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ANOMALOUS BEHAVIOUR OF THE CHEMICAL POTENTIAL IN SUPERCONDUCTORS WITH A LOW DENSITY OF CHARGE CARRIERS

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We discuss the behaviour near T_c of the chemical potential in superconductors with a dilute gas of interacting fermions. It is shown that at T_c there exists an anomaly in the chemical potential that distinguishes superconductors with Δ and E_F of comparable magnitude from ordinary BCS superconductors ($\Delta \ll E_F$). We predict the size of the anomaly for a number of existing superconductors and we argue, that if high-T_c superconductors are indeed special in the above sense, the anomaly is well in the observable range and could be used as an experimental test of the various "exotic" models of the superconducting mechanism.

1. Introduction

Following the discovery of high-T_c superconductivity in a large number of ceramic materials, various theoretical models for the mechanism of high temperature superconductivity have been proposed [1]. In spite of the large variety of proposed mechanisms, most of these models have in common that they deal with dilute gases of strongly interacting particles. It is therefore interesting to study the physics of strongly interacting dilute fermion systems, even without knowing the specific nature of the interaction. Already long before the discovery of high-T_c superconductivity the physics of tightly bound Cooper pairs in the dilute limit had been studied by Eagles [2], Leggett [3], Nozieres and Schmitt-Rink [4]. A very recent discussion was made by Randeria et al. [5]. In these papers it has been shown that there exists a gradual transition from a ground state with large, overlapping Cooper pairs to a Bose condensate of composite bosons formed out of tightly bound pairs of fermions. One can, for example show that the BCS ground state wavefunction and the ground state wavefunction of Bose condensed electron-pairs [6] have the same mathematical form.

A key element in the analysis of superconductors with a large fraction of Cooper pairs in the ground state is the fact that in a dilute system the opening of a gap will, in principle, affect the position of the Fermi level. As the electron density of a macroscopic 3D system is a fixed quantity the chemical potential will adjust itself to the change in the electron configuration self-consistently in order to obey macroscopic number conservation [7]. Although this self-consistent adjustment has been taken into account in several papers, it has not been widely realized that this shift in Fermi level is in fact an experimentally observable quantity. Although it is not the purpose of this paper to explain in detail the various available experimental techniques for studying temperature dependent changes in the chemical potential, we will briefly point out the basic experimental ingredients. In short one has to measure the workfunction of the superconductor as a function of temperature. In principle the workfunction is the sum of three components: (1) the chemical potential of the metal, (2) the potential drop at the surface due to the surface electronic structure and (3) the potential drop just outside the surface due to absorbed gas molecules. Due to the presence of the latter two components a workfunction measurement never gives an

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absolute value of the chemical potential. However, quite often, as in the present case, one is merely interested in temperature dependent changes of the chemical potential. Under proper experimental conditions contributions (2) and (3) can be made almost temperature independent, so that in principle it should be possible to get a proper measurement of the temperature induced changes in contribution (1). A summary of the available techniques for workfunction determinations can be found in a review article by Cardona [8]. The best resolution (better than 1 meV) can probably be obtained with either the Kelvin probe method [8] or the capacitive temperature modulation technique [9]. A prerequisite for reliable results at low temperatures is true ultra high vacuum (better than 10^{-10} Torr), which makes this type of experiment far from trivial. An early attempt to look experimentally at workfunction changes in classical BCS superconductors was made by de Waele [9], who was in search of the superconducting analogue of the fountain effect in superfluid He II [10].

In this paper we will show that in systems with a Debye energy comparable to or larger than the Fermi energy there is a kink in the chemical potential at T_c. The size of this effect depends strongly on the ratio of Δ/μ, where Δ is the superconducting gap at $T=0$ and μ is the Fermi energy relative to the bandbottom. To our knowledge the only paper where this effect has been displayed is the paper by Robaszkiewicz and coworkers from 1982, on the Hartree theory for the negative U Hubbard model [11]. In the present paper we will consider a more general form of the interaction and find qualitative agreement with the above mentioned work. For clarity we have to add, that in our discussion we reserve the term Debye energy for any cutoff energy D due to retardation effects, regardless of the microscopic origin of the interaction (i.e. phonon mediated or other mechanisms). We make numerical estimates of the size of the anomaly for some existing superconductors and show that the kink in the chemical potential should be fairly large and well inside the observable range. Experimental verification or falsification would put a constraint on many of the proposed theories for the mechanism(s) of high temperature superconductivity. As a kink in the chemical potential is related to a jump in the specific heat on thermodynamical grounds, we will furthermore derive the expressions for the resulting modification of the BCS specific heat jump and show that the absolute jump is only slightly reduced due to this effect. From numerical examples we will prove, however, that the relative specific heat jump may be enhanced due to thermal excitations of the electron gas in the normal state.

2. Solution of the coupled gap equations

The coupled BCS equations at finite temperature are

$$2\Delta_k = \sum_q V_{kq} \frac{1-2f(\beta E_q)}{E_q} \Delta_q , \tag{1}$$

$$N = \sum_k \left(\frac{E_k - \epsilon_k}{E_k} + 2\frac{\epsilon_k}{E_k} f(\beta E_k) \right) , \tag{2}$$

where $E_k = \sqrt{\epsilon_k^2 + \Delta_k^2}$ are the quasiparticle energies and $\epsilon_k = \xi_k - \mu$ are the single electron energies relative to the Fermi energy. The usual way to decouple the gap equation is to replace the interaction term V_{kq} with a separable form $V\gamma_k\gamma_q^*$, resulting in a k-dependence of Δ of the form $\Delta_k = \Delta\gamma_k$. To simplify matters further we will replace the summation in k-space with an energy integration over a constant density of states n. In terms of the γ's the gap equation becomes:

$$\frac{2}{nV} = \int_{-\mu}^{\infty} \frac{1-2f(\beta\sqrt{\epsilon^2+\Delta^2}}{\sqrt{\epsilon^2+\Delta^2}} |\gamma(\epsilon)|^2 \mathrm{d}\epsilon . \tag{3}$$

In the present case, where the Debye energy D is no longer small compared to the Fermi energy we have to distinguish two different cases: in the first case (1) we make the usual assumption of a retarded potential equal to V in the energy interval $[-D, D]$ around the Fermi level where D is the Debye frequency. As soon as the Fermi energy becomes smaller than D, the lower cutoff in energy space will no longer be the Debye frequency but the bottom of the band. In the second case (2) we introduce an energy dependency of γ, which is fixed in k-space, i.e. it is independent of the position of the Fermi level. This corresponds to the following interaction Hamiltonian, using tight-binding notation for the site-projected electron creation and annihilation operators:

$$H^{\mathrm{I}} = -V\sum_{R}\left(\sum_{r}\tilde{\gamma}_r c^{\dagger}_{k-r/2\uparrow}c^{\dagger}_{R+r/2\downarrow}\right)$$

$$\times\left(\sum_{r'}\tilde{\gamma}^{*}_{r'}c_{R+r'/2\downarrow}c_{R-r'/2\uparrow}\right).$$

Here $\tilde{\gamma}_r$ is the Fourier transform of γ_k. We see that this interaction Hamiltonian is non-retarded. Note, that if we choose γ_k to be k-independent, $\tilde{\gamma}_r$ is a δ-function model. An easily solvable model potential of type (2) is a potential that is zero above a characteristic energy D relative to the bottom of the band and V in the interval $[-\mu, D-\mu]$ around the Fermi level. We will consider both types of interaction here. We introduce the notation $\tilde{D}$ to indicate the upper cutoff in energy space of the interaction potential, which is D in the retarded case and $D-\mu$ in the case of an instantaneous interaction. From direct integration of eq. (2) we find for N:

$$\frac{N}{2n} = \mu_{\mathrm{n}} = \mu + \sqrt{\mu^2+\Delta^2} + \tilde{D} - \sqrt{\tilde{D}^2+\Delta^2}$$

$$+2k_{\mathrm{B}}T\ln\left(1+\mathrm{e}^{-\beta\mu}\right)$$

$$+2k_{\mathrm{B}}T\ln\left(\left(\frac{1+\mathrm{e}^{-\beta\tilde{D}}}{1+\mathrm{e}^{-\beta\sqrt{\tilde{D}^2+\Delta^2}}}\right)\left(\frac{1+\mathrm{e}^{-\beta\sqrt{\mu^2+\Delta^2}}}{1+\mathrm{e}^{-\beta\mu}}\right)\right) \tag{4}$$

where μ_{n} is the value of the chemical potential at $T=0$ relative to the bandbottom if the system was be in the normal state. The chemical potential μ has to be determined from eqs. (4) and (3) and is a function of temperature. The first four terms cause the shift in chemical potential due to the opening of the gap. The fifth term is the usual term that causes a shift in the chemical potential in the normal state of a Fermi gas at finite temperatures. The sixth term is a temperature dependent correction to terms (3) and (4). It is of the order of $\Delta^2/\tilde{D}\mathrm{e}^{-\beta\tilde{D}} - \Delta^2/\mu\mathrm{e}^{-\beta\mu}$ which is small even at elevated temperatures. First we neglect the last two terms and solve the coupled equations at $T=0$. The exact solution of the coupled equations is for cases (1) and (2):

$$\mu = \tilde{\mu}_{\mathrm{n}} - E_{\mathrm{a}}/2 \text{ and } E_{\mathrm{a}} = \frac{\Delta^2}{2\tilde{\mu}_{\mathrm{n}}}, \tag{5}$$

where E_{a} corresponds to the binding energy in the two body problem. For $D \gg \Delta, \tilde{\mu}_{\mathrm{n}}$ reduces to the normal state value of the chemical potential μ_{n} and our result corresponds exactly to the equations given by Randeria et al. [5]. This follows immediately from the exact expression for $\tilde{\mu}_{\mathrm{n}}$:

$$\tilde{\mu}_{\mathrm{n}} = \mu_{\mathrm{n}} + \frac{\sqrt{\tilde{D}^2+\Delta^2}-\tilde{D}}{2}. \tag{6}$$

For the instantaneous interaction the above equation has still to be solved, as μ is implicitly contained in $\tilde{D}$. The solution is most conveniently expressed in the following way:

$$\mu = \mu_{\mathrm{n}} + \left(\mu_{\mathrm{n}} - \frac{D}{2}\right)$$

$$\times\left(\sqrt{1+\frac{\Delta^2}{\mu_{\mathrm{n}}(D-\mu_{\mathrm{n}})}}-1\right). \tag{7}$$

At zero temperature the exact expressions for the gapfunction are for case (1) and (2) respectively:

$$\Delta(1) = \frac{\sqrt{D\mu_{\mathrm{n}}}}{\sinh(1/nV)}\sqrt{1-\frac{D-\mu_{\mathrm{n}}}{D}\mathrm{e}-(2/nV)}, \Delta(2)$$

$$= \frac{\sqrt{\mu_{\mathrm{n}}(D-\mu_{\mathrm{n}})}}{\sinh(1/nV)}. \tag{8}$$

Note, that for $\mu_{\mathrm{n}} \ll D$ and $nV \ll 1$ these two expressions look similar to the standard BCS result, with the Debye frequency replaced by the geometrical mean value of D and μ_{n}. The first expression contains a renormalization factor, that reduces to 1 in the weak coupling limit. As this expression is only valid for $\mu < D$ it should merge into the BCS result at $\mu = D$. We can check now from eqs. (8) and (5) that this is indeed the case. The equation for case (2) is symmetrical for μ_{n} around $D/2$. Of course this symmetry only holds for our particular choice of the interaction potential and it is lost for a more general form of V_{kq}. The symmetry is also lost at finite temperature, due to the fact that the high energy cutoff D is only a cutoff in the energy dependence of V_{kq}. In principle it is not a band edge as long as we take the upper band edge at infinity. We will see later that the temperature dependence of these gapfunctions is very close to the standard BCS behaviour.

We can now further investigate the behaviour of

the gapfunction and the chemical potential by exploring the phase diagram in the parameter space spanned by the dimensionless parameters μ_n/D and $\exp(-2/nV)$. The phase diagrams indicating contours for constant μ and constant Δ are displayed in figs. 1 and 2 for cases (1) and (2) respectively. In fig. 1 the region where $\mu_n/D > 1$ corresponds to the standard BCS case. It merges continuously into the region where $\mu_n/D < 1$, where there is an influence on μ due to the opening of the gap. In case (2) there is no normal BCS region. Instead for $\mu_n/D > 1$ the system is in the normal state for all values of the interaction parameter. It is important to note that for small values of μ_n/D both types of interaction (i.e. retarded and non-retarded) give the same result: there is a depression of the gapfunction, which becomes proportional to $\sqrt{\mu_n}$. Moreover there exists a phase boundary separating a region with the chemical potential situated below the bandbottom from a region where it is inside the band. As has been pointed out by Randeria et al. [5] in this region the single particle excitation gap is $E_g = \sqrt{\mu^2 + \Delta^2}$ instead

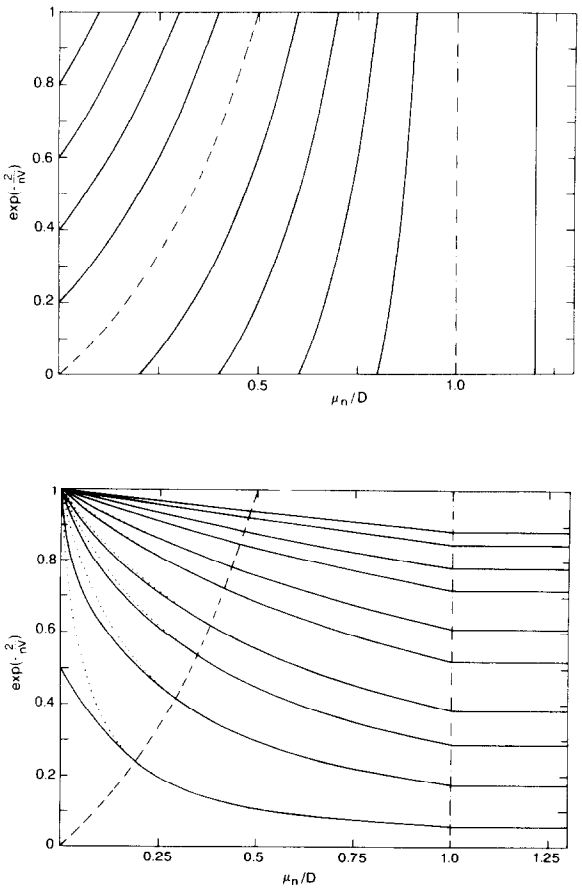

Fig. 1. (a) Curves of constant μ/D for a retarded interaction: from left to right: $\mu/D = -0.8, -0.6, -0.4, -0.2, 0.0, 0.2, 0.4, 0.6, 0.8, 1.0, 1.2$. Dashed curve: $\mu/D = 0.0$. Dash-dotted curve: 1.0. (b) Curves of constant single particle gap (solid curves). For $\mu < 0$ we indicate both the curves of constant gap parameter Δ/D (dotted) and constant single particle excitation gap E_g/D (solid). The values are from top to bottom: 16, 12, 8, 6, 4, 3, 2, 1.5, 1.0, 0.5.

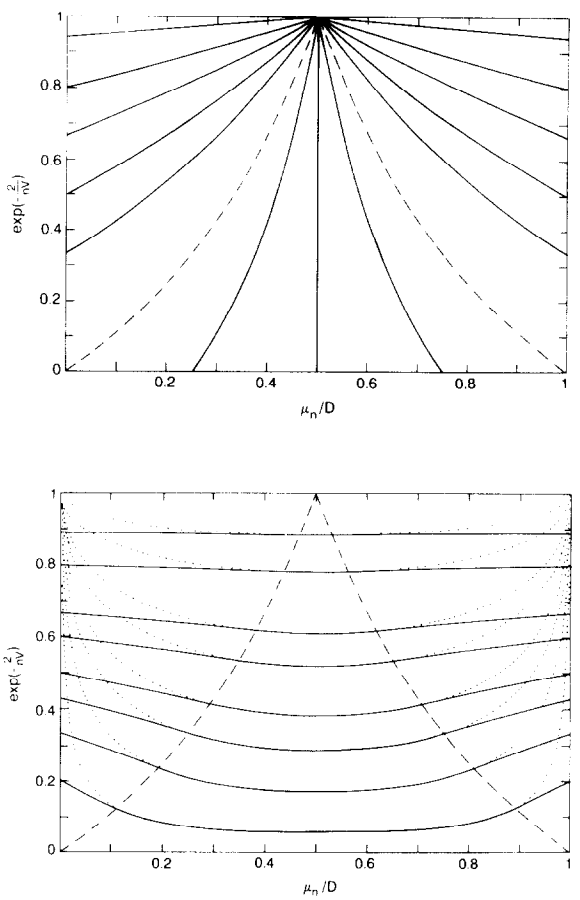

Fig. 2. (a) Curves of constant μ/D for an instantaneous interaction: from left to right: $\mu/D = -16, -4, -2, -1, -0.5, 0.0, 0.25, 0.5, 0.75, 1.0, 1.5, 1.5, 2, 3, 5, 17$. Dashed curves: $\mu/D = 0$ and 1. (b) Curves of constant single particle gap (solid curves). For $\mu < 0$ we indicate both the curves of constant gap parameter Δ/M (dotted) and constant single particle excitation gap E_g/D (solid). The values are from top to bottom: 8, 4, 2, 1.5, 1, 0.75, 0.5, 0.25.

of Δ. Using eqs. (5) we immediately find, that for $\mu<0$, the single particle gap is given by $\tilde{\mu}_n+E_a/2$. For the two types of interaction E_g is respectively:

$$E_g(1)=De^{(-2/nV)}+\mu_n\left(\frac{1+\exp(-4/nV)}{1-\exp(-2/nV)}\right)$$

$$E_g(2)=\frac{D}{\exp(2/nV)-1}+\mu_n\,. \qquad (9)$$

Note, that in the empty band limit ($\mu_n\to 0$) this becomes equal to half the binding energy of an isolated pair of electrons $E_a/2$ rather than 0 [2]. We also indicate the contours of constant E_g in both figures by solid curves. We see that there is a weak singularity at the phase boundary for this parameter. It has been pointed out by Nozieres and Schmitt-Rink [4] and especially by Randeria et al. [5], that this phase boundary may mark the border between a Bose condensate of paired electrons and the BCS ground state. Although we also believe that a boundary of this type may exist, we think that in order to make a distinction between Bose condensation and BCS superconductivity an analysis of the ground state wavefunction could, at least in principle, be insufficient. In this context it is perhaps interesting to point out that the $\mu=0$ border can also be regarded as a manifestation of an effect that likewise exists in non-superconducting Fermi gases at elevated temperatures: the superconducting ground state wavefunction at $T=0$ is a coherent superposition of Slater determinants characterized by an electron distribution function $|v_k|^2=(E_k-\epsilon_k)/(2E_k)$ which is similar (but not equivalent) to a Fermi–Dirac distribution at finite temperature. Even if μ is at the bottom of the band this distribution function will mix a finite number of electrons into the superconducting ground state. This is precisely represented by the first term in eq. (2), apart from a factor of 2 due to spin degeneracy. Note that this term gives a non-zero contribution to the number of electrons, even if μ is at the bottom of the band. If the constraint on macroscopic number density requires a lower number of electrons, the chemical potential must drop below the bottom of the band, resulting in an enlarged gap. A similar situation exists in a (non-superconducting) Fermi gas in the absence of interactions, where the chemical potential drops below the bottom of the band above $T=E_F/(2k_B \ln 2)$, again due to the constraint on macroscopic number density. This follows directly from eq. (4) if we put Δ equal to zero. Note that also in the latter case there is a gap in the single particle excitation spectrum, which is however related to the formation of an incoherent state, rather than a coherent one. The discontinuous behaviour at $\mu_n=D$ in both plots is due to the choice of a sharp cutoff in the energy dependence of V_{kq} and is absent if one chooses a more realistic interaction potential. In our numerical procedures we tried a few interaction potentials that varied smoothly around $\mu_n/D=1$ and found similar results as discussed above in the left side of the plots and a smooth cross-over on the right side. Estimates for the ceramic high-T_c superconductors put the Fermi energy in the range of 50 to 100 meV [12,13], with a gap parameter of 14 to 40 meV and a Debye energy scale of 50 meV or higher. This puts this class of materials in the region where μ_n/D is of the order 1, or smaller. This is still far removed from the region where we have $\mu<0$. Nevertheless, as the gap parameter is quite large, a distinct shift of the chemical potential due to the opening of the gap has to be expected. There are other examples of materials with a small μ_n/D ratio, like the In/InO_x system, Bi, $SrTiO_3$ and also the heavy fermion superconductors. However, in all these cases the gap parameter is small compared to both D and μ_n, so that the shift of the chemical potential is probably difficult to detect experimentally.

3. Temperature dependence of μ and Δ

We can get a qualitative understanding of what happens at finite temperatures by extending the use of figs. 1 and 2 somewhat beyond the $T=0$ limit, where they are strictly applicable. Suppose we have an electron gas with a low density of electrons, e.g. $\mu_n/D=0.25$. We now turn on the interaction at zero temperature and constant electron density. As a result we move upward in figs. 1 and 2 and two things happen: in the first place we move toward lower values of μ (figs. 1a and 2a) and in the second place the gap increases (figs. 1b and 2b). On further increasing the interaction we cross the $\mu=0$ border and the chemical potential drops below the bottom of the band. In the case of the retarded interaction (fig. 1) there is a critical value of the electron density ($\mu_n/$

$D=0.5$) above which the chemical potential never becomes negative at $T=0$. Suppose that the interaction is small, so that we are in the region where $\mu>0$. If we now increase the temperature the main effect of this will be that the gap decreases. Effectively this means that we move vertically down in figs. 1 and 2, until we reach the point where $\Delta=0$, so that we are back at the normal state chemical potential.

We now turn to the solution of the temperature dependent coupled gap equations. We have to consider the effect of a finite value of Δ on eq. (4), which modifies the value of μ. This modification of μ has again to be included in eq. (3), but usually (and especially close to T_c) the change in chemical potential is small enough in order to make the influence hereof on the gap equation neglegible. Also if we are in the parameter range where μ and Δ are of comparable size, some insight can be gained from considering the effect of Δ on μ at $T=0$. Just below T_c the gap is small and we can neglect the sixth term in eq. (4), so that eqs. (5) are again applicable, with μ_n now the normal state chemical potential at finite temperature. Adopting the standard BCS form for the temperature dependence of Δ we obtain

$$\mu(T)=\nu_n(T)-\frac{\Delta_0^2(1-T/T_c)}{4\mu_n(T)} \qquad (10)$$

i.e., there is a discontinuity in the first derivative of $\mu(T)$ at T_c. In fig. 3 we give numerical examples of the solution of the full temperature dependent coupled gap equations (eqs. (3) and (4)), where the interaction parameters were chosen such as to give a critical temperature in the range of values of high-T_c superconductors. We see that there is a kink at T_c in the meV range. In spite of its smallness this is a value, that is in principle experimentally accessible. In this particular example we display the result for a retarded interaction of the type discussed above (i.e. with a sharp cutoff in the range $[-\mu, D]$ around the Fermi level, where $\mu<D$). We also tried some other choices for the function $\gamma(\epsilon)$, in particular the retarded form $\gamma=(1+(\epsilon/D)^2)^{-1}$, the non-retarded form discussed in relation to fig. 2 and the non-retarded form $\gamma=\exp(-(\epsilon+\mu)/D)$. The behaviour of both the gapfunction and the chemical potential turned out to be more or less universal functions of μ_n, T_c and temperature. As a consequence the $2\Delta/k_BT_c$ ratio is quite generally equal to 3.5, at least in the limit of a weak interaction. In the region where $\mu<0$ there is a reduction of the $2\Delta/T_c$ ratio. On the other hand, in those case the ratio $2E_g/k_BT_c$, is larger than 3.5. Of course it is the latter quasiparticle gap and not the gapfunction Δ that is determined experimentally, so that an enhanced gap over k_BT_c ratio is to be expected for superconductors in the extremely dilute limit. The top curve in fig. 3 corresponds to $\mu_n/D=1$. From fig. 1a we already know that this is just inside the region of standard BCS behaviour, where there is no kink in the chemical potential at T_c. As can be seen in fig. 3 the critical temperature decreases on decreasing the density of electrons and a pronounced kink in μ occurs at T_c. One should not conclude from this result that the size of the kink in μ is a decreasing function of T_c: if we had chosen to vary the interaction parameters nV instead of the density of charge carriers, we would have found that the size of the kink increases with increasing T_c. Even for the lowest density of electrons in fig. 3 we still have $\mu>0$ at all temperatures. So the examples in fig. 3 are all in the middle section of fig. 1.

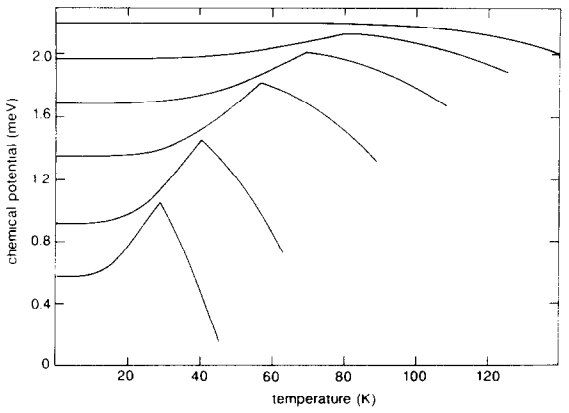

Fig. 3. Temperature dependence of the chemical potential for a superconductor with $\exp(-2/nV)=0.0183$, where V is a retarded potential with a Debye cutoff of 0.05 (eV). The Fermi energy at zero temperature is from top to bottom: 0.05 (eV), 0.04 (eV), 0.03 (eV), 0.02 (eV), 0.01 (eV) and 0.005 (eV). We assumed a band with constant density of states and with a bandwidth of 0.2 (eV).

We need a few words of caution at this point: so far we have restricted the discussion to a mean field description of the interaction particle system. This

may be inappropriate at finite temperatures in the the very dilute limit, even though the ground state wavefunction is still correct. In particular we have to realize that the thermodynamics of an extremely dilute superconductor may no longer be dominated by the quasiparticle degrees of freedom, especially near T_c. A quite extreme example of this would be if we have pre-existing Cooper pairs above T_c, that Bose-condense at the superconducting transition. This notion has been widely discussed, in particular by Robaszkiewicz, Micnas and Ranninger [14] in the context of the bipolaron model for superconductivity, and in their treatment of the negative U Hubbard model. In the extreme case of pure Bose condensation of non-interaction bosons the behaviour of the chemical potential is somewhat similar to our results shown in fig. 3. As is treated in many textbooks on statistical mechanics (e.g. ref. [15]) one can easily show, that in a boson gas above T_c, μ lies below the bottom of the boson band. The chemical potential increases on decreasing the temperature, until it reaches the bandbottom at T_c. Below T_c, μ remains pinned to the bottom of the band due to macroscopic occupation of the lowest boson state. It is not our aim at this stage to calculate the behaviour of the chemical potential beyond the mean field approach given above, despite of its likely inappropriateness in the very dilute limit.

4. Effect on the specific heat

In principle one might expect a contribution to the step in the specific heat at T_c due to the presence of a kink in μ. We can see this by considering the fact that the C_{NV} can be expressed as $k_B T$ times the temperature derivative of the entropy at constant volume and constant particle number:

$$C_{NV} = T\left(\frac{\partial S}{\partial T}\right)_{NV} . \tag{11}$$

Normally the entropy is obtained by differentiating the thermodynamic potential at constant V and μ, so that the entropy is an explicit function of μ. Hence differentiation at constant N involves two terms:

$$\left(\frac{\partial S}{\partial T}\right)_N = \left(\frac{\partial S}{\partial T}\right)_\mu + \left(\frac{\partial S}{\partial \mu}\right)_T \left(\frac{\partial \mu}{\partial T}\right)_N . \tag{12}$$

Clearly, a kink in μ results in a step in the temperature derivative of μ in the above expression. From differentiation of the thermodynamical potential with respect to T [6], we obtain the standard expression for the entropy of a non-interacting gas of quasiparticles obeying Fermi statistics:

$$\begin{aligned} S &= -\left(\frac{\partial \Omega(\mu, T)}{\partial T}\right)_\mu \\ &= -k_B \sum_k \left[(1-f(\beta E_k)) \ln (1-f(\beta E_k)) \right. \\ &\quad \left. + f(\beta E_k) \ln (f(\beta E_k)) \right] . \end{aligned} \tag{13}$$

Combining eqs. (11), (12) and (13) we obtain the final expression for the specific heat:

$$\begin{aligned} C_{NV} = \int_{-\mu}^{\infty} n(\epsilon) \frac{\partial f}{\partial E} \left(\frac{-2E^2}{T} + \frac{\partial \Delta^2}{\partial T} \right. \\ \left. - 2\epsilon \frac{\partial \mu}{\partial T} + \frac{\partial \Delta^2}{\partial \mu} \frac{\partial \mu}{\partial T} \right) d\epsilon . \end{aligned} \tag{14}$$

In the standard analysis of the specific heat jump, only the first and second term are present, and the jump is due to the second term. The fourth term has zero contribution at T_c, whereas the third term is small due to the fact that $\partial f/\partial E$ is non-zero in the region where $\epsilon \simeq 0$. Again we have to take into account the proximity of the bandbottom, which influences the third and second terms. The result for the jump in the specific heat is for $D/\Delta \to \infty$:

$$\begin{aligned} C_{NV}(S) - C_{NV}(N) = \frac{n\Delta_0^2}{T_c} \left(1 - \frac{1/2}{1+e^{\beta_c \mu_n}} \right. \\ \left. + \frac{1}{2\beta_c \mu_n} \ln (1+e^{-\beta_c \mu_n}) \right) \end{aligned} \tag{15}$$

where we used eq. (10) for μ. So we see that there is indeed a small reduction of the specific heat jump, due to the fact that there is a kink in the chemical potential at T_c. In fig. 4 we display a few numerical examples of C_{NV}/T, using the same parameters as in fig. 3. It is evident from this figure, that the most drastic change is not in the specific heat jump, but in the specific heat of the normal phase, resulting in an enhanced value of $(C_{NV}(S) - C_{NV}(N))/C_{NV}(N)$.

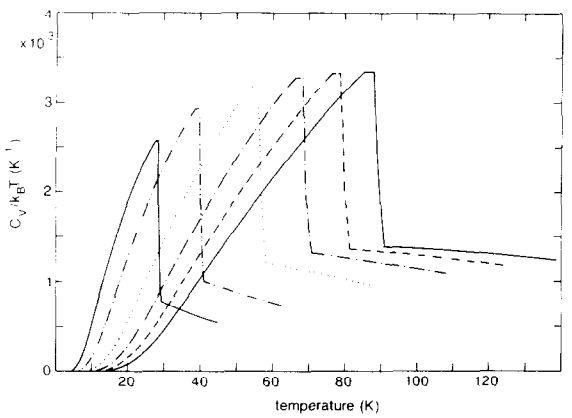

Fig. 4. Temperature dependance of the specific heat divided by temperature for the same parameters as in fig. 3.

This is also a direct consequence of the low density of charge carriers: at elevated temperatures the statistics of the electron gas crosses over from Fermi statistics to the classical Boltzmann distribution, so that the specific heat saturates at k_B per electron. This behaviour of the normal state specific heat is not unexpected in view of the fact that high-T_c superconductors are often regarded as heavily doped semiconductors. An experimental study of the deviations in the normal state specific heat would be quite interesting, although it is probably very difficult to distinguish these rather small deviations from the large phonon background in the specific heat.

5. Conclusions

We conclude, that in superconductors with a large Debye energy relative to the Fermi energy, there exists a kink at T_c in the temperature dependence of the chemical potential. This kink can in principle be observed experimentally, especially if the gap and the Fermi energy are of comparable magnitude. In this parameter range our result is insensitive as to whether one considers a retarded or an instantaneous interaction. Our analysis is not restricted to a particular type of pairing interaction. In the parameter range of the recently found ceramic high-T_c superconductors we calculate shifts in μ due to the opening of the gap, which are of the order of 0.1 to 1 meV.

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