First-Order Phase Transitions in Superconductors and Smectic-A Liquid Crystals

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The superconducting phase transition is predicted to be weakly first order, because of effects of the intrinsic fluctuating magnetic field, according to a Wilson-Fisher ϵ-expansion analysis, as well as a generalized mean-field calculation appropriate to a type-I superconductor. Similar results hold for the phase transition from a smectic-A to a nematic liquid crystal.

According to the BCS theory of superconductivity, the transition between the normal and superconducting states of a metal is a classical second-order phase transition. McMillan[1] has shown that according to a mean-field model, the transition between the smectic-A and nematic phases of a liquid crystal can also be second order, for an appropriate range of parameters. According to current theories of critical phenomena, fluctuations left out of the classical theories do not, generally, convert a second-order transition to first order, although they do modify the nature of the singularity at the critical point.[2] The superconductor and the smectic-A liquid crystal, however, have the special feature that their order parameters are coupled to "gauge fields"[3] (the vector potential for the superconductor, the director in the smectic-A liquid crystal) whose fluctuations also diverge at long wavelengths. In the present paper, we shall argue that when the gauge fields are taken into account, the transition for a superconductor (or a charged superfluid) is always weakly first order. In a separate paper[4] it will be shown that the "critical properties" of the smectic-A liquid crystal are isomorphic to those of the superconductor, so that the transition between the smectic-A and nematic phases should also be at least weakly first order in all materials.

Roughly, the driving force for the first-order transition is the partial expulsion of the "blackbody radiation," (or of the director fluctuations) from the low-temperature phase. The "size" of the first-order transition is at most a few microdegrees for superconductors, but should be of order 10^{-2} K or larger for the liquid crystal.[4] Our arguments for a first-order transition have been obtained both from a generalized mean-field approximation appropriate to a type-I superconductor, and from the renormalization group methods of Wilson, evaluated to first order in ϵ, the deviation of the space dimensionality from four.[5] We have also considered a generalization where the order parameter is a vector with $n/2$ complex components. We find that for sufficiently large n a critical-point transition can exist but with exponents that are greatly affected by the coupling to the gauge fields.

According to the Ginzburg-Landau theory, one may define a combined "free-energy functional" for the superconductor and the electromagnetic field in the form

$$F\{\psi, \vec{A}\} = \int d^3r [a|\psi|^2 + \tfrac{1}{2}b|\psi|^4 + \gamma|(\nabla - iq_0\vec{A})\psi|^2 + (8\pi\mu_0)^{-1}\sum_{i>j}(\nabla_j A_i - \nabla_i A_j)^2]. \quad (1)$$

In Eq. (1), μ_0 is the magnetic permeability of the normal metal, which is always very close to unity, $q_0 = 2e/\hbar c$, and $a = a'(T - T_c)/T_c$. The parameters a', b, and γ may be considered temperature-dependent for T near the transition temperature T_c. We work in the Coulomb gauge where $\nabla \cdot \vec{A} = 0$. In addi-

tion we note that (1) is only valid for long-wavelength variations—in particular we consider only Fourier components of ψ and $\vec{A}$ with wave vector k less than a cutoff Λ, which is normally taken to be the inverse of the zero-temperature coherence length in a superconductor. If $\psi(\vec{r})$ and $\vec{A}(\vec{r})$ are treated as fields in classical statistical mechanics,[6] the relative probability of finding a given configuration $\{\psi(\vec{r}), \vec{A}(\vec{r})\}$ is given by

$$\mathcal{P}(\psi, \vec{A}) = e^{-F\{\psi, \vec{A}\}/T}. \tag{2}$$

This probability is clearly maximized by choosing $\vec{A}=0$, and ψ independent of $\vec{r}$. Moreover, for $T > T_c$ we maximize $\mathcal{P}$ by choosing $\psi = 0$, while for $T < T_c$, we have $|\psi|^2 = |a|/b > 0$.

According to the "Ginzburg criterion,"[7] fluctuations in ψ should have no significant effect on the thermodynamics of the transition, except in the region

$$\frac{|T - T_c|}{T_c} < \epsilon_c \equiv \frac{1}{32\pi^2}\frac{b^2}{a'}\frac{T_c^2}{\gamma^3}. \tag{3}$$

In the case of a good type-I superconductor, we shall ultimately be interested in $|T - T_c|$ of the order of 10^{-6} K. Since the right-hand side of (3) is typically of order $(T_c/E_F)^4 \approx 10^{-16}$, we shall ignore fluctuations in ψ, and assume that ψ is a constant. We can now define a free energy $F(\psi)$, as a function of the single variable ψ, by taking the trace over the configurations of the vector potential:

$$e^{-F(\psi)/T} = \int d\{\vec{A}\} e^{-F\{\psi, \vec{A}\}/T}. \tag{4}$$

It follows from (1) that

$$\frac{1}{2\Omega}\frac{dF}{d|\psi|} = a|\psi| + b|\psi|^3 + q_0^2\gamma|\psi|\langle A^2\rangle_\psi, \tag{5}$$

where Ω is the volume of the system, and $\langle A^2\rangle_\psi$ is the expectation value of $|\vec{A}(\vec{r})^2|$ when ψ has the given (constant) value. Since (1) is quadratic in A, this expectation value can be evaluated by the equipartition theorem. One finds

$$\langle A^2\rangle_\psi = \frac{T_c\mu_0}{8\pi^3}\int_{|k|<\Lambda} d^3k \frac{8\pi}{k^2 + k_s^2}, \tag{6}$$

where k_s, the inverse of the London penetration depth, is given by

$$k_s^2 = 8\pi\gamma q_0^2\mu_0|\psi^2|. \tag{7}$$

If $|\psi|^2$ is sufficiently small so that $k_s \ll \Lambda$, Eq. (6) becomes

$$\langle A^2\rangle_\psi = 4\mu_0 T_c \Lambda\pi^{-1} - (32\pi\gamma q_0^2\mu_0)^{1/2}\mu_0 T_c|\psi|. \tag{8}$$

When (8) is inserted in (5), the first term of (8) leads to a slight renormalization of the Ginzburg-Landau T_c, which is not very interesting. The second term of (8), however, leads to a term in $F(\psi)$ which has negative sign and is proportional to $|\psi|^3$. Such a term inevitably leads to a first-order transition, as F develops a minimum at a finite value of ψ when the coefficient of the quadratic term is still slightly positive. Let us define the *size* of the first-order transition, ΔT_1, as the ratio of the latent heat L to the jump in specific heat, $\Delta C_p = (a')^2/bT_c$, predicted by Ginzburg-Landau. We find

$$\Delta T_1 = \tfrac{128}{9}\pi T_c^3\gamma^3 q_0^6\mu_0^3/a'b = \tfrac{8}{9}\epsilon_c T_c\kappa^{-6}. \tag{9}$$

In the last line, κ is the ratio of the London penetration depth to the temperature-dependent coherence length in the superconducting state, a number of order 0.02 for the best type-I materials. The theoretical limits of metastability of the normal and superconducting phases, T_n* and T_s*, lie below and above the first-order transition temperature by the amounts $\Delta T_1/2$ and $\Delta T_1/16$, respectively. Just below the transition, $|\psi|^2$ is equal to $a'\Delta T_1/b$.

According to the BCS theory, Eq. (9) can be expressed as

$$\Delta T_1 = 2.6\times 10^{-11} T_c^3 [H_c(0)]^2 \xi_0^6, \tag{10}$$

with temperatures in kelvin, H_c in oersteds, and ξ_0 in micrometers. For aluminum, which appears to be the most favorable case, we find $\Delta T_1 \approx 7$ μK, using the tabulated values $T_c = 1.19$ K, $H_c(0) = 99$ Oe, $\xi_0 = 1.6$ μm. Note, however, the extreme sensitivity of the estimate to the assumed value of ξ_0. It is not clear whether it is possible to prepare a sample with the homogeneity necessary to observe this first-order transition.

A useful self-consistency check on the validity of neglecting fluctuations in ψ is obtained from the fluctuation diamagnetism above T_c[8]:

$$-4\pi\chi' \approx \tfrac{1}{6} q_0^2 T_c(\gamma/a_{\rm eff})^{1/2}, \tag{11}$$

where $a_{\rm eff}$, the coefficient of the quadratic term in $F(\psi)$, is equal to $a'(T - T_n$*). The value of $4\pi|\chi'|$ just above the first-order transition is found to be $\frac{1}{8}\kappa\sqrt{2}$, which is small compared to unity for a type-I superconductor.

The case of a type-II superconductor is considerably more complicated. Here the size of the first-order transition will be equal to or smaller than $\epsilon_c T_c$, and fluctuations in ψ cannot be neglect-

ed. The problem is then too complicated to solve directly by any known technique. We are forced to consider generalizations of (1) to an $n/2$-dimensional complex order parameter and/or to noninteger spatial dimensionality d, and study the behavior of the transition in the limits $d \to 4$ or $n \to \infty$.

The limit $d \to 4$ can be studied by a generalization of the Wilson-Fisher recursion relations.[5] We consider repeated transformations in which we integrate out fluctuations with wave vectors between Λ/B and Λ, rescale all lengths by the factor B^{-1}, and rescale $\psi(\vec{r})$ and $\vec{A}(\vec{r})$ by factors $B^{(1/2)(d-2+\eta)}$ and $B^{(1/2)(d-2+\eta_A)}$, respectively. The result, correct to first order in $\epsilon \equiv 4-d$, is a new free-energy functional of the same form as (1), but with renormalized parameters[9]:

$$
\begin{aligned}
a_{l+1} &= B^{2-\eta}\{a_l + (b_l/\gamma_l)(4\pi)^{-2}(n+2)[\tfrac{1}{2}\Lambda^2(1-B^{-2}) - a_l \ln B] + q_l^2\mu_l\gamma_l(3/4\pi)\Lambda^2(1-B^{-2})\},\\
b_{l+1} &= B^{\epsilon-2\eta}[b_l - (b_l^2/\gamma_l^2)(n+8)\ln B/16\pi^2 - 12q_l^4\mu_l^2\gamma_l^2 \ln B],\\
\gamma_{l+1} &= B^{-\eta}\gamma_l[1 - q_l^2\mu_l 3\ln B/2\pi];\\
1/\mu_{l+1} &= (B^{-\eta_A}/\mu_l[1 + q_l^2\mu_l n \ln B/12\pi],\\
q_{l+1} &= B^{(1/2)(\epsilon-\eta_A)}q_l.
\end{aligned}
\tag{12}
$$

(Here we have assumed that a, b, and $q^2\mu$ are all of order ϵ, and have set $T_c = 1$.) For $n > 365.9$, (12) has a fixed point with

$$\eta = -18\epsilon n^{-1} + O(\epsilon^2), \tag{13}$$

$$\eta_A = \epsilon, \tag{14}$$

and finite positive values of $q^2\mu/\epsilon$, $b/\gamma\epsilon$, and $-a/\gamma\Lambda^2\epsilon$. The exponent ν may be calculated in the usual way, and one finds

$$1/\nu = 2 - \tfrac{1}{2}\epsilon(n+8)^{-1}[n+2-216n^{-1} + (n+2)n^{-1}(n^2-360n-2160)^{1/2}] + O(\epsilon^2). \tag{15}$$

[Equations (13) and (15) may be compared with the results for the uncharged case ($q_0 = 0$): $\eta_0 = O(\epsilon^2)$ and $\nu_0^{-1} = 2 - \epsilon(n+2)/(n+8) + O(\epsilon^2)$.] The critical exponents α, β, γ, and δ are determined from η and ν by the usual scaling laws. Furthermore, (14) implies that the observed magnetic permeability μ above T_c goes to zero as $(T-T_c)^{\epsilon\nu} \sim \xi^{-\epsilon}$, whenever a critical point exists, as predicted from the simple Ginzburg-Landau equations.[8]

For $n < 365.9$, there is no fixed point for nonzero charge. In particular, μ_l/ϵ becomes negative for sufficiently large l and approaches $-\infty$ as $l \to \infty$. This must be interpreted as signaling a first-order transition for $n < 365.9$ and ϵ sufficiently small.

The phase transition can also be studied in the limit $n \to \infty$ for fixed dimensionality d, by methods similar to those employed in the neutral case.[10] One finds that a critical point can exist in this limit with

$$
\begin{aligned}
\nu &= 1 - 9.72n^{-1} + O(n^{-2}),\\
\eta &= -4.053n^{-1} + O(n^{-2}), \quad \text{for } d = 3.
\end{aligned}
\tag{16}
$$

Presumably, at $d = 3$ there will again be a critical value n_c such that for $n < n_c$, the transition must always be first order. Although n_c no longer will be 365.9 at $d = 3$, it seems most unlikely that the critical value could be as small as 2, the value of n for the superconductor. We therefore conclude that the superconductor will always have a small first-order transition in three dimensions, even for the type-II case.[11] We expect that for large κ, the "size" of the first-order transition should have the form

$$\Delta T \approx \text{const} \times \epsilon_c T_c \kappa^{-2/\varphi}, \tag{17}$$

where the "crossover exponent"[12] φ is equal to $\epsilon\nu_0$ (≈ 0.67 for $d = 3$, $n = 2$).

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[6]Our use of classical statistical mechanics should be valid because the relaxation rate for fluctuations of the magnetic field in a metal is generally much smaller than $T_c/\hbar$, for all wave vectors less than Λ.

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[9]Actually, the momentum cutoff used in Eq. (1) is inconsistent with the requirements of gauge invariance. This introduces a spurious term in the free-energy functional proportional to $|\vec{A}(\vec{r})|^2$, which must be subtracted off at each iteration.

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[11]We may note in this connection that values of $\eta < 2-d$, or $\nu < 0$, such as are predicted by the $1/n$ terms of (16) for $n = 2$, are unphysical.

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Resistivity of Liquid Sodium-Cesium Alloys up to 300°C

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For a number of liquid sodium-cesium alloys the electrical resistivity ρ has been measured as a function of temperature T in the range 50–300°C. As a function of the cesium concentration c, $(\partial\rho/\partial T)_p$ exhibits a distinct minimum for $c = 0.6$, which gradually disappears at higher temperatures. This minimum is related to the results for the resistivity at high pressure recently obtained by Tamaki, Ross, Cusack, and Endo.

Measurements of the electrical resistivity ρ of liquid sodium-cesium alloys as a function of the temperature T have been communicated recently.[1,2] It was demonstrated that, at 100°C, $(\partial\rho/\partial T)_p$, plotted as a function of the atomic concentration c of cesium exhibits a pronounced relative maximum for $c \sim 0.60$. The maximum was ascribed to an ordering phenomenon, more particularly to the formation of a compound Na_3Cs, in the liquid at temperatures close to the melting point. The existence of such a compound was strongly suggested by the results of Kim and Letcher[3] on ultrasonic absorption. This ordering was supposed to disappear gradually at temperatures above the melting point, thus giving rise to a larger value of $(\partial\rho/\partial T)_p$ in that particular temperature range. The maximum was then expected to disappear at higher temperatures.

In order to check this supposition, the measurements were extended towards higher temperatures, and, for some of the alloy compositions, also to lower temperatures. The experimental equipment used for the measurements above 100°C was basically the same as the one described by Hennephof, van der Lugh, and Wright,[4] but the whole system was made of stainless steel. The results are shown in Fig. 1.

Fair agreement with earlier results has been obtained.[5-7] Furthermore, it is evident that it is not the maximum of $(\partial\rho/\partial T)_p$ that disappears at higher temperatures, but rather the minimum: $(\partial p/\partial T)_p$ varies strongly as a function of temperature in this part of the concentration range, whereas for $c < 0.25$, $(\partial^2\rho/\partial T^2)_p$ almost vanishes. This is in contradiction with our former supposition.

It is interesting to compare our results on the temperature dependence of ρ with those at high pressure obtained by Tamaki *et al.*[8] for the same alloy system. According to their measurements, $(\partial\rho/\partial p)_T$, plotted as a function of c, changes sign twice. It is negative for $c < 0.25$ and for $c > 0.80$ (as it is for all pure liquid alkali metals except Li), whereas it is positive for intermediate concentrations. The central composition range for which $(\partial\rho/\partial p)_T > 0$ corresponds fairly well to the valley found for $(\partial\rho/\partial T)_p$. The two quantities are related by

$$\left(\frac{\partial\rho}{\partial T}\right)_V = \left(\frac{\partial\rho}{\partial T}\right)_p + \left(\frac{\partial\rho}{\partial p}\right)_T \left(\frac{\partial p}{\partial T}\right)_V. \quad (1)$$

For the pure alkali metals except Li, $(\partial\rho/\partial T)_V$, $(\partial\rho/\partial T)_p$, and $(\partial p/\partial T)_V$ are positive quantities and $(\partial\rho/\partial p)_T$ is negative.[9-13] Consequently $(\partial\rho/$