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Quantum-Gas Model Estimate for Wide Range of Superconducting Critical Temperatures

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A quantum mechanical model requiring only strong quantum interaction for a charged particle gas estimates the superconducting transition temperature for wide-ranging states of matter. A general equation is derived which estimates the critical temperature T_c the energy gap, and the coherence length for the classical metallic superconductors, heavy-electron superconductors, the perovskites, metallic hydrogen, and neutron stars. Estimates for T_c, the coherence length, and the energy gap which are model independent for coupling mechanisms agree well with accepted values for these materials. Estimates are made for three-dimensional quasi-two- and quasi-one-dimensional states.

1. THREE-DIMENSIONAL QUANTUM GAS

With the discovery of higher temperature superconductivity at 35 K in the perovskites (Bednorz and Muller, 1986) and the increase of the critical temperature T_c to 125 K and possibly higher (Wu *et al.*, 1987; Huang *et al.*, 1987; Sheng and Hermann, 1988), there is uncertainty regarding electron pairing mechanisms, strengths, dimensionality of the superconductivity, and expected limits for critical temperatures. Thus, insight may be gained by means of a quantum mechanical charged gas model that is essentially independent of any assumed coupling mechanisms and coupling strengths. The first objective of this paper is to derive an upper limit for T_c for different classes of superconducting materials in different dimensionalities. The second object is to derive an approximate coupling strength, i.e., the energy gap and hence also the coherence length for these classes.

In a Bose gas, particles should start a Bose–Einstein condensation into a ground state in momentum space when the quantum mechanical wavelength is much greater than the interparticle spacing (one-fourth the de Broglie wavelength is the approximation here), i.e., at T_c. For a degenerate

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system of Fermi particles (electrons or protons here) superconductivity can exist if the particles pair near the Fermi energy level. When this happens, the paired particles will have integral spin (singlet state of zero spin for electrons, although the triplet state of spin one can also participate) and obey Bose-Einstein statistics rather than Fermi-Dirac statistics. This can lead to the appearance of superconductivity, just as the pairing of ^{3}He atoms in the triplet state leads to superfluidity.

Thus, the only requirement we shall impose is that for strong quantum effects, the quantum mechanical wavelength λ is long compared with the interparticle spacing of the particle pairs. This occurs when there is a multiple occupancy of energy levels, as in a Bose gas. At temperature $T \leq T_c$ we have as a necessary (but not sufficient) condition

$$\tfrac{1}{4}\lambda \geq n_s^{-1/3} \tag{1}$$

where

$$n_s \sim \frac{kT_c}{E_F} n \tag{2}$$

n_s is the number density of particle pairs which can have an effective interaction for condensation because they have energies within kT_c of the Fermi surface. E_F is the Fermi energy, k is the Boltzmann constant, and n is the number density of free particles (assumed to be fermions above T_c).

Since we are interested in general results related to classes of materials, we will neglect detailed structure related to a specific material. Thus, for the Fermi energy of a three-dimensional conductor, we use the standard result for a three-dimensional box of infinite potential outside the box and zero potential inside,

$$E_F = \frac{h^2}{2m}\left(\frac{3n}{8\pi}\right)^{2/3} = \frac{h^2}{8m}\left(\frac{3}{\pi}\right)^{2/3} n^{2/3} \doteq \frac{h^2}{8m} n^{2/3} \tag{3}$$

where m is the mass of the unpaired charge carrier. (In a solid m may be different than for a free particle. Except for the heavy-electron metals, the mass of a free electron and the mass of a free proton will be used here in the calculation of T_c.)

For a particle pair gas of momentum p, mass $2m$, and incremental energy E above the Fermi energy, relating the minimum de Broglie wavelength to T_c

$$\lambda_{\min} = \frac{h}{p} = \frac{h}{[2(2m)E]^{1/2}} = \frac{h}{[4m(\frac{1}{2}fkT_c)]^{1/2}} \tag{4}$$

where f is the number of degrees of freedom per particle. (The mean thermal wavelength of the pair is shorter than by λ a factor of $[f/2\pi]^{1/2}$.) For a particle pair in three dimensions, there are three translational degrees of freedom for the center of mass. (Combining equations (1) and (4) leads to an interparticle spacing which is $4f^{1/2}/(2.612)^{1/3}(2\pi)^{1/2} = 1.16f^{1/2}$ smaller than for a condensed ideal monatomic Bose gas of mass $2m$ in three dimensions. So later when f is set equal to 1, these spacings differ by only 16% in the quasi-one dimensional case which is the one of greatest interest.)

Combining equations (1)-(4), we find

$$T_c \sim \frac{h^2 n^{2/3}}{8f^3 mk} = \frac{E_F}{64f^3 k} = \frac{h^6 D_F^2}{2^{13}\pi^2 (fm)^3 k} \tag{5}$$

where D_F is the density of states at the Fermi surface.

Let us estimate n for various materials, to determine the estimated T_c as given by equation (5). For the classical metallic superconductors, the number density of conduction electrons is $\sim 10^{29}/\mathrm{m}^3$. This is of the same order as the number density of atoms. So, for a three-dimensional classical superconductor equation (5) estimates $T_{c3} = 54.3 \sim 50$ K. This is in good agreement for these materials with the highest known transition temperature of 23.2 K for Nb_3Ge.

For the heavy-electron metals (Fisk *et al.*, 1986), the Hall coefficient is of the same order as for the classical metallic superconductors. This implies that the number density of conduction electrons is roughly the same, $\sim 10^{29}/\mathrm{m}^3$. The mass varies from about 10 to 100 times greater than the mass of a free electron. Thus, the estimate from equation (5) is that $T_{c3} \approx 0.5$–5 K. The experimental values are between 0.5 and 1.5 K (Fisk *et al.*, 1988). So again there is good agreement between the experimental data and equation (5).

The generality of equation (5) permits us to make estimates for states of matter that do not occur on the earth. Let us look at metallic hydrogen and neutron stars. To estimate the number density of free electrons for metallic hydrogen, we assume one free electron per atom and that the center-to-center spacing between atoms is equal to two Bohr radii, $2a_0$. Thus,

$$n \doteq (2a_0)^{-3} = [2(5.3 \times 10^{-11}\mathrm{m}]^{-3} = 8.4 \times 10^{29}\text{–}10^{30}/\mathrm{m}^3 \tag{6}$$

For three-dimensional metallic hydrogen, equation (5) gives $T_{c3} \approx 300$ K as an upper limit. This is in good agreement with results calculated in the literature (Jaffe and Ashcroft, 1983; Overhauser, 1987) of 120–260 K.

Ginzburg (1969) reports that neutron stars have densities of 10^{13}–$10^{15}\,\mathrm{g/cm}^3$. In the case of neutron stars, the supercurrents are thought to be due to coherent circulation of proton pairs. The given mass density gives

an upper limit of 10^{43}–10^{45} protons/m^3. Equation (5) yields $T_{c3} \approx 10^8$–10^9 K. This is in good agreement with the literature value (Ginzburg and Kirzhnits, 1965) of 10^{10}–10^{11} K when one considers the complexity of the detailed calculations and the uncertainties in the many parameters that are used.

2. QUASI-LOWER-DIMENSIONAL SYSTEMS

In order to estimate T_c for the ceramic oxides, we must also consider two- and one-dimensional cases, as there is a possibility that in some of them, such as $Y_1Ba_2Cu_3O_{7-y}$, the superconductivity may be two or even one dimensional in nature. These oxide systems are strictly not of lower dimensionality, as mechanisms such as Josephson tunneling through nonconducting regions and pair tunneling into and through normal-conducting regions tend to produce in equilibrium a Fermi energy corresponding to three dimensions E_F rather than to two- or one-dimensional Fermi energies E_{F2} or E_{F1}. Anisotropy may produce a sufficiently higher effective mass in some directions as to effectively reduce the dimensionality. I envisage these systems to be of quasi-lower dimensionality where only the degrees of freedom of the paired fermions f_2 and f_1 are restricted, respectively, to two and one dimension in their nontunneling conduction paths, hence the designation here of quasi-two or quasi-one dimensionality.

For a quasi-two-dimensional system, the effective two-dimensional number density of interacting pairs is

$$n_{s2} = (n_{s3})^{2/3} = \left(\frac{kT_c}{E_F} n\right)^{2/3} \tag{7}$$

Thus

$$\lambda = 4n_{s2}^{-1/2} = 4\left(\frac{kT_c}{E_F} n\right)^{-1/3} \tag{8}$$

In a quasi-one-dimensional system, the effective one-dimensional number density of interacting pairs is

$$n_{s1} = (n_{s3})^{1/3} = \left(n \frac{kT_c}{E_F}\right)^{1/3} \tag{9}$$

Thus

$$\lambda = 4n_{s1}^{-1} = 4\left(n \frac{kT_c}{E_F}\right)^{-1/3} \tag{10}$$

Equations (8) and (10) for λ are the same as the combination of equations (1) and (2). Thus we obtain equation (5) for the three-, quasi-two-, and

Table I. Comparison of Estimated T_c and Energy Gap with Data for a Wide Range of Matter in Three Dimensions, and Quasi-Two- (Q2) and Quasi-One- (Q1) Dimensional Systems

Material	n	Dim.	Estimated T_c, K	Experimental literature T_c, K	$2\Delta'$, meV	2Δ, meV	$2\Delta_{BCS}$, meV
Metallic superconductor	$10^{29}/m^3$	3	50	23.2	2.0	10	7.04
		Q2	200	—	35	140	—
		Q1	1000	—	160	560	—
Heavy electron metal	$10^{29}/m^3$	3	0.5–5	0.5–1.5	0.16	0.68	0.304
		Q2	2–20	—	0.70	2.9	—
		Q1	10–100	—	3.2	11	—
Ceramic oxide	$10^{28}/m^3$	3	10	13	3.5	19	3.95
		Q2	40	35	8.1	44	10.6
		Q1	300	125	23	110	38.0
Li–Be–H	$5\times10^{29}/m^3$	3	200	—	38	160	60.8
		Q2	500	—	84	330	—
		Q1	4000	—	680	2600	—
Metallic H	$10^{30}/m^3$	3	300	120–260	45	180	79.0
		Q2	800	—	130	520	—
		Q1	7000	—	1200	4800	—
Neutron star	10^{43}–$10^{45}/m^3$	3	10^8–10^9	10^{10}–10^{11}	3.0×10^9	1.8×10^{10}	3.04×10^9

quasi-one-dimensional cases, where f represents the degrees of freedom for the fermion pairs in the given dimensions, i.e., $f_3 = 3$, $f_2 = 2$, and $f_1 = 1$.

We can now estimate T_c for the ceramic oxides. Here n is less than for the metallics, with $n \approx 10^{28}/\text{m}^3$ as a representative number. The estimates from equation (5) are $T_{c3} \sim 10$ K, $T_{c2} \sim 40$ K, $T_{c1} \sim 300$ K, for three, two, and one dimensions, respectively. The agreement with experiment (Wu *et al.*, 1987; Huang *et al.*, 1987; Sheng and Hermann, 1988) is reasonable if one may assume that the primary conduction mechanism in the perovskites is two- or one-dimensional along the copper oxide planes or chains. Conduction along the c axis may occur by Josephson tunneling between copper-oxide planes or chains.

If three-dimensional superconductivity is assumed for $LiTiO_4$ with $T_c = 13.7$ K (Johnston *et al.*, 1973) and $BaPb_{1-x}Bi_xO_3$ with $T_c = 13$ K (Sleight *et al.*, 1975), the agreement with equation (5) is good. If two-dimensional superconductivity is assumed for the original Bednorz and Muller Ba-La-Cu-O system, with $T_c = 35$ K, the agreement is good. If the $Y_1Ba_2Cu_3O_{7-y}$ is assumed to be a quasi-one and quasi-two dimensional superconductor, its established $T_c = 94$ K and reports of $T_c \approx 200$ K are in accord with equation (5) (Wu *et al.*, 1987; Huang, *et al.*, 1987). The Tl-Ca-Ba-Cu-O system has a $T_c = 120$–125 K (Sheng and Hermann, 1988) and the potential for reduced ac power loss (Rabinowitz, 1987). For a combination of linear and planar structure in which the interchain interactions are equal to the intrachain interactions, then $T_c = (T_{c1}T_{c2})^{1/2} = (300\text{ K} \times 40\text{ K})^{1/2} = 110$ K.

Overhauser (1987) has speculated that lithium beryllium hydride compounds, if metallic may be high-temperature superconductors. He points out a similarity with metallic hydrogen and notes that whereas Pd is not a superconductor, PdH has a $T_c \approx 10$ K. He observes that the $LiBeH_3$ and Li_2BeH_4 have a modified perovskite structure. For the latter he calculates the conduction electron density $n = 4.71 \times 10^{23}/\text{cm}^3 = 4.71 \times 10^{29}/\text{m}^3$. No estimates of T_c are presented. For m equal to the free electron mass, equation (5) predicts $T_{c3} \sim 200$ K, $T_{c2} \sim 500$ K, $T_{c1} \sim 4000$ K. These high values indicate that systems like this may indeed be promising areas to investigate.

Table I summarizes the results for various states of matter (material) and the dimensionality of the superconductor.

3. ENERGY GAP

Let us see what constraint must be placed on the Bose–Einstein gas to meet the requirement of an energy gap, since most superconductors, including the new high-temperature ceramic oxide superconductors, have an energy gap. If the Bose gas were an ideal gas, with no potential energy of interaction of the particles, then the condensed phase might not be expected

to exhibit superfluidity, as the smallest infinitesimal energy input would excite it. It appears that this increased kinetic energy would dissipate as heat, resulting in viscosity for an ideal neutral Bose gas or resistance for an ideal charged noninteracting Bose gas, and the critical velocity would be zero.

For any real neutral or charged gas, there is an interaction potential energy between the particles which can result in an energy gap. The particles exhibit no flow viscosity when $kT <$ energy gap, because this minimum energy must be supplied before they can leave the states they are in. One might think that in the limit as the interaction goes to zero, the energy gap may be expected to go to zero and frictionless flow to cease. However, the existence of "gapless superconductivity" is an indication that in addition to the energy gap, the existence of strong correlation of the pair wave function plays an important role in all superconductors. The addition of magnetic impurities, magnetic field, etc., can lower the energy gap more rapidly than T_c. Instead of there being an energy gap in which there is a total absence of states, "gapless superconductivity" merely has an extremely low density of states in the gap region.

However, without assuming any particular coupling mechanism or coupling strength, let us introduce a minimum excitation energy or binding energy Δ per particle which is needed to break up a particle pair. The energy gap is designated as 2Δ here to be in accord with the BCS gap. In our formalism, let us first introduce Δ into equation (4), modifying it thus

$$\lambda = \frac{h}{[2(2m)(\frac{1}{2}fkT_c - \Delta)]^{1/2}} \tag{11}$$

Here $(\frac{1}{2}fkT_c - \Delta)$ represents the translational energy of the particle pair, so that the number of degrees of freedom must be increased from the three translational ones (in three-dimensions) to include the vibrational and rotational degrees of freedom related to Δ. Heuristically, with an additional energy $\frac{1}{2}kT_c$ for the vibrational potential energy (or possibly other than $\frac{1}{2}kT_c$, since the potential energy here is not necessarily a quadratic function of position and the statistics are other than Boltzmann), and $3(\frac{1}{2}kT_c)$ associated with the kinetic energies of vibration and rotation it would be tempting to set

$$\Delta = 2kT_c \tag{12}$$

which is similar to the original BCS (Bardeen, Cooper, and Schrieffer 1957) result

$$\Delta_{BCS} = 1.76kT_c \tag{13}$$

However, we may go beyond the heuristic result of $\Delta = 2kT_c$. Combining equations (11), (1), (2), and (3) we find

$$2\Delta = fkT_c - \tfrac{1}{4}(kT_c)^{2/3}E_F^{1/3} = fkT_c - \tfrac{1}{8}(hkT_c)^{2/3}n^{2/9}m^{-1/3} \tag{14}$$

where the first term is like the BCS result. Equation (14) predicts that T_c may be >0 for $\Delta = 0$, whereas equation (13) yields $T_c = 0$ for $\Delta_{BCS} = 0$. In fact, equation (14) reduces to equation (5) for gapless superconductivity. Experimental values rather than equation (5) should be used as input to equation (14). At most $f_3 = 3$ translational + 2 vibrational + 2 rotational = 7 degrees of freedom in three-dimensions. As before, equation (14) is also obtained for quasi-two and quasi-one dimensions where at most $f_2 = 2$ translational + 2 vibrational + 1 rotational = 5 degrees of freedom in two-dimensions, and $f_1 = 1$ translational + 2 vibrational = 3 degrees of freedom in one dimension. Depending on temperature, some of the degrees of freedom may not be excited. Let us use $f_3 = 5$, $f_2 = 4$, and $f_1 = 3$ at this time for the 2Δ column of Table 1. Since equation (14) involves the difference between two terms which may be close in value, let us derive an alternate equation which avoids this as well as questions about the additional degrees of freedom.

Rather than introducing Δ into equation (4), let us consider equation (2). Twice the number of particle pairs is roughly the fraction $\frac{1}{2}\Delta/E_F$ of conduction electrons that have a strong interaction near the Fermi level. This fraction may be a function of the class of superconductors as the number of states expelled from the gap is related to the size of the gap and the density of normal states. Thus, in place of equation (2), we have

$$2n_s \sim \frac{\frac{1}{2}\Delta}{E_F} n \tag{15}$$

Now combining equations (15), (1), (3), and (4) we obtain

$$2\Delta = 8(4fkT_c)^{3/2}E_F^{-1/2} = 128(2m)^{1/2}(fkT_c)^{3/2}h^{-1}n^{-1/3} \tag{16}$$

As before, equation (16) is obtained for quasi-two and quasi-one dimensions. Here f represents only the translational degrees of freedom, where $f_3 = 3$, $f_2 = 2$, and $f_1 = 1$. (If equations (11), (15), (1) and (3) are combined, a cubic equation in Δ is obtained.) Similarly, a cubic equation in T_c results when Δ is included as in equation (11).

Table I shows the results of equations (14) and (16) in comparison with the original BCS result, equation (13). Although only one significant figure may be warranted, two are listed for the purposes of comparing Δ and Δ'. This simple theory predicts energy gaps ranging over nine orders of magnitude, in fair agreement with BCS from the smallest of tenths of an meV for the heavy Fermion metals to tenths of an MeV for neutron

stars. It gives a better representation than BCS for the ceramic oxides. When T_c from equation (5) is used, $2\Delta/kT_c = 8$. Using experimental values of T_c in equation (16) causes this ratio to vary. The values of Δ and Δ' are reasonably self-consistent. Furthermore, since the coherence length $= \hbar v_F/\pi\Delta$, this theory also yields approximately correct coherence lengths over this range.

A mass of fifty electron masses ($50m_e$) was used as the representative mass for the heavy Fermion metals with $T_{c3} = 1$ K, $T_{c2} = 4$ K, $T_{c1} = 20$ K. A mass of $4m_e$ was used for the ceramic oxides. Except for the ceramic oxides, Δ_{BCS} was computed only for the three dimensional cases. Wherever possible, the energy gaps were computed using the experimental values, T_c.

For Table 1, equation (16) is considered independent of equation (5) and only experimental values of T_c should be input. If we combine equations (5) and (16) then

$$2\Delta = 8kT_c \tag{17}$$

in good agreement with the ceramic oxides.

4. CONCLUSIONS

Table I illustrates that equation (5) does well in representing experimental and calculated results over a range for T_c of nine orders of magnitude. It is indicative of the T_c that may be expected for a given class of materials in a given conduction dimensionality. The experimental and literature data are presented in support of the estimates calculated from equation (5). In addition to crystallographic evidence, the agreement of equation (5) with a wide variety of states of matter is indicative that the ceramic oxides are quasi-one-dimensional (Q1) and quasi-two-dimensional (Q2) for the higher T_c. Because of the low number density of electrons, equation (5) indicates that they are not likely to be three-dimensional superconductors except at the lower transition temperatures.

What is interesting is that this simple equation does so well with only three variables, f, n, and m, which can be determined from experiment. The variation of m from that of a free electron mass may be able to account for small differences in T_c within a given class of materials, as would more detailed knowledge of the Fermi surface in general. The mass variation appears to work well for the heavy electron metals, where $T_c \propto 1/m$, as predicted by equation (5). Crystallographic information can help yield the f that applies for a given dimensionality. The combination of different dimensions, such as Q1 and Q2 in the ceramic oxides, may be an important factor in determining T_c.

What has been shown here is that consideration of the Bose–Einstein condensation as a general feature common to superconductivity for a broad range of states of matter may be equal to the importance of the diversity of mechanisms responsible for the energy gap. It is noteworthy that without specifying a coupling mechanism or coupling strength, this simplified general theory does well in predicting coherence lengths transition temperatures and coupling strengths over nine orders of magnitude (1 K to 10^9 K and meV to MeV) from the heavy electron metals to neutron stars.

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