

Universal Jump in Slope of the Chemical Potential at Second-Order Phase Transitions

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(Received 26 June 1992)

We point out that in systems exhibiting a second-order phase transition, the chemical potential has a jump in slope at the critical temperature, *provided that* T_c depends on particle density. We derive a generally valid thermodynamic relation between the specific heat jump, the jump in $d\mu/dT$, and $d\ln T_c/dn$, with μ the chemical potential and n the density of the particles causing the transition. This relation is similar, but not equivalent, to the more familiar Ehrenfest relation between expansivity, specific heat, and $d\ln T_c/dp$, with p the externally applied pressure.

PACS numbers: 74.30.Ek, 05.70.Fh, 75.40.Cx

In a number of papers [1–5] it has been shown that a jump in slope occurs in the temperature dependence of the chemical potential of narrow band superconductors. The earliest paper where this effect is displayed is to our best knowledge by Robaszkiewicz, Micnas, and Chao on the Hartree approximation of the negative- U Hubbard model [1]. One of us analyzed this effect [2] using different approximations to the retarded interaction, mainly to draw attention to the fact that this kind of shift in the chemical potential can be observed experimentally, and may give important information about the nature of high- T_c superconductivity. Khomskii and Kusmartsev [3] showed that if there is more than one band involved, the change of μ could be partly screened due to an anomalous charge transfer between the bands.

In a quite different model of *bosons* exhibiting a phase transition to a paired state due to an effective attractive interaction, Rice and Wang [4] predicted a temperature dependence of μ very similar to the case of fermions. No discontinuity in slope of $\mu(T)$ occurs for noninteracting bosons in 3D, while in 2D and 1D T_c is zero. If one assumes, without specifying the physical origin, that the boson density of states has an algebraic energy dependence $\rho(E) \propto E^\alpha$, a jump in $d\mu/dT$ can occur at the phase transition provided that $\alpha \geq 1$ [5].

Although derived so far for specific models of superconductivity, this behavior of μ is a generic property of second-order phase transitions, with a direct link to the specific heat and the dependence of the critical temperature on particle density. In this paper we will derive this relation from general thermodynamic considerations, as well as from the Ginzburg-Landau expression for the free energy.

The order parameter ψ is solved from the Ginzburg-Landau expression for the difference in free energy density [6] between the ordered (index ψ) and normal state (index n) $f_\psi(n, T, \psi) - f_n$, which is given by $a(T/T_c - 1)|\psi|^2 + b|\psi|^4$. The order parameter has a nontrivial solution for $T < T_c$, with a free energy difference $-a^2(4b)^{-1}(1 - T/T_c)^2$. As we want to determine the

chemical potential ($\mu = \partial f/\partial n$), it is important to realize that the n dependence of f enters through the parameters a , b , and T_c . The expression for the chemical potential becomes

$$\mu_\psi - \mu_n = -\frac{a^2 T}{2b T_c} \frac{d\ln T_c}{dn} \left(1 - \frac{T}{T_c}\right) - \frac{d(a^2/4b)}{dn} \left(1 - \frac{T}{T_c}\right)^2. \quad (1)$$

Clearly the first term gives rise to discontinuous behavior of $d\mu/dT$ at the phase transition, while the second term has a discontinuity in $d^2\mu/dT^2$. We can combine the expression for the jump in $d\mu/dT$ with the expression for the jump in the specific heat [$c_n - c_\psi = -a^2(2bT_c)^{-1}$] to obtain the central equation

$$\left. \frac{d}{dT} (\mu_n - \mu_\psi) \right|_{T=T_c} = \frac{d\ln T_c}{dn}. \quad (2)$$

Alternatively this relation can be derived from general thermodynamic considerations [7]. The temperature derivative of the chemical potential and the specific heat can both be expressed as derivatives of the entropy density: $d\mu/dT = -ds/dn$, and $c_V = T ds/dT$. In the T vs n phase diagram (Fig. 1) the second-order phase transition is indicated as the curve $T_c(n)$ separating the two phases. As the entropy is continuous at the transition, $s_1 = s_2$ and $s_3 = s_4$ if the pairs (1,2) and (3,4) are infinitesimally close to the $T_c(n)$ curve. Using an expansion for small δn and δT we can write

$$s_3 = s_1 + \frac{\partial s_n}{\partial T} \delta T + \frac{\partial s_n}{\partial n} \delta n + \dots$$

and a similar expression connecting s_4 to s_2 . Employing the property of continuity of s at a second-order phase transition, and using the fact that T is varied along the $T_c(n)$ curve, we obtain

$$-\frac{\partial s_n}{\partial n} + \frac{\partial s_\psi}{\partial n} = \left(\frac{\partial s_n}{\partial T} - \frac{\partial s_\psi}{\partial T} \right) \frac{dT_c}{dn} \quad (3)$$

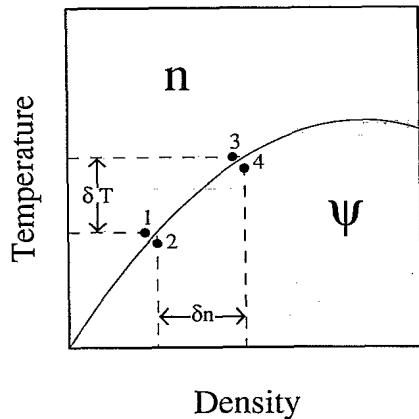


FIG. 1. Phase diagram in the temperature vs particle-density plane. Solid curve: T_c as a function of n , separating the low-temperature (ψ) from the high-temperature (n) phase.

which is equivalent to Eq. (2).

So far the expressions were derived for a system at constant volume. If we want to describe a solid held at constant pressure, small modifications enter because the density n now also depends on temperature. The expansivity coefficient is $\alpha \equiv V^{-1}dV/dT = -n^{-1}dn/dT$, so that corrections of the type $-\alpha n(d\mu/dn)$ and $-\alpha nT(ds/dn)$ occur in the expressions for $d\mu/dT$ and c . As α behaves discontinuously at the phase transition [8] the jump at T_c is altered for both c and $d\mu/dT$. However, because of the smallness of α and the jump therein the corrections are negligible in a solid.

It is interesting to compare our central result Eq. (2) to the more common Ehrenfest relation [8]

$$\frac{\alpha_n - \alpha_\psi}{c_n - c_\psi} \Big|_{T=T_c} = \frac{d \ln T_c}{dp} \quad (4)$$

Although this relation looks similar to Eq. (2), there is an important difference: Equation (4) links three quantities, each of which can be measured separately. Hence this relation can be used to check the validity of the thermodynamic relations and the assumption of a second-order phase transition. In Eq. (2) only the temperature dependence of the chemical potential and the specific heat can be measured directly, but the particle density is an intrinsic property of a material, which is usually difficult to control.

In many cases one expects a strong dependence of T_c on n , especially if the interactions between particles leading to the phase transition affect a large fraction of the states out of which the many-body wave function is formed. To give an example, let us briefly discuss the superconducting critical temperature in a 2D negative- U Hubbard model, treated in the Hartree approximation. In the low density limit T_c is proportional to $Wan^{1/2}e^{(-1/g)}$, where a is the lattice constant, W is the bandwidth, n is

the density of electrons, and g is the attractive electron-electron coupling constant [9]. If we change the external hydrostatic pressure with an amount δp , the volume changes by an amount $\delta V = -V\delta p/B$, where B is the bulk modulus. Both n and the lattice constant change, but as the total number of electrons is conserved, the product na^2 is a constant. W and g also have a pressure dependence, so that

$$d \ln T_c / dp = -B^{-1}(d \ln W / d \ln V + g^{-1} d \ln g / d \ln V).$$

The pressure derivative differs strongly from the derivative with respect to n , for which we obtain $d \ln T_c / dn = (2n)^{-1}$. This model can easily be shown to be in agreement with the thermodynamic relation Eq. (2). Using the fact that within the framework of this model the specific heat $c_n - c_\psi \approx \rho |\Delta(T)|^2 / dT$, with ρ the density of states, while the carrier density is given by $n = 2\rho\mu_n$, we obtain the familiar equation [2, 3] $\mu_\psi \approx \mu_n - |\Delta(T)|^2 / 4\mu_n$.

Hence Eq. (2) gives us access to a quantity which is otherwise difficult to determine, namely, the density dependence of the critical temperature. Recently a successful series of measurements of the jump in slope of μ at T_c have been performed on high- T_c cuprates [10], and the value obtained for $d \ln T_c / dn$ was compared to microscopic models of the density dependence of T_c . Other examples where strong renormalizations of the many-body wave function occur at a second-order phase transition are ferro- and antiferromagnetic phase transitions and charge density waves. Experiments aimed at the determination of $d\mu/dT$ could, in combination with specific heat data, provide new and valuable information about the microscopic nature of these phase transitions.

As it is now possible to measure dT_c/dn experimentally, there is a way to predict from a set of data on a single material in which direction doping levels have to be changed in order to reach an optimal transition temperature. In combination with studies of the pressure dependence it is possible to disentangle, at least in part, the contributions of the various microscopic parameters to the pressure dependence. This way one can supply relevant experimental information in, e.g., the quest for the mechanism of high-temperature superconductivity.

In conclusion we have demonstrated from an analysis of thermodynamic relations valid for second-order phase transitions, that the availability of a new type of experimental data, namely, the temperature dependence of the chemical potential, can provide information on the density dependence of the critical temperature. It is particularly interesting to analyze this type of experimental information together with specific heat data, thermal expansivity, and the pressure dependence of the critical temperature. From such an analysis one can decide to which extent pressure dependencies of T_c are due to changes of particle density or changes of other microscopic parameters. Also the size and sign of the experi-

mental value of dT_c/dn can be used as a guide to develop materials with higher (or, if required, lower) transition temperatures.

We gratefully acknowledge G. M. Eliashberg for inspiring comments, and J. M. J. van Leeuwen for illuminating discussions.

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