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Specific heat jump in BCS superconductors

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Abstract. An exact analytical expression for the specific heat jump ΔC at the critical temperature T_c has been obtained directly from the BCS gap equation for any shape of the energy dependent electronic density of states (DOS). We consider a model which takes into consideration electron-electron repulsion, formulated in the Hubbard model along with the electron-electron attraction due to electron-phonon interaction in the BCS formalism. We have analyzed this expression for constant as well as for the Lorentzian forms of DOS. It is shown that the constant DOS in the simple BCS theory cannot explain the large values of $\Delta C/T_c$, found in some superconductors. The specific heat *versus* temperature curve has been found to have a peak, similar to that of Eliashberg theory of superconductivity. The influence of repulsive interaction is very small and occurs mainly at higher temperatures.

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The specific heat is an important tool to investigate the excitation pectrum in the superconducting state [1]. It also informs us about the nature of phase transition [2] and the symmetry of the pairing state [3]. The specific heat is specially suitable to study the BCS superconductors [2]. For example all the parameters in the BCS formula $T_c = 1.14\ \theta_D e^{-1/\lambda}$ can in principle be determined by a single specific heat measurement. It gives the critical temperature, T_c, from the position of the jump, the Debye temperature, θ_D, from the slope of the specific heat *versus* T^3 in the limit $T_c \to 0$, and λ from the ratio of high and low temperature values of the Sommerfeld constant.

In BCS theory the ratio, $\Delta C/T_c$, is a constant quantity. In many conventional superconductors like Pb and Nb_3Sn [4], in alkali doped fullerenes [5] and also in high temperature cuprates superconductors [2] this ratio has been found to be greater than the BCS value. Recently the explanation of this discrepancy has been attributed to the logarithmic van-Hove singularity in the normal state electronic density of states (DOS) in the BCS theory [6,7].

Here we consider a model which in addition to electron-phonon induced attractive interaction between electrons, takes into account a repulsive Coulomb interaction, formulated in the Hubbard model. This model has recently been considered by Hocquet *et al.* [9] to study the critical temperature and the isotope effect. Within the Bogoliubov-Valatin [10] approximation for the above model, one obtains the BCS gap equation as

$$\Delta_{\mathbf{k}} = -\frac{1}{2}\sum_{\mathbf{k}'} \frac{(V_{\mathbf{k}\mathbf{k}'} + \frac{U}{N})\Delta_{\mathbf{k}'}}{\sqrt{E_{\mathbf{k}'}^2 + \Delta_{\mathbf{k}'}^2}} \tanh\left(\frac{\sqrt{E_{\mathbf{k}'}^2 + \Delta_{\mathbf{k}'}^2}}{2kT}\right), \tag{1}$$

where, $E_{\mathbf{k}} = \epsilon_{\mathbf{k}} + Un/2 - \epsilon_f$, is the Hartree Fock one particle energy, U is the repulsive intra-atomic interaction of the Hubbard model, N is the total number of sites, n is the average number of electrons per site, $\epsilon_{\mathbf{k}}$ is the bare particle energy in the band, and ϵ_f is the Fermi energy. We shall measure the energy such that the sum of the Hartree-Fock shift $Un/2$ and the energy of the middle of the band is equal to zero. The width of the band is taken equal to $2W$. Following BCS the scattering matrix element $V_{\mathbf{k}\mathbf{k}'}$ due to phonon mediated interaction is assumed to have a nonvanishing value $-V/N$ with $V > 0$ only if both $|E_{\mathbf{k}}|$ and $|E_{\mathbf{k}'}|$ are smaller than the Debye energy $\hbar\omega_D$.

The specific heat jump, ΔC, at the critical temperature T_c is related to the temperature derivative of the square of the gap parameter by the expression [11],

$$\Delta C = -\sum_{\mathbf{k}} \left(-\frac{\partial f_{\mathbf{k}}}{\partial \epsilon_{\mathbf{k}}}\right) \left[\frac{d\Delta_{\mathbf{k}}^2}{dT}\right]_{T=T_c} \tag{2}$$

where $f_{\mathbf{k}}$ is the Fermi distribution function for electrons of wave vector $\mathbf{k}$ at the critical temperature T_c. The temperature derivative of the square of the gap parameter, can be obtained from the numerical solutions of the BCS gap equation. However, usually this derivative is obtained from the approximate analytical expression for the gap parameter near T_c. In this paper, we show that it is

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not necessary to have an explicit expression of the gap parameter near T_c to obtain its derivative at T_c.

For the simple BCS form of the scattering matrix element, as described above, the solutions of the BCS gap equation (1) have the following structure

$$\begin{aligned} \Delta_{\mathbf{k}} &= \Delta_1 \quad \text{if} \quad |E_{\mathbf{k}}| < \hbar\omega_D, \\ &= \Delta_2 \quad \text{if} \quad |E_{\mathbf{k}}| > \hbar\omega_D. \end{aligned} \tag{3}$$

Upon substituting the solutions (3) in equations (1, 2), one obtains the equations for ΔC, Δ_1 and Δ_2 as

$$\begin{aligned} \Delta C = &\left[\frac{d\Delta_1^2}{dT}\right]_{T=T_c} \langle\eta(\epsilon)\rangle_D \\ &+ \left[\frac{d\Delta_2^2}{dT}\right]_{T=T_c} (\langle\eta(\epsilon)\rangle_W - \langle\eta(\epsilon)\rangle_D) \end{aligned} \tag{4}$$

$$\begin{aligned} \Delta_1 &= (V-U)\Delta_1 F_1^D - U\Delta_2(F_2^W - F_2^D), \\ \Delta_2 &= -U\Delta_1 F_1^D - U\Delta_2(F_2^W - F_2^D) \end{aligned} \tag{5}$$

where

$$\begin{aligned} F_\alpha^D &= \int_{-\hbar\omega_D}^{\hbar\omega_D} d\epsilon \frac{\eta(\epsilon+\epsilon_f)\tanh\left(\frac{\sqrt{\epsilon^2+\Delta_\alpha^2}}{2kT}\right)}{2\sqrt{\epsilon^2+\Delta_\alpha^2}}, \\ F_2^W &= \int_{-W-\epsilon_f}^{W-\epsilon_f} d\epsilon \frac{\eta(\epsilon+\epsilon_f)\tanh\left(\frac{\sqrt{\epsilon^2+\Delta_2^2}}{2kT}\right)}{2\sqrt{\epsilon^2+\Delta_2^2}}, \end{aligned} \tag{6}$$

$\eta(\epsilon)$ is the electronic density of states (DOS) per spin, $\alpha = 1, 2$, and $\langle\eta(\epsilon)\rangle_D$ and $\langle\eta(\epsilon)\rangle_W$ are the thermally averaged DOS, given as

$$\begin{aligned} \langle\eta(\epsilon)\rangle_D &= \int_{-\hbar\omega_D+\epsilon_f}^{\hbar\omega_D+\epsilon_f} d\epsilon\eta(\epsilon)\left(-\frac{\partial f}{\partial\epsilon}\right), \\ \langle\eta(\epsilon)\rangle_W &= \int_{-W}^{W} d\epsilon\eta(\epsilon)\left(-\frac{\partial f}{\partial\epsilon}\right). \end{aligned} \tag{7}$$

A simple algebraic manipulation of the set of equations (5) shows that

$$\Delta_2 = (1 - VF_1^D)\Delta_1. \tag{8}$$

Upon substituting the expression (8) for Δ_2 in equations (5), we get

$$1 = \left(V - \frac{U}{1+U(F_2^W - F_2^D)}\right) F_1^D. \tag{9}$$

We shall use equations (8, 9) to calculate the temperature derivative of the square of the gap parameters Δ_1 and Δ_2 at the critical temperature T_c in order to obtain the specific heat jump ΔC. Differentiating equation (8) with respect to T and taking the limit $\Delta_1 \to 0$ as $T \to T_c$ we get

$$\left[\frac{d\Delta_2^2}{dT}\right]_{T=T_c} = (1 - VF_D)^2 \left[\frac{d\Delta_1^2}{dT}\right]_{T=T_c}, \tag{10}$$

Similarly differentiating equation (9) with respect to T and taking the limits $\Delta_1, \Delta_2 \to 0$ as $T \to T_c$ we get

$$\begin{aligned} &F_D U^{*^2}(G_W - G_D)\left[\frac{d\Delta_2^2}{dT}\right]_{T=T_c} + (V - U^*)\frac{\partial F_D}{\partial T_c} \\ &+ (V - U^*)G_D\left[\frac{d\Delta_1^2}{dT}\right]_{T=T_c} + F_D U^{*^2}\frac{\partial(F_W - F_D)}{\partial T_c} = 0 \end{aligned} \tag{11}$$

where

$$\begin{aligned} F_D &= \int_{-\hbar\omega_D/2kT_c}^{\hbar\omega_D/2kT_c} d\epsilon \frac{\eta(2kT_c\epsilon + \epsilon_f)\tanh(\epsilon)}{2\epsilon}, \\ F_W &= \int_{(-W-\epsilon_f)/2kT_c}^{(W-\epsilon_f)/2kT_c} d\epsilon \frac{\eta(2kT_c\epsilon + \epsilon_f)\tanh(\epsilon)}{2\epsilon}, \\ G_D &= -\int_{-\hbar\omega_D/2kT_c}^{\hbar\omega_D/2kT_c} d\epsilon \frac{\eta(2kT_c\epsilon + \epsilon_f)}{(4kT_c)^2} Q(\epsilon), \\ G_W &= -\int_{(-W-\epsilon_f)/2kT_c}^{(W-\epsilon_f)/2kT_c} d\epsilon \frac{\eta(2kT_c\epsilon + \epsilon_f)}{(4kT_c)^2} Q(\epsilon), \\ Q(\epsilon) &= \frac{\tanh^2\epsilon}{\epsilon^2} + \frac{\tanh\epsilon - \epsilon}{\epsilon^3}, \end{aligned} \tag{12}$$

and

$$U^* = \frac{U}{1 + U(F_W - F_D)}\,. \tag{13}$$

Upon substituting $\left[d\Delta_2^2/dT\right]_{T=T_c}$ from equation (10) in equations (11, 4), we get

$$\left[\frac{d\Delta_1^2}{dT}\right]_{T=T_c} = -\frac{(V^*)\frac{\partial F_D}{\partial T_c} + U^{*2}F_D\frac{\partial(F_W - F_D)}{\partial T_c}}{(V^*)G_D + U^{*2}F_D\xi^2(G_W - G_D)}, \tag{14}$$

and the jump in the specific heat at T_c as

$$\Delta C = -\left[\frac{d\Delta_1^2}{dT}\right]_{T=T_c} \{\langle\eta(\epsilon)\rangle_D + \xi^2(\langle\eta(\epsilon)\rangle_W - \langle\eta(\epsilon)\rangle_D)\}. \tag{15}$$

Here $V^* = V - U^*$ and $\xi = 1 - VF_D$. It is possible to eliminate V from equation (14) by using the expression for T_c which can be obtained from equation (9) by taking the limits $\Delta_1 \to 0$ and $\Delta_2 \to 0$. It is given as

$$1 - V^*F_D = 0. \tag{16}$$

Substituting the value of U^* from equation (16) in equation (14) we get

$$\left[\frac{d\Delta_1^2}{dT}\right]_{T=T_c} = -\frac{\frac{\partial F_D}{\partial T_c} + (U^*F_D)^2\frac{\partial(F_W - F_D)}{\partial T_c}}{G_D + (U^*F_D)^4(G_W - G_D)}\,. \tag{17}$$

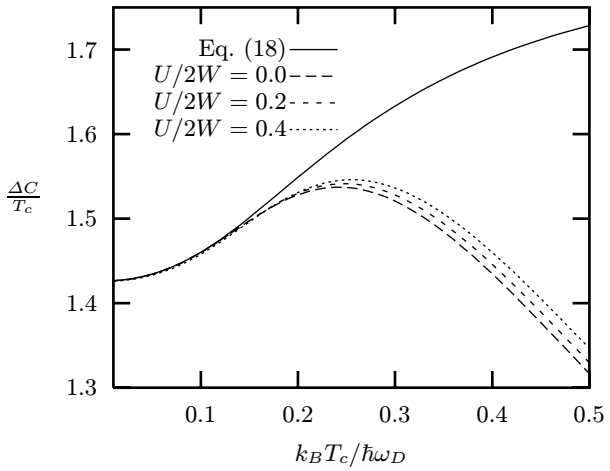

Fig. 1. $\Delta C/T_c$ (in units of $\frac{2\pi^2 k^2}{6W}$) *versus* $kT_c/\hbar\omega_D$ for constant density of states.

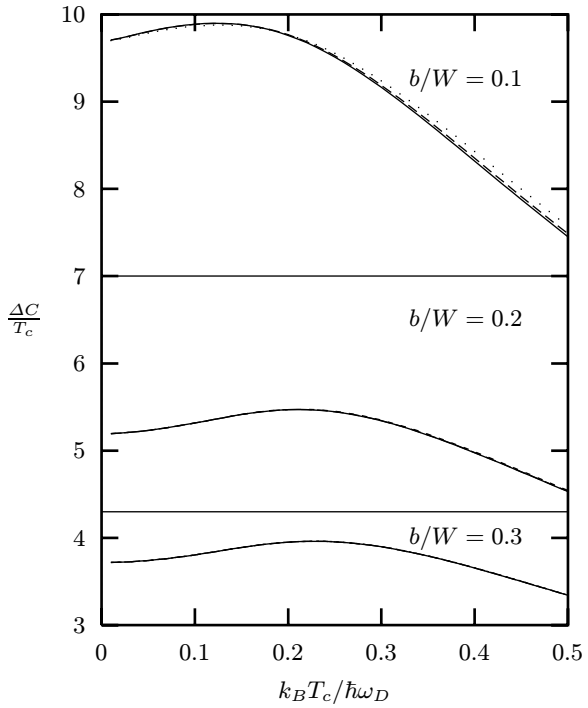

Fig. 2. $\Delta C/T_c$ (in units of $2\pi^2 k^2/6W$) *versus* $kT_c/\hbar\omega_D$ for the normalized Lorentzian density of states, $\rho(\epsilon) = \frac{1}{2\tan^{-1}(\frac{w}{b})}\frac{b}{\epsilon^2+b^2}$, for various values of b/W and $U/2W$. The solid line corresponds to $U/2W = 0.0$, the dashed line corresponds to $U/2W = 0.2$ and the small dashed line corresponds to $U/2W = 0.4$.

It should be noted that equation (15), together with equation (17), is an exact analytical expression for the specific heat jump ΔC within the BCS framework. It can be used to check the validity of other results of ΔC, obtained from the approximate expressions for the gap parameters. For example, recently Nam [12] has calculated the specific heat jump ΔC from the BCS gap equation in absence of short range interactions by expanding the gap parameter near T_c. Considering the constant DOS near the Fermi energy and replacing the thermally averaged DOS $\langle\eta(\epsilon)\rangle_D$ by $\eta(\epsilon_f)$, he showed that at $\hbar\omega_D/2kT_c = 2$ the ratio $\Delta C/T_c$, is equal to 3.4γ compared to the BCS value of 1.4γ. Here γ is the sommerfeld constant $\gamma = 2\pi^2 k^2 \eta(e_f)/3$. Our exact results show that his results are in error. For the constant DOS near the Fermi energy and the thermally averaged DOS $\langle\eta(\epsilon)\rangle_D = \eta(\epsilon_f)$, equations (12–17) show that in absence of repulsive interaction U

$$\Delta C = \frac{16\eta(\epsilon_f)k^2 T_c \tanh(\hbar\omega_D/2kT_c)}{\int_{-\hbar\omega_D/2kT_c}^{\hbar\omega_D/2kT_c} d\epsilon Q(\epsilon)}\,. \qquad (18)$$

From the above equation it is easy to show that in the limit $T_c \to 0$,

$$\frac{\Delta C}{T_c} \to \frac{12}{\pi^2 \int_0^\infty d\epsilon Q(\epsilon)} = 1.43\gamma \qquad (19)$$

and in the limit $T_c \to \infty$,

$$\frac{\Delta C}{T_c} \to \frac{18\gamma}{\pi^2} = 1.82\gamma. \qquad (20)$$

At intermediate temperatures $\Delta C/\ T_c$ increases monotonically with temperature as shown in Figure 1. Thus for the constant DOS $\Delta C/T_c$ cannot reach the value of 3.4γ as obtained by Nam [12].

The temperature dependence of thermal DOS $\langle\eta(\epsilon)\rangle_D$ and $\langle\eta(\epsilon)\rangle_W$, neglected in obtaining equation (18), is to reduce $\Delta C/\ T_c$ and produce a peak at $kT_c/\hbar\omega_D = 0.24$ in absence of repulsive interaction U. As shown in Figure 1 this behavior of $\Delta C/\ T_c$ is very similar to that of Marsiglio *et al.* [13] and Carbotte [14], obtained by using Eliashberg theory of superconductivity. In presence of the repulsive interaction U, $\Delta C/\ T_c$ depends upon the position of the Fermi energy. We have performed calculations for the Fermi energy located at zero of our energy scale. As shown in Figure 1, the effect of repulsive interaction U is very small. Visible effect occurs only at higher temperatures where it increases $\Delta C/\ T_c$. In Figure 2 we have plotted $\Delta C/\ T_c$ *versus* $kT_c/\hbar\omega_D$ for normalized Lorentzian DOS. It is found that $\Delta C/\ T_c$ increases as the sharpness of the Lorentzian DOS peak increases (or the width of the Lorentzian DOS peak decreases). Similar result was found by Tsuei *et al.* [6] in absence of the repulsive interaction U. The effect of U is again very small but increases as the sharpness of the peak increases. This negligible effect of U can also be seen directly from equation (17). In this equation the effect of U on $\Delta C/\ T_c$ over the BCS value appears in second or higher order power of U. Thus for small U (the regime of the validity of the Hartree-Fock approximation) the change in $\Delta C/\ T_c$ over the BCS value is expected

to be small for any form of the DOS. However, the correlation effects which are relevant for high T_c superconductors may change this conclusion. In this case one may also require to consider the DOS with Van-Hove singularity and the d-wave pairing.

Thus we have shown that one can obtain an exact analytical expression for the jump in specific heat at T_c directly from the BCS gap equation. The analysis of this expression shows that the constant DOS in the conventional BCS theory cannot explain the large values of $\Delta C/T_c$ found in many superconductors. Also the electron-electron repulsive interaction treated within Hartree-Fock approximation [10] does not give any appreciable enhancement of the ratio $\Delta C/T$ over BCS value. To explain the higher values of $\Delta C/\ T_c$ within the BCS framework, one may need to take into account the energy dependent density of states with sharper peak at the Fermi level.

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