

Specific heat amplitude ratios for generic competing systems

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Abstract. *The specific heat amplitude ratios for generic anisotropic as well as isotropic Lifshitz critical behaviors for the N -vector model are computed at one-loop level using the ϵ_L -expansion. In the anisotropic case, we show that the universal result obtained reduces very easily to that from the simpler m -axial universality class result. In the isotropic case, if n is the number of neighbors coupled via competing interactions, we demonstrate that the ratio vanishes close to $n = 4$ and becomes negative for $n > 4$ when it is calculated exactly, which is rather odd. The evaluation using the orthogonal approximation is shown to yield positive results for arbitrary n . Explicit computations for the case $n = 2, d = 3, N = 1$ yield an exact amplitude ratio equal to 0.06, with the approximate amplitude ratio being 1.17. We discuss two physical mechanisms to pick out one of the amplitude ratio values. We propose an experiment in homopolymer-diblock copolymer blends in order to determine the amplitude ratio.*

1. Introduction

Competition represents the balance between attractive and repulsive microscopic short range forces in macroscopical systems. Their description is different from ordinary physical criticality where only either attractive or repulsive interactions take place. The main distinction is the need to including additional parameters, the number and kinds of “competing axes” which indicate how far the attractive-repulsive couplings extend themselves along certain space directions [1, 2]. (In the language of magnetic systems n is the number of neighbors interacting via competing forces.)

Specific heat amplitude ratio is an example of a universal critical property which has not been investigated yet for this sort of system. (A recent study of the susceptibility amplitude ratio of this universality class can be found in [3].) In this work we compute this amplitude ratio for anisotropic as well as isotropic systems. In the anisotropic cases we show how general competition universality classes reduce to those from the m -axial Lifshitz criticalities, whereas a similar property is demonstrated for generic isotropic systems too.

Although (second character) m -axial isotropic Lifshitz points [4] have been reported in the literature [7, 8, 9, 10] from theoretical and experimental results in unconventional polymers, recent results taking into account the effect of fluctuations on these systems [11, 12] make the subject far from being completely understood. Besides, the appearance of the isotropic case $n = 6$ at mean-field level has been discussed in mixtures of $(AB - BC)$ diblock copolymers [13].



Hence, we found convenient to propose an experiment in polymers in the attempt to compare our results with real isotropic physical systems with competition.

2. Anisotropic Amplitude ratio

We begin with the renormalized free energy density at one-loop level at the fixed point for the N -vector model describing the generic anisotropic Lifshitz critical behavior. This object is written in terms of the two factor scale, namely, the renormalized temperature (t) and order parameter (M) and is defined up to a polynomial of second order in t . Furthermore, we choose the free energy such that it coincides with the case without competition, *i.e.*, $m_n = 0$ [5], for which $\epsilon_L (= 4 + \sum_{n=2}^L \frac{(n-1)}{n} m_n - d) \equiv \epsilon = 4 - d$. Defining the quantity $y = u_n^* M^2$ (u_n^* is the dimensionless coupling constant at the fixed point useful to our purposes in what follows), the free energy density at one-loop order can be written as

$$F(t, y) = \frac{1}{2u_n^*} \left(ty + \frac{y^2}{12} \right) + \frac{1}{2} \int d^{d-\sum_{n=2}^L m_n} q \prod_{n=2}^L d^{m_n} k_{(n)} \left[(N-1) \ln \left(1 + \frac{t + \frac{y}{6}}{q^2 + \sum_{n=2}^L k_{(n)}^{2n}} \right) \right. \\ \left. + \ln \left(1 + \frac{t + \frac{y}{2}}{q^2 + \sum_{n=2}^L k_{(n)}^{2n}} \right) - \frac{1}{q^2 + \sum_{n=2}^L k_{(n)}^{2n}} \left[N \left(t + \frac{y}{6} \right) + \frac{y}{3} \right] + \frac{1}{4} I_{SP_n} \left[N \left(t + \frac{y}{6} \right)^2 + \frac{2y}{3} \left(t + \frac{y}{3} \right) \right] \right] \\ + O(\epsilon_n^2). \quad (1)$$

The integral I_{SP_n} is the one-loop contribution to the one-particle (1PI) irreducible four-point vertex part computed at fixed external momenta and is defined by

$$I_{SP_{n'}}(K_n^2 = \delta_{nn'} \kappa_n^2) = \int \frac{d^{d-\sum_{n=2}^L m_n} q \prod_{n=2}^L d^{m_n} k_{(n)}}{\left(q^2 + \sum_{n=2}^L k_{(n)}^{2n} \right) \left[(q + K_{(1)})^2 + \sum_{n=2}^L (k_{(n)} + K_{(n)})^{2n} \right]}. \quad (2)$$

Note that at this symmetry point, only the external momenta associated to the n' subspace is fixed at nonvanishing values, whereas all other external momentum scales are set to zero. The specific heat above and below the critical temperature is given by

$$C_{\pm}(t) = -\frac{\partial^2 F(t, M)}{\partial t^2} - \frac{N\nu_n}{2\alpha_L} \left[\kappa_n \frac{\partial I_{SP_n}(\kappa_n)}{\partial \kappa_n} \right]_{\kappa_n^2=1}, \quad (3)$$

and above T_L we should take the derivatives and set $M = 0$ ($y = 0$). Below T_L , we should employ the value of M (y) at the coexistence curve, namely $y = u_n^* M^2 = -6t$. The integral can be computed in a closed analytical form using the orthogonal approximation [1, 2] and is given by $I_{SP_n}(K_{(n)}) = \frac{K_{(n)}^{-n\epsilon_L}}{\epsilon_L} [1 + h_{m_L} \epsilon_L]$ ($h_{m_L} = 1 + \frac{[\psi(1) - \psi(2 - \sum_{n=2}^L \frac{m_n}{2n})]}{2}$). Using this result in conjunction with the fixed point and critical exponents up to two-loop level computed using this approximation given, respectively, by the following expressions [2]

$$u_n^* = \frac{6\epsilon_L}{(N+8)} \left[1 + \epsilon_L \left[-h_{m_L} + \frac{(9N+42)}{(N+8)^2} \right] \right], \quad (4a)$$

$$\nu_n = \frac{1}{n} \left(\frac{1}{2} + \frac{(N+2)}{4(N+8)} \epsilon_L + \frac{1}{8} \frac{(N+2)(N^2+23N+60)}{(N+8)^3} \epsilon_L^2 \right). \quad (4b)$$

$$\alpha_L = \frac{(4-N)}{2(N+8)} \epsilon_L - \frac{(N+2)(N^2+30N+56)}{4(N+8)^3} \epsilon_L^2, \quad (4c)$$

is sufficient to compute the ratio up to one-loop order. After performing the integrals resulting from the derivatives of the free energy with respect to t we identify the specific heat up to one-loop order with the expressions $C_{\pm}(t) = A_{\pm}|t|^{-\alpha_L}$, which yields

$$\frac{A_+}{A_-} = \frac{N}{4} 2^{\alpha_L} (1 + \epsilon_L). \quad (5)$$

Notice that in the above expression the exponent is expressed up to first order in ϵ_L . This formula reduces to the case $m_2 = m$, $m_3 = \dots = m_L = 0$ corresponding to the ratio of the m -axial Lifshitz universality class [6].

3. Exact isotropic amplitude ratio

We write the free energy density for the N -vector model describing the generic isotropic Lifshitz critical behavior using the same ingredients as before, with minor modifications. The expansion parameter is $\epsilon_n = 4n - d$ ($d = m_n$). The free energy is such that it coincides with the case without competition, *i.e.*, $n = 1$ [5], for which $\epsilon_1 \equiv \epsilon = 4 - d$. The free energy density at one-loop order reads

$$\begin{aligned} F(t, y) = & \frac{1}{2u_n^*} \left(ty + \frac{y^2}{12} \right) + \frac{1}{2} \int d^{m_n} k \left[(N-1) \ln \left(1 + \frac{t + \frac{y}{6}}{(k^2)^n} \right) + \ln \left(1 + \frac{t + \frac{y}{2}}{(k^2)^n} \right) \right. \\ & \left. - \frac{1}{k^{2n}} \left[N \left(t + \frac{y}{6} \right) + \frac{y}{3} \right] + \frac{1}{4} I_{SP_n} \left[N \left(t + \frac{y}{6} \right)^2 + \frac{2y}{3} \left(t + \frac{y}{3} \right) \right] + O(\epsilon_n^2) \right]. \end{aligned} \quad (6)$$

Similarly as discussed in the anisotropic case, the integral I_{SP_n} and the condition on the specific heat are both defined by the expressions

$$I_{SP_n}(K) = \left[\int \frac{d^{m_n} k}{k^{2n} (k+K)^{2n}} \right]_{K^2=\kappa_n^2}, \quad (7a)$$

$$C_{\pm}(t) = -\frac{\partial^2 F(t, M)}{\partial t^2} - \frac{N\nu_n}{2\alpha_n} \left[\kappa_n \frac{\partial I_{SP_n}(\kappa_n)}{\partial \kappa_n} \right]_{\kappa_n^2=1}. \quad (7b)$$

Above T_L the derivatives are taken and set $M = 0$ ($y = 0$) afterwards, whereas below T_L we set $y = u_n^* M^2 = -6t$. Now, the exact result $I_{SP_n}(K) = \frac{K^{-\epsilon_n}}{\epsilon_n} [1 + D(n)\epsilon_n]$ ($D(n) = \frac{1}{2}[\psi(2n) + \psi(1)] - \psi(n)$) together with the fixed point and critical indices up to two-loop order given, respectively, by [2]

$$\begin{aligned} u_n^* = & \frac{6\epsilon_n}{(N+8)} \left[1 + \epsilon_n \left[\frac{1}{(N+8)^2} \frac{(-1)^n \Gamma(2n)^2 (2N+4)}{\Gamma(n+1)\Gamma(3n)} + (20N+88)(1-D(n)) - D(n) \right. \right. \\ & \left. \left. + \frac{(20N+88)}{(N+8)^2} \left(\sum_{p=1}^{2n-2} \frac{1}{2n-p} - 2 \sum_{p=1}^{n-1} \frac{1}{2n-p} \right) \right] \right], \end{aligned} \quad (8a)$$

$$\begin{aligned} \nu_n = & \frac{1}{2n} + \frac{(N+2)}{4n^2(N+8)} \epsilon_n + \frac{(N+2)}{4n^2(N+8)^3} \epsilon_n^2 \left[(-1)^n (N-4) \frac{\Gamma(2n)^2}{\Gamma(n+1)\Gamma(3n)} + \frac{(N+2)(N+8)}{2n} \right. \\ & \left. + (14N+40)D(n) \right], \end{aligned} \quad (8b)$$

$$\begin{aligned} \alpha_n = & \frac{(4-N)}{2n(N+8)} \epsilon_n - \frac{(N+2)}{4n^2(N+8)^3} \epsilon_n^2 \left[(-1)^n \frac{4n(N-4)}{\Gamma(n+1)} \frac{\Gamma(2n)^2}{\Gamma(3n)} + (N-4)(N+8) + 4n(14N \right. \\ & \left. + 40)D(n) \right], \end{aligned} \quad (8c)$$

are required to evaluate the exact ratio up to one-loop order. From the identification $C_{\pm}(t) = A_{\pm}|t|^{-\alpha_n}$, one learns that

$$\frac{A_+}{A_-} = \frac{N}{4} 2^{\alpha_n} (1 + 2D(n)\epsilon_n). \quad (9)$$

This formula reduces to the case $n = 1$ from ref.[19], since $D(1) = 1/2$. Nevertheless, as n increases $D(n)$ becomes negative for $n \geq 2$. The choice $\epsilon_n > 0$ leads naturally to *vanishing and even negative values for the amplitude ratio*. Accordingly, perturbation theory in the framework of the ϵ_n -expansion is not a systematic correction to the mean field solution in the case of this amplitude ratio, since neither zero nor negative values are allowed in the later situation. Could this indicate a failure of the ϵ_n -expansion for isotropic systems with n higher enough? Let us compute the amplitude ratio using the generalized orthogonal approximation [1, 2] and try to figure out possible explanations to this odd behavior.

4. Isotropic amplitude ratio in the orthogonal approximation

Now we just have to compute the one-loop integral at the symmetry point, the fixed point and the critical exponents using the orthogonal approximation. The integral at the symmetry point is given by $I_{SP_n}(K) = \frac{K^{-\epsilon_n}}{\epsilon_n} [1 + \frac{\epsilon_n}{2n}]$. The fixed point and critical exponents in this approximation can be obtained from ref.[2] but we do not bother to write them down explicitly. Substitution of these values above and below T_L as explicated before lead to the orthogonal approximation version of the specific heat amplitude ratio, namely

$$\frac{A_+}{A_-} = \frac{N}{4} 2^{\alpha_n} (1 + \frac{\epsilon_n}{n}). \quad (10)$$

This result only agrees with the exact computation for $n = 1$. But the result from last equation has the virtue that it does represent an expansion around the mean field value ($\epsilon_n = 0$) since the positiveness is guaranteed at this loop order.

5. Discussion

In fig. 1 we plot simultaneously the exact amplitude ratios for fixed ϵ_n . Inspired by the traditional use of the ϵ -expansion for three-dimensional systems in order to compare with experiments, we set $\epsilon_n = 1$ for the various values of the space dimension (i.e., below the critical dimension) in the amplitude with the variation of (N, n) . The asymptotes of the orthogonal approximation amplitude curves are defined by the $n \rightarrow \infty$ limit. The inset indicates how different values of N produce a slight deviation in the cancellation of the amplitude ratio as a function of n . For all values of $N \neq 0$, $n \geq 4$ correspond to negative values of the specific heat amplitude ratio in the exact approach.

The amplitude ratio await for experimental applications in generic anisotropic systems yet to be discovered. From the experimental viewpoint, at least the traditional second character case $m_2 \equiv m$ can be compared with theoretical predictions. Suggested theoretically in the context of copolymer-homopolymer ternary blends [7, 8], the first mean-field isotropic experimental realization was reported on symmetric diblock copolymer-homopolymer blends (of polyethylene (PE) and polyethylenepropylene (PEP)) using small angle neutron scattering (SANS) for the case $(N, d, n) = (1, 3, 2)$ [9]. However, a subsequent study showed that the phase behavior of symmetric PE-PEP/PE/PEP mixtures points out to the destruction of the mean-field Lifshitz point [10]. Another polymer system consisting of deuterated polybutadiene (dPB) and polystyrene (PS) homopolymers has also been analyzed with SANS, though its phase diagram was constructed from the temperature and diblock copolymer concentration [11, 12]. The PE-PEP/PE/PEP and dPB-PS/dPB/PS mixtures agree between each other with respect to the disappearance of the Lifshitz point caused by fluctuations, except that in the latter the

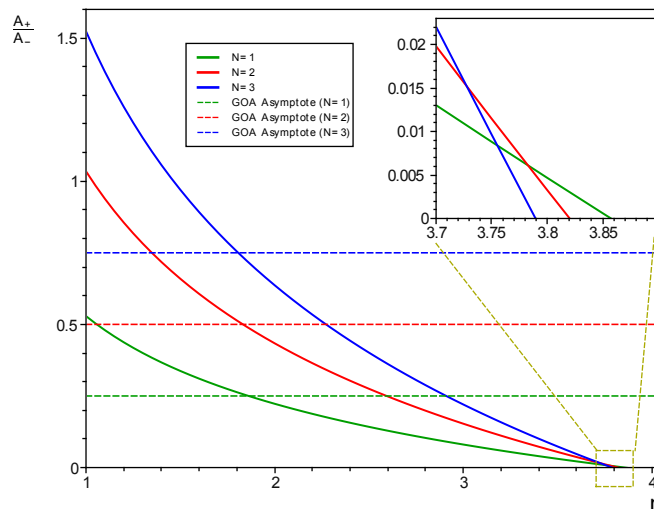


Figure 1. The amplitude ratio plotted as a function of n and N (different collors). The horizontal lines correspond to the value $n \rightarrow \infty$ using the generalized orthogonal approximation (GOA). The inset shows how the amplitude vanish and start to take negative values for different values of N .

fluctuations were explicitly taking into account in the isotropic Lifshitz critical region and produced nontrivial effects on the susceptibility amplitudes and associated critical exponent [12]. The universality class ($N = 1, d = 3, n = 2$) in ref.[12] encountered the susceptibility exponent $\gamma_2 = 1.55 \pm 0.15$ from the isotherm at 69.5°C with concentration of diblock copolymer $\Phi_{DB} = 0.071$. Surprisingly, the exact two-loop value determined from ref.[2] using $\epsilon_2 = 5$ yields $\gamma_2 = 1.50$ which is quite close to the experimental value. Unfortunately, the setup of this experiment was not able to encounter universal values for the susceptibility amplitude ratio.

In the case of the specific heat amplitude ratio we propose the following experiment: using a scanning adiabatic calorimeter [14], determine the mean field Lifshitz temperature T_L in the case of the homopolymer-diblock copolymer blend, for instance in the dPB-PS/dPB/PS system. Next, in the lamellar modulated phase one should measure the amplitude ratio in a certain temperature $T = T_L - \Delta T$ as well as performing the measurement of the amplitude in the disordered phase for $T = T_L + \Delta T$ and dividing the latter result by the former. The result could be checked in principle by measuring the amplitude at $T = T_L - \Delta T$ within the uniformly ordered phase with different diblock copolymer concentration followed by a similar determination at $T = T_L + \Delta T$. Inside the Lifshitz critical region, the two results should be the same. After that, the output should be compared with our theoretical predictions in the present work by setting $d = 3(\epsilon_2 = 5)$, $N = 1, n = 2$: $\left[\frac{A_+}{A_-}\right]_{exact} = 0.06$, whereas $\left[\frac{A_+}{A_-}\right]_{GOA} = 1.17$, which is quite big a difference to clearly distinguish the correct experimental result in comparison with both theoretical predictions and rule out one of the hypotheses raised herein.

If the would be experimental result confirms the exact ratio, then we can conclude for its smallness that this rules out isotropic Lifshitz systems for $n > 3$. In that case, $n = 4$ represents effectively a long range system in the isotropic competitive world, since it is well known that systems with long range order originate negative specific heat [17, 18], even though no pathology occurs to the exponents, leading to a new criterion for stability of isotropic competing systems. On the other hand, if the other possibility prevails, then the propagation of fluctuations must be restricted and the orthogonal approximation is a way out to the issue of thermodynamical instability in higher character isotropic Lifshitz critical behavior.

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