

Critical behavior of energy-energy, strain-strain, higher-harmonics, and similar correlation functions

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The structure factor associated with general biquadratic correlation functions is calculated for an n -component order parameter using ϵ -expansion techniques in $d=4-\epsilon$ dimensions. The results apply to energy-energy and strain-strain correlations as well as to correlations of higher harmonics in density wave systems. We find the correlations of these secondary order parameters to be characterized by a correlation length $\hat{\xi} = \hat{\xi}_0[(T-T_c)/T_c]^{-\nu}$, with the same n -dependent exponent ν as for the correlation length characterizing fluctuations of the primary order parameter, which is denoted by ξ . The amplitude ratio $\hat{X} \equiv (\hat{\xi}_0/\xi_0)^2$ is universal, and we obtain $X_T = \gamma_T/6\gamma + O(\epsilon^3)$ for quadratic order parameters transforming like a traceless spin tensor in n -component space (with γ_T characterizing the divergence of the corresponding susceptibility) and $X_E = \alpha/6\gamma + O(\epsilon^3)$ for energy-energy correlations, where α and γ denote the usual specific heat and susceptibility critical exponents, respectively. The universal amplitude ratio for the second harmonic in density wave systems is given by X_T with $n=2$ and takes the value $X_2 = \epsilon/20 - \epsilon^2/100 + O(\epsilon^3)$, thus being very small. This naturally explains previously puzzling experimental results for the critical behavior of the second harmonic structure factor at the nematic-smectic- A_2 transition of a thermotropic liquid crystal. Applications to sound attenuation in liquids or solids close to critical transitions and to colloidal interactions in near-critical binary mixtures are briefly discussed. [S1063-651X(97)12802-1]

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I. INTRODUCTION

The direct relation between the scattering intensity $G(q)$ near a critical point and the Fourier transform of the two-point correlation function

$$G(\mathbf{q}) \propto \int \frac{d^d \mathbf{x}}{(2\pi)^{d/2}} e^{i\mathbf{q} \cdot \mathbf{x}} \langle \vec{\phi}(\mathbf{0}) \cdot \vec{\phi}(\mathbf{x}) \rangle \quad (1)$$

has made the correlation function of central interest both for theorists and experimentalists. In Eq. (1) the integration extends over a d -dimensional system, with $\vec{\phi}$ denoting an n -component vector field.

The hypothesis of scaling asserts that, when the critical temperature is approached, i.e., when $T \rightarrow T_c$, and $qa \ll 1$ (where a is the lattice spacing), the two-point correlation function has the asymptotic form [1]

$$G(q, t) = \chi_0 t^{-\gamma} f(q^2 \xi^2), \quad (2)$$

which defines the scaling function $f(x^2)$; the reduced temperature t is defined as

$$t \equiv (T - T_c)/T_c.$$

The two-point correlation length ξ varies asymptotically (which means in the limit $t \rightarrow 0$) as

$$\xi(t) = \xi_0 a t^{-\nu}. \quad (3)$$

The susceptibility is obtained from the correlation function at zero momentum $q=0$, and is asymptotically given by

$$\chi(t) \equiv G(0, t) = \chi_0 t^{-\gamma}. \quad (4)$$

The exponents γ and ν give the strength of divergence of the susceptibility $\chi(t)$ and the correlation length $\xi(t)$, respectively, and are universal features of the physical system; they depend only on a few parameters such as dimensionality d and the number of components n of the order parameter.

Apart from a rather natural normalization of $f(x^2)$, given by

$$f(0) = 1, \quad \left. \frac{df(x^2)}{dx^2} \right|_{x=0} = -1, \quad (5)$$

the scaling function $f(x^2)$ is universal to the same degree as the exponents [2]. The second normalization condition in Eq. (5) means that $\xi(t)$ is identified as the second-moment correlation length defined through the second spatial moment of the correlation function $G(\mathbf{r}) = \langle \vec{\phi}(\mathbf{0}) \cdot \vec{\phi}(\mathbf{r}) \rangle$. It follows that the structure factor can, at least for small values of $q^2 \xi^2$, be written in the standard way as

$$G(q, t) = \frac{\chi_0 t^{-\gamma}}{1 + q^2 \xi^2} + O(q^4). \quad (6)$$

The amplitudes χ_0 and ξ_0 are nonuniversal parameters depending explicitly on details of the interaction, lattice structure, etc.

In this paper we extend the analysis to biquadratic correlation functions which describe the fluctuations of secondary, quadratic local order parameters $\varphi(\mathbf{r})$. These secondary order parameters show critical behavior due to a coupling to

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the primary fluctuating field $\vec{\phi}(\mathbf{r})$. Two distinct choices for the symmetry of $\varphi(\mathbf{r})$ emerge: the first choice is given by the local energy density, which is defined by

$$\varphi_E(\mathbf{r}) \equiv \phi_i(\mathbf{r}) \phi_i(\mathbf{r}). \quad (7)$$

The indices refer to the n components of the field $\vec{\phi}$; repeated indices are always summed over. One notes that $\varphi_E(\mathbf{r})$ is isotropic in the n -component space. The second choice is an anisotropic secondary order parameter [3], which can be written as

$$\varphi_T(\mathbf{r}) \equiv \phi_i(\mathbf{r}) \phi_j(\mathbf{r}), \quad (8)$$

with $i \neq j$. Experimental realizations of this order parameter include quite generally anisotropic couplings in ordering systems such as strains in certain crystals (see Sec. III A).

As will be shown in detail in Sec. III B, the field φ_T for the special case $n=2$ corresponds to the second harmonic order parameter in density wave systems. The correlations of fluctuations in this secondary order parameter have recently been determined experimentally for a liquid crystal at the nematic–smectic-*A* transition using high-resolution x-ray scattering techniques [4]. There it was found that the correlation length associated with fluctuations in the second harmonic order parameter scaled rather differently from the correlation length associated with the first harmonic, which is the primary order parameter. Fitting the data to a single Lorentzian, the two exponents for the divergence of the correlation length differed markedly, and hyperscaling was severely violated for the second harmonic. Some of the results described in the present paper were reported previously, together with a detailed comparison with additional measurements, leading to an interesting reinterpretation of these experimental results in accord with scaling theory [5]. In all of what follows, a symbol with a hat stands for the two versions corresponding to the choices $\hat{\varphi} = \varphi_E$ and $\hat{\varphi} = \varphi_T$, which are, only if necessary, distinguished by an index *E* or *T*, respectively.

To summarize our results, the two-point correlation function of the secondary order parameters $\hat{\varphi}$ can be written in the same form as Eq. (2), namely,

$$\hat{G}(q, t) = \hat{\chi}_0 t^{-\hat{\gamma}} \hat{f}(q^2 \hat{\xi}^2), \quad (9)$$

and constitutes a subclass of biquadratic correlation functions obtained from the general four-point correlation function by a pairwise contraction of field coordinates. It is assumed that the identical normalization conditions (5) apply to the biquadratic scaling function $\hat{f}(x^2)$, which naturally defines the biquadratic correlation length $\hat{\xi}$. The critical behavior at zero momentum ($x=0$) is well known; the exponents $\gamma_E \equiv \alpha$ and γ_T are different from the susceptibility exponent γ for the primary order parameter ϕ , and are determined by the respective crossover exponents, see Sec. II A.

Interesting information is obtained about the critical behavior at finite momentum, which can be inferred from the scaling functions $f_E(x^2)$ and $f_T(x^2)$ for $x > 0$. Specifically, it is found that the correlation lengths of all biquadratic and bilinear correlation functions scale with the same exponent

ν , contrary to what had been initially inferred from experiments on second harmonic scattering in liquid crystal systems [4]. Ratios of quantities which diverge with identical exponents commonly approach universal values in the asymptotic limit [6]. The universal amplitude ratios of the different correlation lengths are given by

$$\begin{aligned} X_E \equiv \left(\frac{\xi_0^E}{\xi_0} \right)^2 &= \epsilon \frac{4-n}{12(n+8)} - \epsilon^2 \frac{(n+2)(13n+44)}{12(n+8)^3} + O(\epsilon^3) \\ &= \frac{\alpha}{6\gamma} + O(\epsilon^3), \end{aligned} \quad (10)$$

$$\begin{aligned} X_T \equiv \left(\frac{\xi_0^T}{\xi_0} \right)^2 &= \epsilon \frac{4+n}{12(n+8)} + \epsilon^2 \frac{n^2 - 18n - 88}{12(n+8)^3} + O(\epsilon^3) \\ &= \frac{\gamma_T}{6\gamma} + O(\epsilon^3). \end{aligned} \quad (11)$$

One important feature of these universal ratios is that the first term in these series is already of order ϵ , leading to a logarithmic divergence as $\epsilon \rightarrow 0$. Experimentally relevant is the independent observation that the combinatorial prefactors in Eqs. (10) and (11) are quite small.

In Sec. II we first reproduce the critical behavior for zero momentum; then we present our ϵ -expansion results for the scaling function $\hat{f}(x^2)$ for small momentum $x \ll 1$ and in the limit $x \rightarrow \infty$. Based on the series expansion of $\hat{f}(x^2)$ in terms of x^2 , we give a closed-form approximant for $\hat{f}(x^2)$ which interpolates between and reproduces these two limits. We add a discussion of corrections to scaling and the limit $\epsilon \rightarrow 0$. The latter limit corresponds to the dimensionality $d \rightarrow 4$ for normal short-ranged interactions, but also includes the experimentally relevant dimensionality $d \rightarrow 3$ for dipolar interactions [7]. Section III contains the application of these results to density wave systems, strain-strain correlation functions, and colloidal interactions in near-critical binary mixtures, followed by a discussion and a brief outlook.

II. BIQUADRATIC CORRELATION FUNCTIONS

A. Scaling at zero momentum

The behavior of the $q=0$ part of the structure factor of secondary order parameters can be understood in terms of a simple scaling model for the free energy F [8],

$$F(t, h_T) \sim |t|^{2-\alpha} w(h_T/|t|^{\Phi_T}), \quad (12)$$

where $\Phi_T = \nu \gamma_T$ is the crossover exponent associated with the generating field h_T , which couples linearly to φ_T ; likewise, the energy operator φ_E couples to the temperature t . The scaling function $w(x)$ satisfies $w(0)=1$. From the above ansatz one immediately obtains

$$\langle \varphi_T^2 \rangle_C = \partial^2 F / \partial h_T^2 \sim |t|^{-\gamma_T}, \quad (13)$$

where the subscript *C* denotes the cumulant and $\gamma_T = \alpha - 2 + 2\Phi_T$. Using the result [9]

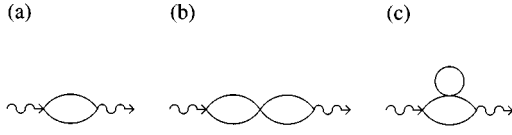


FIG. 1. Graphs that have to be evaluated at finite external momentum \mathbf{q} and finite bare mass r_0 . The graph in (a) is defined by $\Omega(\mathbf{q}, r_0)$, the graph in (b) is then given by $\Omega(\mathbf{q}, r_0)^2$, and the graph in (c) is canceled by mass renormalization.

$$y_T = 2 - \epsilon \frac{2}{n+8} + \epsilon^2 \frac{n^2 - 18n - 88}{2(n+8)^3} + O(\epsilon^3), \quad (14)$$

one obtains for the exponent γ_T the value [8,4]

$$\gamma_T = \epsilon \frac{n+4}{2(n+8)} + \epsilon^2 \frac{(n-2)(n+4)(n+14)}{4(n+8)^3} + O(\epsilon^3). \quad (15)$$

The analogous calculation for the energy-energy correlations trivially yields $\gamma_E = \alpha$. One notes that γ_T as well as α are of leading order ϵ .

B. Scaling at small finite momentum

The Hamiltonian appropriate for the study of the critical scattering of higher-order n vector correlation functions can be written in standard form as [10]

$$\begin{aligned} \mathcal{H}/T = & \int_{\mathbf{q}} \left\{ \frac{1}{2} (r_0 + q^2 + \Lambda^{-2} q^4) \phi_i(\mathbf{q}) \phi_i(-\mathbf{q}) \right\} \\ & + \frac{u}{(2\pi)^d} \int_{\mathbf{q}} \int_{\mathbf{q}'} \int_{\mathbf{q}''} \phi_i(\mathbf{q}) \phi_i(\mathbf{q}') \phi_j(\mathbf{q}'') \\ & \times \phi_j(-\mathbf{q} - \mathbf{q}' - \mathbf{q}''), \end{aligned} \quad (16)$$

with the shorthand notation $\int_{\mathbf{q}} \equiv \int d^d \mathbf{q}$, and with Λ representing a smooth cutoff [11]. In the resulting equations we set $\Lambda = 1$ (the universal results do not depend on Λ). The two-point correlation functions of the quadratic local fields defined in Sec. I are then given by

$$\begin{aligned} \hat{G}(\mathbf{q}, r_0) & \equiv \langle \hat{\phi}(\mathbf{q}) \hat{\phi}(-\mathbf{q}) \rangle \\ & = \frac{1}{(2\pi)^d} \int_{\mathbf{p}} \int_{\mathbf{p}'} \langle \phi_i(\mathbf{p}) \phi_j(\mathbf{q}-\mathbf{p}) \phi_i(\mathbf{p}') \\ & \times \phi_j(-\mathbf{q}-\mathbf{p}') \rangle_C, \end{aligned} \quad (17)$$

with $i=j$ for correlations of the energylike local field φ_E or $i \neq j$ for the traceless local field φ_T . Expanding up to first order in the four-point vertex u (which is a two-loop expansion; see Fig. 1), one obtains the following expression for the correlation function:

$$\frac{\hat{G}(q, r)}{\hat{M}} = 2\Omega(q, r) - 16u\hat{N}\Omega(q, r)^2, \quad (18)$$

with the combinatorial factors \hat{N} and \hat{M} given by

$$\hat{N} = \begin{cases} N_E = 1 + n/2, \\ N_T = 1, \end{cases} \quad (19)$$

$$\hat{M} = \begin{cases} M_E = n, \\ M_T = n(n-1), \end{cases} \quad (20)$$

Ω denotes the subgraph defined by

$$\Omega(q, r_0) \equiv \frac{1}{(2\pi)^d} \int_{\mathbf{p}} G^{(0)}(\mathbf{p} + \mathbf{q}) G^{(0)}(\mathbf{p}), \quad (21)$$

with the bare propagator $G^{(0)}$ given by

$$G^{(0)}(\mathbf{q}) = \frac{1}{\mathbf{q}^2 + r_0 + \Lambda^{-2} \mathbf{q}^4}. \quad (22)$$

The integrals corresponding to the first and second terms in Eq. (18) which are proportional to Ω and Ω^2 are graphically represented in Figs. 1(a) and 1(b), respectively. The graph in Fig. 1(c) is canceled by appropriate mass renormalization, i.e., by replacing the bare parameter r_0 by its renormalized value, the true susceptibility $r \equiv 1/\chi \sim t^\gamma$ [10]. Note that at this level of perturbation theory, no such renormalization takes place for the four-point coupling strength u .

Using the result for Ω derived in the Appendix, Sec. 1, and expanding in powers of ϵ , the correlation function (18) can be written as

$$\begin{aligned} \frac{\hat{G}(q, r)}{\hat{M} K_d \hat{\chi}_0} & = \hat{C} - \ln r + \frac{\hat{z}(u)}{2} \ln^2 r - \frac{q^2}{6r} [1 - \hat{z}(u) \ln r] \\ & + O(\epsilon^2, u^2, \epsilon u, q^4), \end{aligned} \quad (23)$$

with

$$\hat{\chi}_0 \equiv [1 - \hat{z}(u)] \left(1 + \frac{u}{u^*} \frac{2\epsilon\hat{N}}{n+8} \right), \quad (24)$$

and $\hat{C} \equiv -2[1 - \hat{z}(u)]$. In the above equation, u^* denotes the fixed-point value of u , and is given by [10]

$$u^* = \frac{\epsilon}{4K_d(n+8)} + O(\epsilon^2) = \frac{2\epsilon\pi^2}{n+8} + O(\epsilon^2). \quad (25)$$

The function $\hat{z}(u)$ reads

$$\hat{z}(u) \equiv \frac{u}{u^*} \frac{\epsilon}{2} - \frac{2\epsilon\hat{N}}{n+8}. \quad (26)$$

For the calculation of critical exponents and amplitude ratios, one fixes u at its fixed point value u^* ; the critical exponent $\hat{\gamma}$ can be obtained from Eq. (23) by the usual method of exponentiating logarithms according to the expansion

$$r^{-\hat{\gamma}} = 1 - (\hat{z}_1 \epsilon - \hat{z}_2 \epsilon^2) \ln r + \frac{1}{2} \hat{z}_1^2 \epsilon^2 \ln^2 r + O(\epsilon^3), \quad (27)$$

and is given in terms of the function $\hat{z}(u)$ by

$$\hat{\gamma}/\gamma = \hat{z}(u^*) \equiv \hat{z}_1 \epsilon - \hat{z}_2 \epsilon^2 + O(\epsilon^3). \quad (28)$$

Note that, since $\hat{z}(u)$ is only known to order ϵ from our two-loop expansion, we cannot obtain \hat{z}_2 . But, as will be shown below, we can in fact calculate critical amplitude ratios up to $O(\epsilon^2)$. For these calculations we need the values of \hat{z}_2 as well, which are taken from the literature. With the well-known values for the susceptibility and heat-capacity exponents [10]

$$\gamma = 1 + \epsilon \frac{n+2}{2(n+8)} + \epsilon^2 \frac{(n+2)(n^2+22n+52)}{4(n+8)^3} + O(\epsilon^3), \quad (29)$$

$$\alpha = \epsilon \frac{4-n}{2(n+8)} - \epsilon^2 \frac{(n+2)^2(n+28)}{4(n+8)^3} + O(\epsilon^3), \quad (30)$$

and γ_T given by Eq. (15), one obtains the explicit values

$$z_1^E = \frac{4-n}{2(n+8)}, \quad (31)$$

$$z_2^E = \frac{(n+2)(13n+44)}{2(n+8)^3}, \quad (32)$$

$$z_1^T = \frac{4+n}{2(n+8)}, \quad (33)$$

$$z_2^T = \frac{88+18n-n^2}{2(n+8)^3}. \quad (34)$$

With these notations the biquadratic correlation function at the fixed-point coupling strength u^* can be written as

$$\frac{\hat{G}(q,r)}{\hat{M}K_d \hat{\chi}_0} = \hat{C} - \frac{\gamma}{\hat{\gamma}} + \frac{\gamma r^{-\hat{\gamma}/\gamma}}{\hat{\gamma}} \hat{g}(q^2/r) + O(\epsilon^2), \quad (35)$$

with the scaling function $\hat{g}(x^2)$ for small arguments $x^2 \ll 1$ given by

$$\hat{g}(x^2) = 1 - \frac{\hat{\gamma}}{6\gamma} x^2 + O(\epsilon^3, x^4). \quad (36)$$

Comparison with the definition of the scaling function $\hat{f}(x^2)$, Eq. (9), and using the second normalization condition in Eq. (5), one immediately identifies $\hat{f}(\hat{\gamma}x^2/6\gamma) = \hat{g}(x^2)$ and thus

$$\hat{\xi}^2 = \frac{\hat{\gamma}}{6\gamma} r^{-1} + O(\epsilon^3). \quad (37)$$

Noting that, for the Hamiltonian given by Eq. (16), the bilinear correlation length ξ can be calculated to be $\xi = r^{-1/2} + O(\epsilon^2)$, we obtain our two main results from Eq. (37): (i) the bilinear correlation length ξ and the biquadratic correlation lengths ξ_E and ξ_T scale with the same exponent ν to leading order in ϵ , in agreement with the general scaling hypothesis, stating that there is a single length scale in the asymptotic limit; and (ii) the ratio between the two correlation lengths, defined by $\hat{X} \equiv \hat{\xi}^2/\xi^2$, approaches the universal value

$$\hat{X} \equiv \frac{\hat{\xi}^2}{\xi^2} = \frac{\hat{\gamma}}{6\gamma} + O(\epsilon^3) \quad (38)$$

in the asymptotic limit. Using the values for \hat{z}_1 and \hat{z}_2 one obtains the universal amplitude ratios given in Eqs. (10) and (11). For negative values of $\hat{\gamma}/\gamma$ (as, e.g., observed for energy-energy correlation for $n=2$) one therefore obtains a negative value for the amplitude ratio \hat{X} . This at first glance surprising result can be understood since in this case the singular contribution to the biquadratic susceptibility itself is negative, leading to a cusplike finite maximum at the critical point. A negative \hat{X} then corresponds to an attenuation of the singular contribution for increasing values of q , as expected.

C. Scaling at the critical point

Right at the critical point, defined by $r=0$, the biquadratic correlation function scales asymptotically like

$$\hat{G}(q,r=0) \sim q^{\hat{\eta}-2}, \quad (39)$$

defining the exponent $\hat{\eta}$, which can be expressed in terms of the other exponents via the scaling relation

$$2 - \hat{\eta} = \frac{\hat{\gamma}}{\nu}. \quad (40)$$

From the definition of the correlation function (18) and the explicit expression for $\Omega(q,0)$, derived in the Appendix, Sec. 2, one obtains

$$\frac{\hat{G}(q,r=0)}{\hat{M}K_d} = (1 + \epsilon/2) \left[\epsilon \left(1 - \frac{\pi^2}{12} \right) - 2 \ln q (1 - \hat{z}(u) \ln q) \right] + O(u^2, \epsilon^2, u\epsilon), \quad (41)$$

with $\hat{z}(u)$ given by Eq. (26). From the above expansion one readily obtains $2 - \hat{\eta} = 2\hat{z}(u^*) + O(\epsilon^2)$; using $\gamma/\nu = 2 + O(\epsilon^2)$ and Eq. (28), one confirms the scaling relation (40) to order ϵ . Using the knowledge about $\hat{\gamma}$ to order ϵ^2 , and the scaling relation (40), the exponents $\hat{\eta}$ are explicitly given by

$$\eta_E = 2 - \epsilon \frac{4-n}{8+n} + \epsilon^2 \frac{(2+n)(44+13n)}{(n+8)^3} + O(\epsilon^3), \quad (42)$$

$$\eta_T = 2 - \epsilon \frac{4+n}{n+8} + \epsilon^2 \frac{88+18n-n^2}{(n+8)^3} + O(\epsilon^3). \quad (43)$$

These exponents are quite large, unlike the result for η for the bilinear correlation function, and higher-order corrections to the expansion of the scaling function $\hat{g}(x^2)$ for small arguments are expected to be important. Using the definition of the scaling function $\hat{g}(x^2)$, Eq. (35), the functional behavior for large arguments $x \gg 1$ can be calculated to be

$$\hat{g}(x^2) = (1 + 2\hat{\gamma}/\gamma) x^{\hat{\eta}-2} + O(\epsilon^2). \quad (44)$$

A heuristic expression for $\hat{g}(x^2)$, valid for both small and large arguments, will be presented in Sec. II F.

D. Corrections to scaling

In this section we discuss corrections to scaling due to the crossover from mean-field behavior, at high temperatures, to the asymptotic critical behavior below the Ginzburg temperature. This crossover can be calculated explicitly within the ϵ expansion.

Generalizing the analysis of the scaling corrections for the specific heat by Rudnick and Nelson [12], we write the biquadratic correlation function \hat{G} at zero momentum and the inverse susceptibility r as

$$\hat{G}(t) = \frac{\hat{M}}{2(4-n)} \frac{1}{u} \left\{ \left[1 + \frac{u}{u^*} (t^{-\epsilon/2} - 1) \right]^{2\hat{z}_1} - 1 \right\} + O(u^2, \epsilon u, \epsilon^2), \quad (45)$$

$$r(t) = t \left[1 + \frac{u}{u^*} (t^{-\epsilon/2} - 1) \right]^{-(n+2)/(n+8)} + O(u^2, \epsilon u, \epsilon^2), \quad (46)$$

where t is the nonlinear scaling field associated with the temperature. These functions can be derived from approximate solutions of the differential recursion relations [13–15]. Combining these expressions, the biquadratic correlation function for finite momentum can be expressed to the same order of accuracy and including only terms up to q^2 as

$$\frac{\hat{G}(q, r)}{\hat{M}K_d} = \frac{u^*}{\epsilon u \hat{z}_1} \left\{ \left[1 + \frac{u}{u^*} (r^{-\epsilon/2} - 1) \right]^{2\hat{z}_1} - 1 \right\} - \frac{q^2}{6r} r^{-\epsilon/2} \left[1 + \frac{u}{u^*} (r^{-\epsilon/2} - 1) \right]^{2\hat{z}_1 - 1}, \quad (47)$$

with \hat{z}_1 and u^* defined in Sec. II B. For the following, it is useful to separate the regular part of the first term, leading to

$$\frac{\hat{G}(q, r)}{\hat{M}K_d} = \frac{u^*}{\epsilon u \hat{z}_1} \left[1 + \frac{u}{u^*} (r^{-\epsilon/2} - 1) \right]^{2\hat{z}_1} \hat{\mathcal{F}}(q, r) - \frac{u^*}{\epsilon u \hat{z}_1}, \quad (48)$$

with the scaling function $\hat{\mathcal{F}}(q, r)$ defined by

$$\hat{\mathcal{F}}(q, r) = 1 - \frac{q^2}{6r} \frac{\epsilon u \hat{z}_1}{u^*} r^{-\epsilon/2} \left[1 + \frac{u}{u^*} (r^{-\epsilon/2} - 1) \right]^{-1}. \quad (49)$$

Fixing the four-point coupling strength at its fixed-point value, $u = u^*$, one reproduces the results from Sec. II B to $O(\epsilon)$. In contrast, corrections to scaling arise from the slow crossover connected with deviations of the four-point coupling strength u from its fixed-point value. Defining the effective biquadratic susceptibility exponent $\hat{\gamma}_{\text{eff}}$ as

$$\hat{\gamma}_{\text{eff}} \equiv - \frac{\partial \ln[\hat{G}(q=0, r(t))/\hat{M}K_d]}{\partial \ln t}, \quad (50)$$

one obtains (using as a definition for the effective normal susceptibility exponent the expression $\gamma_{\text{eff}} \equiv \partial \ln r / \partial \ln t$) the result

$$\frac{\hat{\gamma}_{\text{eff}}}{\gamma_{\text{eff}}} = \frac{\epsilon u \hat{z}_1}{u^*} r^{-\epsilon/2} \left[1 + \frac{u}{u^*} (r^{-\epsilon/2} - 1) \right]^{-1}. \quad (51)$$

Using this relation, which holds beyond the asymptotic regime since it includes corrections to scaling, one finally obtains for the scaling function the result

$$\hat{\mathcal{F}}(q, r) = 1 - \frac{\hat{\gamma}_{\text{eff}}}{6\gamma_{\text{eff}}} \frac{q^2}{r} = 1 - \frac{\hat{\gamma}_{\text{eff}}}{6\gamma_{\text{eff}}} \xi^2 q^2, \quad (52)$$

and, for the universal amplitude ratio,

$$\hat{X}_{\text{eff}} = \frac{\hat{\gamma}_{\text{eff}}}{6\gamma_{\text{eff}}}, \quad (53)$$

which is a generalization of the asymptotic result (38). The above relation has recently been checked using cluster Monte Carlo simulation techniques for energy-energy correlations in two- and three-dimensional Ising models, and agrees well with the numerical results [16].

E. Behavior for $\epsilon \rightarrow 0$

Since the amplitude ratios \hat{X} calculated in Sec. II B are of leading order ϵ , it is important and interesting to examine the limiting behavior for $\epsilon \rightarrow 0$. This corresponds to the limiting behavior, obtained for normal short-ranged interactions for the (unphysical) dimensionality $d=4$. However, it is important to note that this upper critical dimension is reduced for long-ranged interactions, and is realized at the (physical) dimensionality $d=3$ for dipolar interactions [7].

To obtain the correct behavior for $\epsilon \rightarrow 0$ from the expressions (48) and (49), it is important *not* to set $u = u^*$, since the coupling strength u becomes marginally relevant as $\epsilon \rightarrow 0$, leading to logarithmic correction terms. In the limit $\epsilon \rightarrow 0$, expression (48) for the biquadratic correlation function reduces to

$$\frac{\hat{G}(q, r)}{\hat{M}K_d} \simeq \frac{1}{4u\hat{z}_1 K_d(n+8)} [1 - 2uK_d(n+8) \ln r]^{2\hat{z}_1} \hat{\mathcal{F}}(q, r), \quad (54)$$

with

$$\hat{\mathcal{F}}(q, r) \simeq 1 + \frac{q^2}{3r} \frac{\hat{z}_1}{\ln r}. \quad (55)$$

To obtain the limiting behavior as a function of the temperaturelike scaling field t , one first has to evaluate Eq. (46) in the limit $\epsilon \rightarrow 0$ and $t \rightarrow 0$, which yields

$$r \simeq t \left(- \frac{\epsilon u}{2u^*} \ln t \right)^{-(n+2)/(n+8)}. \quad (56)$$

Inserting this into Eq. (54) and (55), one finally obtains

$$\frac{\hat{G}(q, t)}{\hat{M}K_d} \simeq \frac{1}{4u\hat{z}_1 K_d(n+8)} [1 - 2uK_d(n+8) \ln t]^{2\hat{z}_1} \hat{\mathcal{F}}(q, t) + O(\ln \ln t), \quad (57)$$

with

$$\hat{\mathcal{F}}(q,t) \approx 1 - \frac{q^2 \hat{z}_1}{3t} [2uK_d(n+8)]^{(n+2)/(n+8)} (-\ln t)^{-6/(n+8)} + O\left(\frac{(-\ln t)^{-6/(n+8)} \ln \ln t}{t}\right). \quad (58)$$

Recalling the well-known result for the quadratic correlation length ξ in the limit $\epsilon \rightarrow 0$ and $t \rightarrow 0$ [17],

$$\xi^2 \sim \frac{(-\ln t)^{(n+2)/(n+8)}}{t}, \quad (59)$$

and identifying from Eq. (58) the biquadratic correlation length $\hat{\xi}$ to be given by

$$\hat{\xi}^2 \sim \frac{\hat{z}_1 (-\ln t)^{-6/(n+8)}}{t}, \quad (60)$$

for the ratio of the quartic and quadratic correlation lengths in the limit $\epsilon \rightarrow 0$ one finally obtains the result

$$\frac{\hat{\xi}^2}{\xi^2} \sim \frac{\hat{z}_1}{-\ln t}. \quad (61)$$

The universal amplitude ratio \hat{X} , which was found to be proportional to ϵ , is replaced by a logarithmic singularity as $\epsilon \rightarrow 0$.

As already mentioned, the limit $\epsilon \rightarrow 0$ is realized for certain dipolar Ising ferromagnets [18,19]. Measurements of the biquadratic correlation length $\hat{\xi}$ could in principle be possible using sound-adsorption techniques (see Sec. III), which would allow a direct check of Eq. (59)–(61).

F. Higher-order terms in q^2

Using the expression for \hat{G} in Eq. (18) and the result for Ω including higher powers of q^2 (Appendix, Sec. 1), the biquadratic correlation function can be written as

$$\frac{\hat{G}(q,r)}{\hat{M}K_d\hat{\chi}_0} = \hat{C} - \ln r + \frac{1}{2} \epsilon \hat{z}_1 \ln^2 r + \sum_{i=1}^{\infty} \left(\frac{-q^2}{r}\right)^i \times \left[[1 - \epsilon \hat{z}_1 \ln r + \epsilon Y_1(i)] \Xi(i) - \frac{\epsilon}{4} (1 - 2\hat{z}_1) \Theta(i) Y_1(i) \right] + O(\epsilon^2). \quad (62)$$

The constants $\hat{\chi}_0$ and \hat{C} were previously defined in Sec. II B; the numerical factor $\Theta(i)$ is defined by

$$\left(\sum_{i=1}^{\infty} (-x)^i \Xi(i) \right)^2 = \sum_{i=1}^{\infty} (-x)^i \Theta(i). \quad (63)$$

The first four values of the constants $Y_1(i)$, $\Xi(i)$, and $\Theta(i)$ are given in Table I. The inverse scaling function $\hat{g}^{-1}(q^2/r)$ is obtained by dividing Eq. (62) by $r^{-\hat{\gamma}/\gamma}$ ($\hat{\gamma}/\gamma$), as was done in Sec. II B, leading to

TABLE I. Values of the first numerical coefficients appearing in the scaling function.

	$\Xi(i)$	$Y_1(i)$	$\Theta(i)$
$i=1$	$\frac{1}{6}$	0	0
$i=2$	$\frac{1}{60}$	1/2	1/36
$i=3$	$\frac{1}{420}$	3/4	1/180
$i=4$	$\frac{1}{2520}$	11/12	47/2520

$$\hat{g}^{-1}(x^2) = 1 - \sum_{i=1}^{\infty} (-x^2)^i \Xi(i) \left[\epsilon \hat{z}_1 - \epsilon^2 \hat{z}_2 + \epsilon^2 \hat{z}_1 \times \left(Y_1(i) - \frac{\Theta(i)}{4\Xi(i)} \right) \right] + O(\epsilon^3). \quad (64)$$

In contrast to the analogous results for the scaling function of bilinear correlations [2], here the higher-order terms (in x^2) are of the same leading order in ϵ as the term proportional to x^2 , namely, $O(\epsilon)$. It turns out that the Fisher-Burford approximant [1], which has been successfully used to approximate the quadratic scaling function [2], does not reproduce the epsilon expansion of the quartic scaling function. For a lucid discussion of different phenomenological scaling function approximants, see [20]. In the following, we present a heuristic approximant for the scaling function which is valid both for small and large arguments,

$$\hat{g}^{\text{app}}(x^2) = \frac{\left(1 + \frac{a_1 x^2 + a_2 x^4 + a_3 x^6 + a_4 x^8 + \dots}{1 + a_2 x^2 + a_3 x^4 + a_4 x^6 + \dots} \right)^{\hat{\eta}/2}}{1 + (\hat{X} + a_1 \hat{\eta}/2) x^2}, \quad (65)$$

which reduces to the Fisher-Burford approximant if $a_i = 0$ for $i > 1$. For $x \ll 1$, one has

$$\hat{g}^{\text{app}}(x^2) = 1 - \hat{X} x^2 + O(x^4), \quad (66)$$

which, by construction, agrees with the asymptotic forms (36) and (38), and for $x \gg 1$ (and if $a_i \neq 0$ for at least one i with $i > 1$), one obtains

$$\hat{g}^{\text{app}}(x^2) = \frac{x^{\hat{\eta}-2}}{\hat{X} + a_1 \hat{\eta}/2}. \quad (67)$$

Clearly, the amplitude of $\hat{g}(x^2)$ for $x \gg 1$ fixes the coefficient a_1 . With the result (44), one readily finds

$$a_1 = 1 - \frac{7}{6} \epsilon \hat{z}_1 + O(\epsilon^2). \quad (68)$$

Each term in Eq. (64) of the order $(x^2)^i$ determines a parameter a_i ; going up to x^8 one obtains for the coefficients the values $a_2 = 3/10 + O(\epsilon)$, $a_3 = -199/4900 + O(\epsilon)$, and $a_4 = 2699/147\,000 + O(\epsilon)$, which reproduces the series in Eq. (64) up to order ϵ . In order to reproduce the higher terms including $O(\epsilon^2)$, one would have to know a_1 to $O(\epsilon^2)$, which requires a three-loop calculation.

III. EXPERIMENTAL APPLICATIONS

In the following we discuss some experimental systems where the biquadratic structure factor and the corresponding correlation length can or have been determined experimentally. We distinguish three different mechanisms that allow correlations of quadratic (secondary) order parameters to be measured.

(i) Local strains in a system close to a phase transition usually couple to the order parameter. Due to symmetry reasons, the lowest-order coupling is linear in the strain and quadratic in the order parameter. Measurements of strain-strain correlation functions, for example via sound attenuation experiments, include contributions proportional to biquadratic correlation functions and thus allow comparison with our results. This will be the subject of Sec. III A.

(ii) Colloids in near-critical binary mixtures act as local field and temperature perturbations, leading to mutual interactions that are proportional to bilinear and biquadratic correlation functions, respectively [21]. Under suitable conditions, the field perturbation can be suppressed [22], and the resultant interaction, proportional to the energy-energy correlation function, could be detected by light scattering experiments. Comparison of the resultant decay length ξ_E with the correlation length of the binary mixture, ξ , would then allow a determination of the universal amplitude ratio $X_E = (\xi_E/\xi)^2 \approx \alpha/(6\gamma)$ (with the exponents α and γ taking values according to the Ising universality class of the binary demixing critical point).

(iii) Higher harmonics in density-wave systems are coupled to the first-harmonic order parameter. At the critical point, characterized by the singular behavior of the first-harmonic order parameter, the higher-harmonic structure factors contain contributions which are proportional to higher-order correlation functions of the first-harmonic order parameter. Our results for the biquadratic structure factor correspond to the singular part of the second-harmonic structure factor, as will be explained in Sec. III B.

A. Coupling to elastic degrees of freedom

Elastic deformations of liquids or solids are defined by the strain tensor $e_{\alpha\beta}$, which is related to the displacement vector $\mathbf{u}(\mathbf{r})$ in the usual way by

$$e_{\alpha\beta} \equiv \frac{1}{2} \left(\frac{\partial u_\alpha}{\partial r_\beta} + \frac{\partial u_\beta}{\partial r_\alpha} \right). \quad (69)$$

The order parameter $\vec{\phi}(\mathbf{r})$, governed by the Hamiltonian (16), in general couples to these deformations. In the long-wavelength limit, the bare elastic Hamiltonian including the coupling terms can be written as [23,24]

$$\mathcal{H}_{\text{el}}/T = \int_{\mathbf{r}} \left\{ \frac{1}{2} \lambda_{\alpha\beta\gamma\delta} e_{\alpha\beta} e_{\gamma\delta} + b^{(E)} \phi_i \phi_i e_{\alpha\alpha} + b_{ij\alpha\beta}^{(T)} \phi_i \phi_j e_{\alpha\beta} \right\}. \quad (70)$$

Note that the bare coupling constants are only weakly temperature dependent. In a typical sound adsorption experiment, one measures the frequency-dependent attenuation coefficient, which is, via the fluctuation-dissipation theorem, directly related to the generalized elastic correlation function

$C_{\text{el}}(\omega, \mathbf{q}) = \int d\tilde{t} e^{i\omega\tilde{t}} \langle e_{\alpha\beta}(0, \mathbf{q}) e_{\alpha\beta}(\tilde{t}, -\mathbf{q}) \rangle$ [25], with \tilde{t} denoting time. Based on the simple Hamiltonian (70) we distinguish two contributions to the frequency-dependent strain-strain correlation function: (i) a temperature-independent background at zero frequency and zero wave vector, proportional to the inverse elastic modulus tensor λ , and (ii) singular contributions $C_{\text{el}}^{(E)}(\omega, \mathbf{q})$ and $C_{\text{el}}^{(T)}(\omega, \mathbf{q})$, which arise for nonvanishing constants $b^{(E)}$ and $b^{(T)}$, respectively, and are due to coupling of the elastic strain to the order parameter. The first is the isotropic coupling, and is present in liquids and solids alike, the latter anisotropic coupling is only present in solids and depends on the detailed lattice structure. These frequency-dependent correlation functions $C_{\text{el}}^{(E)}$ and $C_{\text{el}}^{(T)}$ are related to the equal-time structure factors $G_E(\mathbf{q})$ and $G_T(\mathbf{q})$, which were defined and calculated in Sec. II, simply by the Fourier transform

$$\hat{G}(\mathbf{q}) \sim \int_{-\infty}^{\infty} d\omega \hat{C}_{\text{el}}(\omega, \mathbf{q}), \quad (71)$$

where the caret stands for the subscripts T or E , as in Sec. II.

In analyzing experimental results, such an integral might be hard to perform in practice. Alternatively, one can use the dynamic scaling hypothesis, which predicts the frequency-dependent correlation functions to have the scaling form [26]

$$\hat{C}_{\text{el}}(\omega, \mathbf{q}) \sim t^{-z\nu} \hat{Y}(q^2 \xi^2, \omega\tau). \quad (72)$$

Here z denotes the dynamic exponent. So in principle the correlation lengths ξ_E and ξ_T might directly be calculated from $C_{\text{el}}(\omega, \mathbf{q})$ by fitting data at constant scaling variable $\omega\tau$, where $\tau \sim t^{-z}$ is the relaxation time, which diverges on approaching the critical point.

The energy-energy correlation function can thus be measured via sound attenuation in liquids close to a binary demixing or liquid-gas critical point; experimental realizations for the latter include ultrasonic attenuation in xenon near its critical point [27]. One notes that in order to determine the universal amplitude ratio between the two correlation lengths, one has to determine the ordinary correlation length independently with some light-scattering experiment.

Sound attenuation in crystals allows to access the tensorial structure factor as well [24]. The most prominent examples are structural phase transitions in perovskites, where measurements of longitudinal and transverse modes along different lattice directions allow independent determinations of the structure factors $G_E(\mathbf{q})$ and $G_T(\mathbf{q})$ [28,29].

B. Density wave systems

The order parameter of density waves (DW's) in a uniaxial system is characterized by the complex amplitude $\psi_1 = \psi_1^x + i\psi_1^y$, determined by the contribution $\text{Re}(\psi_1 e^{iq_0 z})$ to the density modulation, which runs parallel to the z axis. The wave vector q_0 is determined by the wavelength of the modulation. Since the order parameter ψ_1 has two independent components, the critical behavior associated with a continuous symmetry breaking of the thermal average of ψ_1 is described by the XY-model universality class. Examples in solids include charge density wave systems such as NbSe₃ [30], spin density wave systems such as Cr [31], and rare-

earth magnets. Two-dimensional freezing from a hexatic fluid to a solid is another example [32]. In three-dimensional complex fluids, such behavior is provided by the smectic-A phase of thermotropic liquid crystals [33]. The nematic phase of these rodlike liquid crystal molecules shows orientational order, but is positionally disordered. The nematic–smectic-A phase transition corresponds to the establishment of a one-dimensional mass density wave in the three-dimensional fluid with the mass density wave along the direction of orientational order. The smectic phase and the critical fluctuations associated with the onset of smectic ordering can be represented in terms of the above defined order parameter ψ_1 [34]. High-resolution x-ray scattering and ac-calorimetry experiments have indeed shown that many features of the nematic–smectic-A phase transition in liquid crystals are well described by the three-dimensional XY model, although the correlation lengths exhibit weakly anisotropic scaling [35].

Recently, there has been considerable interest in the critical behavior of higher harmonics, associated with the contributions $\text{Re}(\psi_m e^{imq_0 z})$ to the density modulation. Theoretically, the exponents describing correlation functions of the order parameters ψ_m were derived from the XY model which describes the leading order parameter ψ_1 [8], and the results were nicely confirmed by measurements of the bond orientational order harmonics in hexatic liquid crystals [36].

More recently, experiments on the nematic–smectic-A₂ (N–Sm-A₂) transition in the polar thermotropic liquid crystal material 4'-n-heptyloxy carbonylphenyl-4'-(4"-cyanobenzoyloxy) benzoate (7APCBB) succeeded in observing the critical fluctuations associated with the second harmonic of the DW order parameter [4]. Although these experiments confirmed the theoretical predictions for the second-harmonic susceptibility χ_2 fits of the second-harmonic structure factor $S_2(\mathbf{q})$ to a single Lorentzian shape yielded correlation lengths $\xi_{\parallel 2}$ and $\xi_{\perp 2}$, which seemed to scale very differently than 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_m 's for the different harmonics would imply that the N–Sm-A₂ transition involves more than one critical length scale, and that it cannot be simply described by the XY model. Furthermore, the fitted exponents $\nu_{\parallel 2}$ and $\nu_{\perp 2}$ severely violated the hyperscaling relation $2\nu_{\perp 2} + \nu_{\parallel 2} = 2 - \alpha$, with no explanation. The results presented in this paper clarify the critical behavior of higher harmonics in DW and similar systems. Specifically, all the harmonics are still dominated by the critical behavior of the XY model, and $\xi_m^2 = X_m \xi_1^2$ where X_m is a universal number; in particular, $X_2 = X_T$ with $n=2$, which was calculated in Sec. II. Since X_m may be quite small, the structure factor of the m th harmonic $S_m(\mathbf{q})$ may be strongly influenced by its bare (noncritical) value. Furthermore, since at the transition $S_m \sim q^{\eta_m - 2}$, with large values of η_m , deviations from the Lorentzian shape are also important. These theoretical results have been used to reinterpret the experimental results of Ref. [4], together with some measurements [5].

To proceed, we define the “local” m th harmonic order parameters as the slowly varying complex functions $\psi_m(\mathbf{r})$ determining the density:

$$\rho(\mathbf{r}) = \rho_0 + \text{Re} \sum_{m=1}^{\infty} \psi_m(\mathbf{r}) \exp(iq_0 m z). \quad (73)$$

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

$$\mathcal{H}_m = \int d^d \mathbf{r} \left\{ \frac{1}{2} r_{m0} [|\psi_m|^2 + \xi_{\parallel mb}^2 |\nabla_{\parallel} \psi_m|^2 + \xi_{\perp mb}^2 |\nabla_{\perp} \psi_m|^2] + u_m |\psi_m|^4 \right\}. \quad (74)$$

The distinct prefactors $\xi_{\parallel mb}^2$ and $\xi_{\perp mb}^2$ of the parallel and perpendicular gradient terms take into account the experimental fact of anisotropic correlation lengths. We must also take into account the coupling terms [5]

$$\mathcal{H}_{m,\text{int}} = \mu_m \int d^d \mathbf{r} (\psi_1^m \psi_m^* + \psi_1^{*m} \psi_m). \quad (75)$$

The correlation functions of the secondary order parameters, ψ_m 's with $m > 1$, can in principle be derived from Eqs. (74) and (75).

Assuming T_m to be far enough below T_1 , one has a single phase 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_m 's, and set $u_m = 0$ in Eq. (74). Thus the ψ_m 's for $m > 1$ can be treated in the harmonic approximation, and we can solve the partition function for ψ_m exactly in terms of the correlation functions of ψ_1 . For example, the average density modulation with the wave vector $m q_0 \hat{\mathbf{z}}$ is determined by

$$\Psi_m \equiv \langle \psi_m \rangle = \mu_m \chi_{mb} \langle \psi_1^m \rangle, \quad (76)$$

where $\chi_{mb} = 1/r_{m0}$ is the bare susceptibility for the m th harmonic. Since χ_{mb} is not singular at T_1 , the singularity comes only from $\langle \psi_1^m \rangle \propto |t|^{\beta_m}$, where $t = (T - T_c)/T_c$, $\beta_m = 2 - \alpha - \phi_m$ and ϕ_m is the crossover exponent associated with m th order anisotropy near the rotationally invariant XY model fixed point [8]. Specifically, ϕ_2 is the crossover exponent for a uniaxial anisotropy term, proportional to $\text{Re}(\psi_1^2) = (\psi_1^x)^2 - (\psi_1^y)^2$ or to $\text{Im}(\psi_1^2) = 2\psi_1^x \psi_1^y \equiv 2\varphi_T$. Indeed, the experiments on bond orientational harmonics confirmed these predictions [36].

The above theory can now be extended to the structure factor [37,38]

$$S_m(\mathbf{q}) = \langle \psi_m(\mathbf{q}) \psi_m^*(\mathbf{q}) \rangle = S_{mb}(\mathbf{q}) + \mu_m^2 S_{mb}(\mathbf{q})^2 \tilde{S}_m(\mathbf{q}), \quad (77)$$

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

$$S_{mb}(\mathbf{q}) = \frac{k_B T \chi_{mb}}{1 + \xi_{\parallel mb}^2 q_{\parallel}^2 + \xi_{\perp mb}^2 \mathbf{q}_{\perp}^2} \quad (78)$$

is the bare m th harmonic structure factor. Here

$$\widetilde{S}_m(\mathbf{q}) = \langle \psi_1^m(\mathbf{q}) \psi_1^{*m}(\mathbf{q}) \rangle \quad (79)$$

has to be calculated with the XY model Hamiltonian \mathcal{H}_1 [39,40]. Asymptotically close to T_1 , and for very small \mathbf{q} , $S_{mb}(\mathbf{q})$ is practically temperature independent, and the divergent part of S_m is proportional to \widetilde{S}_m , 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_{mb} cannot be ignored [5]. 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 $\widetilde{S}_m(\mathbf{q})$. Apart from a trivial phase shift, which interchanges the real and imaginary parts, we have seen that the local field $\text{Re}(\psi_1^2)$ corresponds to the tensorial operator φ_T with $n=2$, which was introduced and defined in Sec. I. Consequently, the structure factor $\widetilde{S}_2(\mathbf{q})$ is proportional to the biquadratic correlation function $G_T(q)$ with $n=2$, which has been calculated in Sec. II. The higher harmonics ($m>2$) correspond to operators which are of higher order in the primary field ϕ , which have not been considered in this paper.

In analogy to the results for biquadratic correlation functions of Sec. II, one expects the scattering functions for all harmonics to be dominated by the critical behavior of the XY model represented by \mathcal{H}_1 ; therefore they should have the asymptotic scaling form $\widetilde{S}_m(\mathbf{q}) = \chi_m g_m(q^2 \xi_1^2)$, where $\chi_m \sim |t|^{-\gamma_m}$, with $-\gamma_m = 2 - \alpha - 2\phi_m$ [4,8], and g_m is a universal scaling function [6]. For $x \ll 1$, $g_m(x^2)$ may be expanded in powers of x^2 and thus be approximated by a Lorentzian, that is, $g_m(x^2) = 1/[1 + X_m x^2 + O(x^4)]$, and X_m is a universal amplitude ratio [5]. Rewriting $\widetilde{S}_m(\mathbf{q}) = \chi_m/[1 + \xi_m^2 q^2 + \dots]$, this yields $\xi_m^2 = X_m \xi_1^2 = X_m \xi_{10}^2 |t|^{-2\nu}$; 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_m , are universal. Indeed, our ϵ -expansion calculations in Sec. II confirm these expectations for the case $m=2$. In addition, these expansions show that X_m can be small compared to unity, causing the \mathbf{q} dependence of \widetilde{S}_m to become dominant only very close to T_c . For $x \gg 1$, $g_m(x^2) \sim x^{-(2-\eta_m)}$, with $2 - \eta_m = \gamma_m/\nu$. For $m>1$, η_m is quite large, and we expect significant deviations from the Lorentzian shape at large x . To approximate the crossover between these limits, one can use the approximant $\hat{g}^{\text{app}}(x^2)$, given in Eq. (65).

Considering the isotropic case ($\xi_{\parallel mb} = \xi_{\perp mb}$), the results derived in Sec. II can be directly applied. For the experimentally relevant case of anisotropic correlation lengths ($\xi_{\parallel mb} \neq \xi_{\perp mb}$), one can still use our results by making the replacement $\xi_1^2 q^2 = \xi_{\parallel 1}^2 q_{\parallel}^2 + \xi_{\perp 1}^2 q_{\perp}^2$. In Ref. [5] experimental data were fitted using the Fisher-Burford expression, which follows from our extended approximant (65) by setting $a_i = 0$ for $i>1$; the resulting expression reads

$$\widetilde{S}_2(\mathbf{q}) = \frac{k_B T \chi_2 [1 + a_1 (\xi_{\parallel 1}^2 q_{\parallel}^2 + \xi_{\perp 1}^2 q_{\perp}^2)]^{\eta_2/2}}{1 + (X_2 + a_1 \eta_2/2) (\xi_{\parallel 1}^2 q_{\parallel}^2 + \xi_{\perp 1}^2 q_{\perp}^2)}. \quad (80)$$

Determining the parameters occurring in $S_{2b}(\mathbf{q})$ from fits far from the nematic-smectic- A_2 transition, and using these values for all temperatures, the parameters occurring in $\widetilde{S}_2(\mathbf{q})$ had been set to the following values: η_2 at $2 - \gamma_2/\nu \approx 1.5$ and $\xi_{\parallel 1}$ and $\xi_{\perp 1}$ at their values determined from $S_1(\mathbf{q})$ at each temperature. X_2 was set at its ϵ -expansion value of 0.04, as given by Eq. (11) and using $n=2$. Using the Fisher-Burford approximant (80) in Eq. (77), the structure factor S_2 was fitted for $10^{-5} < t < 10^{-4}$, close to T_c , and good fits were obtained for $a_1 \approx 0.01$. Setting a_1 at this value for all temperatures, one was left with a single temperature-dependent parameter $\mu_2^2 \chi_2$; the resultant fits to both the transverse and longitudinal scans over the complete temperature range from $t \sim 10^{-2}$ to $t \sim 10^{-5}$ were very good [5].

As noted already in Sec. II F, the Fisher-Burford approximant gives a good description of data but is not consistent with a systematic expansion in powers of ϵ . However, setting $\epsilon=1$, one can obtain the value of a_1 from our epsilon-expansion results by matching the general expression (65) with $a_i=0$ for $i>1$ to the asymptotic result valid in the limit $x^2 \gg 1$, Eq. (44); this yields the estimate $a_1 \approx 0.07$, which is considerably larger than the experimentally determined value. Clearly, a fit of the experimental data using the extended scaling function (65) would be desirable.

IV. DISCUSSION

The momentum-dependent scaling behavior of biquadratic correlation functions has been determined. Depending on the symmetry of the quadratic fields in the n -component space, one either describes energy-energy correlations or correlations of a local operator which transforms like a traceless tensor in the component space. The latter correlation function describes strain-strain correlations in certain anisotropic solids and, for the special case $n=2$, describes the fluctuations of the second-order harmonic in density-wave systems. We show that the exponent ν , which measures the divergence of the correlation length, is the same for the biquadratic and the regular quadratic correlation function, which indicates the existence of a single diverging length scale. The ratios between the quadratic and biquadratic correlation lengths are universal and proportional to ϵ ; also, the numerical prefactors of these ratios are quite small.

This theory is completely consistent with the experimental data on the second harmonic critical fluctuations in 7APCBB, including the ϵ -expansion estimate for X_2 , as has been shown in detail in Ref. [5]. It would be most valuable to search for similar effects in other systems with XY -like DW ordering. Also, the critical behavior of energy-energy correlations or correlations of other secondary order parameters in systems showing continuous phase transitions would provide more insight into the interesting phenomena discussed in this paper.

Some preliminary Monte Carlo simulations of two- and three-dimensional Ising systems exhibit good agreement with the nonasymptotic amplitude-exponent relation (53) for energy-energy correlation [16]. Extensions of these numerical results into the asymptotic regime and for vector order parameters would be useful to check our results, and could provide an independent access to the experimentally relevant

numerical values of the universal amplitude ratios in three dimensions.

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APPENDIX: EVALUATION OF THE INTEGRALS

In this section we determine the integral Ω defined by

$$\Omega(\mathbf{q}, r_0) \equiv \frac{1}{(2\pi)^d} \int_{\mathbf{p}} G^{(0)}(\mathbf{p} + \mathbf{q}) G^{(0)}(\mathbf{p}). \quad (\text{A1})$$

It is convenient to introduce a smooth cutoff and define the bare propagator as [11]

$$G^{(0)}(\mathbf{p}) \equiv \frac{1}{r_0 + \mathbf{p}^2 + \Lambda^{-2} \mathbf{p}^4} = \frac{1}{r_0 + \mathbf{p}^2} - \frac{1}{\Lambda^2 + \mathbf{p}^2} + O(r_0). \quad (\text{A2})$$

Thus, the integral Ω can to $O(r_0^0)$ be written as

$$\begin{aligned} \Omega(\mathbf{q}, r_0) &= \int \frac{d^d \mathbf{p}}{(2\pi)^d} \left(\frac{1}{\mathbf{p}^2 + r_0} - \frac{1}{\Lambda^2 + \mathbf{p}^2} \right) \\ &\quad \times \left(\frac{1}{[\mathbf{p} + \mathbf{q}]^2 + r_0} - \frac{1}{\Lambda^2 + [\mathbf{p} + \mathbf{q}]^2} \right) \\ &\equiv \mathcal{I}_1 + \mathcal{I}_2 - \mathcal{I}_3 - \mathcal{I}_4. \end{aligned} \quad (\text{A3})$$

The four product integrals can be solved using the Feynman-reparametrization technique defined by the equality

$$\frac{1}{AB} = \int_0^1 \frac{d\alpha}{[\alpha(A-B) + B]^2}. \quad (\text{A4})$$

Applying this trick to the first integral yields

$$\begin{aligned} \mathcal{I}_1 &\equiv \int \frac{d^d \mathbf{p}}{(2\pi)^d} \frac{1}{(\mathbf{p}^2 + r_0)([\mathbf{p} + \mathbf{q}]^2 + r_0)} \\ &= \int_0^1 d\alpha \int \frac{d^d \mathbf{p}}{(2\pi)^d} \frac{1}{\{[\mathbf{p} + \alpha \mathbf{q}]^2 + r_0 + \alpha \mathbf{q}^2(1 - \alpha)\}^2}. \end{aligned} \quad (\text{A5})$$

The origin of the \mathbf{p} integration can be shifted, since there is no cutoff involved, and the integration can be performed; the result is

$$\begin{aligned} \mathcal{I}_1 &= \frac{K_d}{2} \Gamma(2 - \epsilon/2) \Gamma(\epsilon/2) r_0^{-\epsilon/2} \\ &\quad \times \int_0^1 d\alpha [1 + \alpha(1 - \alpha)q^2/r_0]^{-\epsilon/2}. \end{aligned} \quad (\text{A6})$$

The constant K_d is defined by $K_d \equiv S_d/(2\pi)^d$, and S_d is the surface of a d -dimensional sphere given by $S_d \equiv 2\pi^{d/2}/\Gamma(d/2)$. The analogous results for the other product integrals are

$$\begin{aligned} \mathcal{I}_2 &\equiv \int \frac{d^d \mathbf{p}}{(2\pi)^d} \frac{1}{(\Lambda^2 + \mathbf{p}^2)(\Lambda^2 + [\mathbf{p} + \mathbf{q}]^2)} \\ &= \frac{K_d}{2} \Gamma(2 - \epsilon/2) \Gamma(\epsilon/2) \Lambda^{-\epsilon} \\ &\quad \times \int_0^1 d\alpha [1 + \alpha(1 - \alpha)q^2/\Lambda^2]^{-\epsilon/2}, \end{aligned} \quad (\text{A7})$$

$$\begin{aligned} \mathcal{I}_3 &\equiv \int \frac{d^d \mathbf{p}}{(2\pi)^d} \frac{1}{(\Lambda^2 + \mathbf{p}^2)([\mathbf{p} + \mathbf{q}]^2 + r_0)} \\ &= \frac{K_d}{2} \Gamma(2 - \epsilon/2) \Gamma(\epsilon/2) \\ &\quad \times \int_0^1 d\alpha [\alpha r_0 + (1 - \alpha)\Lambda^2 \\ &\quad + \alpha(1 - \alpha)q^2]^{-\epsilon/2}, \end{aligned} \quad (\text{A8})$$

$$\begin{aligned} \mathcal{I}_4 &\equiv \int \frac{d^d \mathbf{p}}{(2\pi)^d} \frac{1}{(\mathbf{p}^2 + r_0)(\Lambda^2 + [\mathbf{p} + \mathbf{q}]^2)} \\ &= \frac{K_d}{2} \Gamma(2 - \epsilon/2) \Gamma(\epsilon/2) \\ &\quad \times \int_0^1 d\alpha [\alpha \Lambda^2 + (1 - \alpha)r_0 \\ &\quad + \alpha(1 - \alpha)q^2]^{-\epsilon/2}. \end{aligned} \quad (\text{A9})$$

1. Expansion in terms of the momentum

To proceed, we expand the integrands of \mathcal{I} in powers of q^2 , defining the closed-form binomial expansion

$$(1+x)^{-\epsilon/2} = 1 + \frac{\epsilon}{2} \sum_{i=1}^{\infty} \frac{(-x)^i}{i} Y(i), \quad (\text{A10})$$

with the function

$$Y(i) \equiv \prod_{j=1}^{i-1} \left(1 + \frac{\epsilon}{2j} \right) = 1 + \epsilon Y_1(i) + O(\epsilon^2). \quad (\text{A11})$$

The integrals appearing in \mathcal{I}_1 and \mathcal{I}_2 can then be performed for general powers of q^2 and are given by

$$\frac{1}{n} \int_0^1 d\alpha [\alpha(1 - \alpha)]^i = \frac{(i!)^2}{i(2i+1)!} \equiv \Xi(i). \quad (\text{A12})$$

Rescaling the integrals by $\mathcal{I} = \tilde{\mathcal{I}} K_d \Gamma(2 - \epsilon/2) \Gamma(\epsilon/2)/2$, one obtains

$$\tilde{\mathcal{I}}_1 = r_0^{-\epsilon/2} \left[1 + \frac{\epsilon}{2} \sum_{i=1}^{\infty} \left(\frac{-q^2}{r_0} \right)^i \Xi(i) Y(i) \right], \quad (\text{A13})$$

$$\begin{aligned}\tilde{\mathcal{I}}_2 &= \Lambda^{-\epsilon} \left[1 + \frac{\epsilon}{2} \sum_{i=1}^{\infty} \left(\frac{-q^2}{\Lambda^2} \right)^i \Xi(i) Y(i) \right] \\ &= \Lambda^{-\epsilon} \left[1 + \frac{\epsilon}{2} \sum_{i=1}^{\infty} \left(\frac{-q^2}{r_0 \Lambda^2} \right)^i O(r_0^i) \right].\end{aligned}\quad (\text{A14})$$

A similar calculation for the integrals appearing in \mathcal{I}_3 and \mathcal{I}_4 leads to the result

$$\tilde{\mathcal{I}}_3 + \tilde{\mathcal{I}}_4 = \frac{2\Lambda^{-\epsilon}}{1-\epsilon/2} + O(r_0) + \sum_{i=1}^{\infty} \left(\frac{q^2}{r_0} \right)^i O(r_0). \quad (\text{A15})$$

Neglecting terms of $O(r_0)$ is consistent with the initial simplification made for the bare propagator, Eq. (A2). The prefactor of the integrals can be written as

$$\Gamma(2-\epsilon/2)\Gamma(\epsilon/2) = \frac{\epsilon\pi/2}{\sin(\epsilon\pi/2)} \frac{2(1-\epsilon/2)}{\epsilon}, \quad (\text{A16})$$

where for later calculations we will use the expansion

$$\frac{\epsilon\pi/2}{\sin(\epsilon\pi/2)} = 1 + \frac{\epsilon^2\pi^2}{24} + O(\epsilon^4). \quad (\text{A17})$$

Putting everything together, setting the cutoff to $\Lambda=1$, the integral Ω is given, to all orders in q^2 and ϵ , by

$$\begin{aligned}\Omega(q, r_0) &= -K_d \frac{\epsilon\pi/2}{\sin(\epsilon\pi/2)} \left[1 - \frac{1-\epsilon/2}{\epsilon} (r_0^{-\epsilon/2} - 1) \right. \\ &\quad \left. - r_0^{-\epsilon/2} \frac{(1-\epsilon/2)}{2} \sum_{i=1}^{\infty} (-1)^i \left(\frac{q^2}{r_0} \right)^i \Xi(i) Y(i) \right].\end{aligned}\quad (\text{A18})$$

The result, to first order in ϵ , as sufficient for the calculation of the scaling function up to two loops, is given by

$$\begin{aligned}\Omega(q, r_0) &= -K_d \left[1 + \frac{1}{2} (1-\epsilon/2) \ln r_0 - \frac{\epsilon}{8} \ln^2 r_0 \right. \\ &\quad \left. - \frac{1}{2} \left(1 - \frac{\epsilon}{2} - \frac{\epsilon}{2} \ln r_0 \right) \right. \\ &\quad \left. \times \sum_{i=1}^{\infty} (-1)^i \left(\frac{q^2}{r_0} \right)^i \Xi(i) [1 + \epsilon Y_1(i)] \right],\end{aligned}\quad (\text{A19})$$

with

$$Y_1(i) = \sum_{j=1}^{i-1} \frac{1}{2j}. \quad (\text{A20})$$

2. Result for vanishing mass

For the case $r_0=0$ the integral Ω can be written after a calculation similar to the last section to all orders in ϵ as

$$\begin{aligned}\Omega(q, 0) &= K_d \frac{\epsilon\pi/2}{\sin(\epsilon\pi/2)} \left[\frac{1-\epsilon/2}{\epsilon} q^{-\epsilon} \frac{\Gamma(1-\epsilon/2)^2}{\Gamma(2-\epsilon)} \right. \\ &\quad \left. - \frac{1+\epsilon/2}{\epsilon} + O(q^2) \right],\end{aligned}\quad (\text{A21})$$

where $\Lambda=1$ has been set for simplicity. Using the expansion

$$\frac{\Gamma(1-\epsilon/2)^2}{\Gamma(2-\epsilon)} = 1 + \epsilon + (1-\pi^2/24)\epsilon^2 + O(\epsilon^3), \quad (\text{A22})$$

the value of $\Omega(q, 0)$ is given by

$$\begin{aligned}\Omega(q, 0) &= \frac{K_d}{2} [\epsilon(1-\pi^2/12) - (2+\epsilon)\ln q + \epsilon \ln^2 q] \\ &\quad + O(\epsilon^2, q^2).\end{aligned}\quad (\text{A23})$$

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