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The Ginzburg Criterion Applied to a Weak First Order Phase Transition

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The range of validity of a mean field theory near a second order phase transition can be estimated using the Ginzburg criteria. Previous attempts to apply this principle to weakly first order transitions such as the nematic-isotropic transition fail to simplify to the form of the Ginzburg criteria for a second order transition and also predict fluctuations becoming less significant as the transition is approached. I calculate a Ginzburg criteria in the nematic phase that simplifies to the accepted solution as the transition becomes second order.

Keywords: mean field theory, Landau theory

Mean field theories which ignore the effects of fluctuations are successful in qualitatively describing many disparate physical systems. Mean field theories are usually least successful in describing behavior near a phase transition where the role of fluctuations are crucial. A mean field approach to estimating when the fluctuations are sufficiently large as to make the mean field approach incorrect was developed by Ginzburg[1] and subsequently applied to a wide range of phase transitions.

The Ginzburg criterion states that fluctuations of the order parameter over a coherence volume must be much smaller than the value of the order parameter and is written as

$$\langle Q(0)\ Q(r)\rangle << \langle Q(0)\rangle^2. \tag{1}$$

For a second order phase transition described by a Landau[2] theory of the form

$$F = 1/2\ a(t - T_c)/T_c\ Q^2 + 1/4\ C\ Q^4, \tag{2}$$

the order parameter is $Q = (a/c)^{1/2}\ (T_c - t)/T_c$ where T_c is the transition temperature. The correlation function is of the form[2,3] $\langle Q(0)\ Q(r)\rangle \approx k\ T \exp(-r/\xi(t))/\xi_0$ where the bare correlation length is defined as $\xi(t) = \xi_0/\varepsilon^{1/2}$ and $\varepsilon = (T_c - t)T_c$. As we are averaging over a volume of length ξ the inequality (Equation 1) becomes

$$K\ T/\xi_0^3\ e^{-1}\ \varepsilon^{1/2} << a/C\ \varepsilon.$$

Making use of the relation between the expansion coefficients and the discontinuity of the specific heat (ΔC_p), the Ginzburg criteria may be written

$$[k/(\Delta C_p\ \xi_0^3)]^2 << \varepsilon \tag{3}$$

Thus, as long as ε is sufficiently large, i.e., far enough away from the transition, the condition is satisfied and the system has mean field behavior. When the inequality is no longer satisfied close to the transition, mean field theory will no longer describe the critical behavior. Two examples[3] showing the utility of the Ginzburg criteria are provided by the superconducting transition of tin and the ferromagnetic transition of iron. In the first case, the bare correlation length is large, 2300 angstroms, and the transition can be approached very closely before deviations from mean field behavior are important. In the latter case, the bare correlation length is only 2 angstroms and deviation from mean field behavior is seen much farther from the transition.

Most mean field theories have been concerned with second order transitions as it is these that show interesting critical behavior. The nematic-isotropic phase transition exhibited by many liquid crystal systems is a counter example that shows a weak first order transition, yet still displays critical divergences that are often well described by mean field theories.[4]

It has been argued that the Ginzburg criterion for the weak first order nematic-isotropic transition can be written as[5]

$$b\ \xi^3 >> kT, \tag{4}$$

where b is the height of the energy barrier separating the nematic and isotropic phases. Calculation of the height of the energy barrier converts this equation to

$$(\Delta H\ \xi_0^3/kT)^2 >> \varepsilon, \tag{5}$$

where ΔH is the latent heat. This result suffers from a number of flaws. First, it does not reduce to the second order Ginzburg result when the latent heat vanishes. Secondly, the inequality improves as the transition is approached indicating that fluctuations become less important at a phase transition. These problems result because Equation (4) only represents a limiting condition that fluctuations of the order of kT do not carry the system from the ordered phase to the disordered phase. Equation 4 has also appeared reversed elsewhere.[6]

The Landau theory describing the nematic-isotropic transition is the Landau-de Gennes[7] theory that expands the free energy as a power series of the tensor order parameter,

$$F_n = F_i + 1/2\ a\ \varepsilon\ Q_{\alpha\beta}\ Q_{\beta\alpha} - 1/3\ B\ Q_{\alpha\beta}\ Q_{\beta\gamma}\ Q_{\gamma\alpha} + 1/4\ C\ (Q_{\alpha\beta}\ Q_{\beta\alpha})^2, \tag{6}$$

where a, B and C are positive constants, Q the tensor order parameter and $A = a\ \varepsilon$ with $A > 0$ in the isotropic phase and $A < 0$ in the ordered phase. The coefficient of the cubic term drives the transition first order and is also responsible for an

asymmetry in critical behavior on both sides of the transition.[8] From the isotropic phase, fluctuations diverge at a temperature designated T^* so that the closest approach to the critical point is given by $(T_c - T^*)$, while in the nematic phase the divergence occurs at T^{**} and the closest approach is $(T^{**} - T_c)$. The relation $(T^{**} - T_c) = 1/8\ (T_c - T^*)$ can be derived from the Landau expansion.

For a uniaxial nematic, the order parameter may be written as $Q_{\alpha\beta} = S(n_\alpha\ n_\beta - 1/3\delta_{\alpha\beta})$, where S is a scaler order parameter in the range from 0 to 1 and n_α is the component of the molecular axis along the α axis.

Substitution of this expression into Equation (6) gives the reduced free energy density

$$F_n = F_i + 1/3\ a(t - T^{**})/T^{**}\ S^2 - 2/27\ B\ S^3 + 1/9\ C\ S^4. \tag{7}$$

The order parameter in the nematic phase is found by minimizing the free energy density of Equation (7) with respect to S to give

$$S = B/(4C)\ (1 + (1 + 24\ |a|\ C(T^{**} - t)/(B^2\ T^{**}))^{1/2}). \tag{8}$$

Squaring Equation (8) gives

$$S^2 = 3/2\ a/C\ \varepsilon + B^2/(8C^2)\ (1 + \sqrt{}(1 + 24\ |a|\ C\ \varepsilon/B^2), \tag{9}$$

where $\varepsilon = (T^{**} - t)/T^{**}$. To second order in S (Gaussian approximation) the fluctuations of the order parameter may be written[9] as $\langle S(0)S(r)\rangle = kT \exp(-R/\xi(t))/(6\ \pi\ L\ R)$, where L is related to the elastic constants which are assumed to be equal and ξ is the correlation length which is given by $\xi(t) = \xi_0/\varepsilon^{1/2} = (L/a\ \varepsilon)^{1/2}$. The expression for the correlation function has been qualitatively verified to hold in the nematic phase[8] as well as the isotropic phase near the transition. Averaging over a correlation volume is equivalent, to within numerical factors, of replacing R by ξ. Making this replacement and rewriting L in terms of the correlation length reduces this equation to

$$\langle S(0)S(r)\rangle \approx kT\ \varepsilon^{1/2}/(6\pi e\xi_0^3 a). \tag{10}$$

The Ginzburg criterion, Equation (1) is then

$$kt\ \varepsilon^{1/2}/(6\pi e\xi_0^3 a) << (3/2\ a/C\ \varepsilon + B^2/(8C^2)\ (1 + \sqrt{}(1 + 24\ |a|\ C\varepsilon/B^2)). \tag{11}$$

Near the transition ε is small and aC/B^2 is of order unity so the square root term may be expanded to yield, to first order in epsilon,

$$kT\ \varepsilon^{1/2} << 6e\pi\xi_0^3 a(B^2/(4C^2) + 3\ a\varepsilon/C). \tag{12}$$

This expression consists of two parts, one containing the cubic coefficient B, which is nonzero for the first order transition, and a part independent of B. It is

the first term that gives a solution of the form of Equation (5). In the limit of $B \rightarrow 0$ Equation (12) becomes

$$(kT/\xi_0^3)^2 << \varepsilon, \tag{13}$$

which is of the same form as the Ginzburg criterion for a second order phase transition (Equation (3)).

It is possible to rewrite Equation (12) in terms of physically accessible quantities by using the latent heat, $\Delta H = a\,B^2/(27C^2)$, and $\varepsilon_c = (T_c - T^{**})/T_c = B^2/27aC$ to get

$$kT/(6e\pi\,\xi_0^3\,\Delta H) << (27/(4\sqrt{\varepsilon}) + 3\sqrt{\varepsilon}/\varepsilon_c. \tag{14}$$

The right hand side of Equation (14) remains finite as $\varepsilon \rightarrow \varepsilon_c$ at the transition and is a minimum at $\varepsilon = 9/4\ \varepsilon_c$.

Equation (14) still retains the unphysical behavior of Equation (5) where the inequality improves as the transition is more closely approached in the range $\varepsilon_c < \varepsilon < (9/4\ \varepsilon_c)$. The value of the RHS of Equation (14) does not, however, change appreciably from its minimum value as the transition is approached as the ratio of the minimum value to the value at the transition is 12/13.

Putting in values for *p*-methoxybenzlidene-*p*-*n*-butylaniline (MBBA), Latent heat[9] is $1.6\ 10^6\ J\ m^{-3}$ and $(T_c - T^*)$ is experimentally determined[10] to be about 1 *K* which means $(T^{**} - T_c)$ is 1/8 *K*. The bare correlation length is about 7 angstroms.[11] Substitution of these values into Equation (14), at $\varepsilon = \varepsilon_c$, yields $.15 << 490$. While the inequality is true, it is not clear if the right hand side is sufficiently large to preclude observing departures from mean field results, especially given the inexact nature of these calculations.

It is, never the less, well established that deviations from mean field results are seen from light scattering in the isotropic phase in MBBA[10] as well as other liquid crystals.[12] This discrepancy could arise for a number of reasons, including a significant temperature dependence of the cubic and quartic coefficients or the need to consider refinements to the Gaussian approximation.[13]

In conclusion, the Ginzburg criterion for a first order phase transition has been developed that simplifies to the usual result when the transition becomes second order. This new formulation suffers the same problem as the earlier derivation in that the inequality improves as the transition is approached, thus implying that fluctuations become less important at the transition. The magnitude of the improvement is small, less than 10 percent.

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References

1. V. L. Ginzburg, Sov. Phys.—Solid State 2, 1824 (1960).
2. L. D. Landau and E. M. Lifshitz, *Statistical Physics*, Vol. 1 3rd edition (Pergamon Press, Oxford, 1980).

3. See, for example, R. M. White and T. H. Geballe, *Long Range Order in Solids*, (Academic Press, New York 1979).
4. See M. J. Stephen and J. Straley, *Rev. Mod. Phys.*, **46**, 617 (1974) and references therein.
5. C. P. Fan and M. J. Stephen, *Phys. Rev. Lett.*, **25**, 500 (1970) and T. W. Stinson and J. D. Litster, *Phys. Rev. Lett.*, **25**, 503 (1970).
6. E. F. Gramsbergen, L. Longa and W. H. de Jeu, Physics Reports, 135, 195 (1986).
7. P. G. de Genes, *The Physics of Liquid Crystals*, (Clarendon Press, Oxford, 1974).
8. J. P. McClymer and P. H. Keyes, *Phys. Rev. A*, **42**, 4767 (1990).
9. See G. Vertogen and W. H. de Jeu, *Thermotropic Liquid Crystals, Fundamentals*, (Springer-Verlag, New York, 1988).
10. T. W. Stinson and J. D. Litster, loc. cit.
11. T. W. Stinson and J. D. Litster, *Phys. Rev. Lett.*, **30**, 688 (1973).
12. H. Zink and W. H. de Jeu, *Mol. Cryst. Liq. Cryst.*, **124**, 287 (1985).
13. See reference #6 for a clear presentation of other explanations of deviations from Gaussian behavior and references contained there in.