), and (10) form our theoretical predictions, to be compared with experimental data below. At this stage A_2 must be determined from experiment.

All of these results can be easily generalized to other secondary order parameters. If an order parameter ψ_m couples to some combination of the (primary) order parameter components, which involves a sum over products of m factors of these components, like $x_1 x_2 \cdots x_m$, then the structure factor $S_m = \langle \psi_m(\mathbf{q}) \psi_m^*(\mathbf{q}) \rangle$ is also given by equations similar to Eqs. (5), (6), and (7), and one should expect a universal ratio $X_m = (\xi_m/\xi_1)^2$. For example, energy-energy correlations involve the correlation function $\tilde{S}_E = \langle |\psi|^2(\mathbf{q}) |\psi|^2(-\mathbf{q}) \rangle$, and a calculation similar to the one presented above for the n-component Heisenberg-like model yields $X_E = (4 - n)\epsilon/12(n + 8) - (n + 2)(13n + 44)\epsilon^2/12(n + 8)^3 + O(\epsilon^3)$. Similar results apply for elastic degrees of freedom, where the components of the elastic strain $e_{\alpha\beta}$ couple to $x_\alpha x_\beta$, etc. [15].

As noted earlier, the above theoretical developments were stimulated by recent experiments on the second harmonic critical fluctuations at the $N-$Sm-A_2 transition in the polar thermotropic liquid crystal material 7APCBB. In light of this new theory we have reanalyzed the data of Ref. [5], using Eq. (5). In addition, new experiments have been carried out, extending the data out to $t = 10^{-2}$ [6]. We first noticed that the data around $t \sim 10^{-2}$ are fitted excellently by a simple Lorentzian around $2q_0\hat{\mathbf{z}}$, with correlation lengths which show little temperature dependence. We interpret this by assuming that far away from the transition Eq. (5) is dominated by the first term that is by the bare structure factor. We have thus fitted S_2 for scans at $t = 10^{-2}$ with Eq. (6), and found the values $\xi_{\|2b} = 80$ Å and $\xi_{\perp 2b} = 11$ Å. We have also set the amplitude χ_{nb} to the value found by these fits. A representative fit is shown in the lower part of Fig. 1. Having set $S_{2b}(\mathbf{q})$ at these values for all temperatures, we have also fixed X_2 at its ϵ-expansion value of 0.04, η_2 at $2 - \gamma_2/\nu \approx 1.5$, and $\xi_{\|1}$ and $\xi_{\perp 1}$ at their values determined from $S_1(\mathbf{q})$ at each temperature (shown in Fig. 2). Using Eq. (10) in Eq. (5), we have then fitted the structure factor S_2 for $10^{-5} < t < 10^{-4}$, close to T_c, and found good fits for $A_2 \approx 0.01$. At these temperatures, S_2 is dominated by the second term in Eq. (5) (see top of Fig. 1). Setting $A_2 = 0.01$ for all T, we were left at each temperature with the single adjustable parameter $\mu_2\chi_2$. Finally, we fitted $S_2(\mathbf{q})$ at each temperature, and found the value of this parameter. As can be seen from Fig. 1, the fits to both the transverse and longitudinal scans over the complete temperature range from $t \sim 10^{-2}$ to $t \sim 10^{-5}$ are very good, comparable in quality to the original single Lorentzian fits reported in Ref. [5]. This gives strong support to the above theory. The critical second harmonic susceptibility so obtained is also shown in Fig. 2. Fits by a single power law give $\gamma_2 = 0.44 \pm 0.1$, again in agreement with the theoretical prediction $\gamma_2 = 0.32 \pm 0.04$ [3].

Clearly, this new theory is completely consistent with the experimental data on the second harmonic critical fluc-

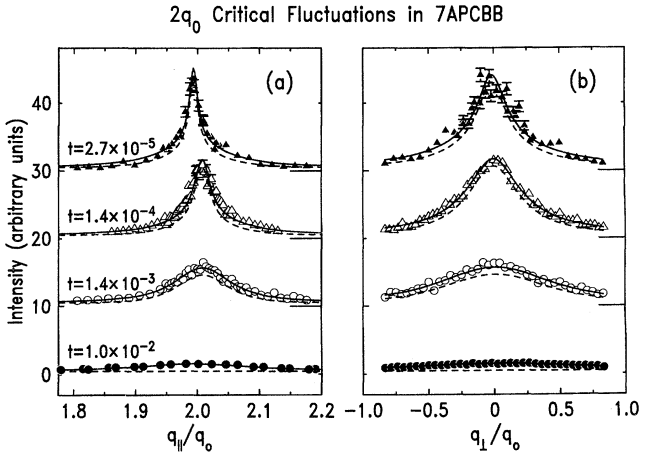

Fig. 1. (a) Longitudinal x-ray scans through the $2q_0$ peaks in 7APCBB at various reduced temperatures, $t = (T - T_c)/T_c$. (b) Corresponding transverse x-ray scans. For clarity, each scan is shifted by 10 counts/s in intensity. The solid lines are the results of least squares fits by Eq. (5), as explained in the text, convoluted with the instrumental resolution. The dashed lines correspond to the contributions from the second term of Eq. (5). The data at $t = 1.0 \times 10^{-2}$ (and at eight lower temperatures) were taken with a lower resolution and then normalized to match the intensity of the earlier measurements in the overlap region.

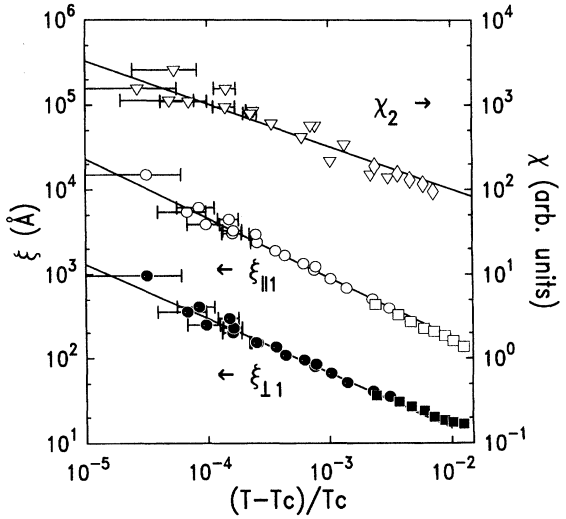

Fig. 2. The susceptibility χ_2 for the second harmonic at $2q_0$ in the nematic phase of 7APCBB. The solid line shows a single power law with the exponent 0.44. Also shown are data for the longitudinal and transverse correlation lengths for the first harmonic, $\xi_{\|1}$ and $\xi_{\perp 1}$, respectively, with the XY model exponent $\nu = 0.669$. The eight points farthest from T_c are additional data taken on the same sample at a later date and normalized to match the intensity of the earlier data [6].

tuations in 7APCBB, including the ϵ-expansion estimate for X_2. Proving uniqueness as well as further optimization of the parameters would require a detailed theoretical expression replacing our approximate Eq. (10), as well as more precise experimental data. It would be most valuable to search for similar effects in other systems with XY-like DW ordering, and in systems exhibiting critical fluctuations in other secondary order parameters. As seen from our Eqs. (4) and (5), the chances to observe higher harmonics are increased when the couplings among the harmonics, represented by the coupling coefficients μ_n, are strong, and when the bare susceptibilities χ_{nb} are large, that is, the T_n's are not too far from each other.

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