Chemical Physics of Phonons and Superconductivity: A Heuristic Approach

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Abstract-Several potential heuristic angles are explored with regard to the parametrization of the superconducting transition temperature, T(c), and its relationship to the chemical physics of bonding. Fruitful angles explored in this paper include the relationship of the gas of Cooper pairs in a superconductor to a van der Waals equation of state for such a fluid and how it may be controlled and exploited through the consideration of such variables as pressure, P, and volume, V, of the fluid of Cooper pairs resident in a superconductor. Other angles explored, in an attempt to get a heuristic handle on the superconducting transition temperature, T(c), for superconducting compositions across the Periodic Table, include the introduction of a Morse's anharmonic chemical bond potential for the Debeye frequency of the phonons as it emerges from the central result for T(c) in superconductors from the Bardeen-Cooper-Schreifer (BCS) formulation of superconductivity. Yet another angle explored in this heuristic reasoning, is the use of a Badger's relationship between chemical bond force constant, k, and equilibrium internuclear distance, $r_{(e)}$, to try to gain some understanding of the nature of the electron-phonon coupling mechanism in superconductors. A relationship between $r_{(e)}$ and $D_{(e)}$ emerges as a result of this line of thought, given as $r_{(e)}D_{(e)}$ = "critical temperature constant", from which examination of spectroscopic data across the Periodic Table may yield a compositional solution of the appropriate chemical bonding, with the assumption of the proper electron-phonon coupling constant, C, and density of states, N(0), that ultimately may be yield more desirable superconductivity transition temperatures.

I. Superconductivity and the Gas Laws

Considering our Equation (1) from the microscopic version of the BCS theory[1]:

(1) $$k \cdot T(c) = 1.14 \cdot h\omega_{(D)} \cdot \exp(-1/\lambda)$$

[1] J. Bardeen, L.N. Cooper and J.R. Schreiffer, *Physical Review*, **108**, 1175 (1957).

One can multiply both sides by N_A, the Avogadro constant, to yield a corresponding macroscopic version of this Equation (1), as Equation (2), our macroscopic BCS theory result.

(2) $$N_A \cdot k \cdot T(c) = N_A \cdot 1.14 \cdot h\omega_{(D)} \cdot \exp(-1/\lambda)$$

Using the identites $N_A \cdot k \cdot T(c) = R \cdot T$, and $P \cdot V = R \cdot T$, for an ideal gas, we have Equation (3):

(3) $$P \cdot V = N_A \cdot 1.14 \cdot h\omega_{(D)} \cdot \exp(-1/\lambda)$$

Assuming the Bose gas of Cooper pairs inside the superconducting lattice behaves as an ideal gas, then there seemingly is nothing we can do with this macroscopic BCS theory expression at all. P and V would thus be the thermodynamic values of the Bose gas of Cooper pairs as their pressure and volume they occupy, for a mole of Cooper pairs constrained within a mole of superconducting material.

But what if the Bose gas of Cooper pairs is non-ideal, what if it obeys a van der Waals equation of state for a gas, as Equation (4) suggests:

(4) $$(P + (a^2/V^2)) \cdot (V - b) = N_A \cdot 1.14 \cdot h\omega_{(D)} \cdot \exp(-1/\lambda)$$

Therefore, if one could measure the vdW parameters, "a" the attractive force between Cooper pairs, and "b" the finite volume occupied by Cooper pairs, one would have a means of controlling the superconductivity mechanism somewhat and possibly affecting the superconducting temperature onset, T(c) through a control of these

thermodynamic variables.

II. Superconductivity and the Electron-Phonon Coupling Parameter, λ

An article by the Mao-Hemley group[2] at the Geophysical Laboratory in Washington, D.C., describes measurements of conductivity and superconductivity in B allotropes under pressure. They cite an expression for the electron-phonon coupling of superconductivity, the parameter λ in Equation (1) above. The expression is for s-p metals & superconductors, whatever that means, and is given as Equation (5):

$$\lambda = ((N(0) \cdot C) / \langle \omega^2 \rangle) \tag{5}$$

The parameter "C" is supposed to be a numerical constant, so we don't worry about that. N(0) is the DOS(E_f) = density of states at the Fermi energy, E_f. And, importantly, $\langle \omega^2 \rangle = (k/\mu)$ is the averaged phonon frequency squared.

So we see that the phonon frequencies and ultimately the phonon width at the Fermi energy, play an important role twice in the BCS theory result given in Equation (1) here. In the term, $h\omega_{(D)}$, in Equation (1), it seems that the higher the phonon frequencies attained in the BCS mechanism, the higher will be the transition temperature, T(c). But in the electron-phonon coupling parameter, because of the inverse exponential-type function it enters as in Equation (1), it seems that the higher the phonon frequencies contributing to the BCS mechanism, the lower will be the transition temperature, T(c).

It is as if the two effects in the BCS theory result of Equation (1) are indeed opposed to each other. I have not plotted this exponential function so I am not sure if I am right because it is also a reciprocal function, i.e. exp(-1/λ) as well.

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[2] M.I. Eremets, V.V. Struzhkin, H-K. Mao and R.J. Hemley, *Science*, **293**, 272 (2001).

At this point I would throw my hands up and give up. The BCS theory doesn't seem to give a monotonic-type, useful predictive result. It contains parameters that work at cross-purposes to each other. I think, also, judging from the paper I cited[3], where I note there is yet another expression for the superconducting transition temperature T(c), that indeed there may be a plethora of such expressions for T(c). Indeed, it seems that there is no concensus in the physics community over what the proper physical expression should be for the behavior of T(c) in superconductors.

My earlier result for substituting into (1) the classical Morse potential, U(r), to yield a semiclassical BCS-type theory with maximum contributions, in a continuum of states, from anharmonicity and anharmonic vibrations of the lattice, would seem to work to increase the transition temperature, T(c), were it not for the term in the electron-phonon coupling, given by $\exp(-1/\lambda)$, which suggests such anharmonicity corrections would serve to SUPPRESS the superconducting transition temperature, T(c).

Finally, there is the term N(0) which is $DOS(E_f)$. Clearly the bigger the $DOS(E_f)$ the bigger will be the contribution to increasing the transition temperature of superconductivity, T(c). In this instance, and only in this instance, does it seem that a band structure can play a role. And the flatter the bands are at the Fermi energy, the more so will N(0) contribute to a higher transition temperature, T(c).

This seems to be all I can gather from Equation (1) and the other references I have studied thus far. It is odd that the BCS theory has this competition built into it from contributions of the lattice vibrations. It is a conundrum indeed.

III. Superconductivity and the Morse Potential & Badger's Rule

In treating anharmonicity in the BCS expression for superconductivity, one can start

[3] Ibid (2)

with Equation (6), which is the ordinary result from the BCS theory, in which one approximates phonons in a harmonic potential:

(6) $$k \cdot T(c) = 1.14 \cdot h\omega_{(D)} \cdot \exp(-1/\lambda)$$

And thus one can use an anharmonic Morse's potential[4], $U(r) = D_{(e)}(1 - e^{(-a(r - r_e)2)})$, where the anharmonicity parameter is given by, $a = \sqrt{(k/2D_{(e)})}$, to solve the Schroedinger equation for the diatomic molecular potential, and thus to replace the phonon energy term in (6), $h\omega_{(D)}$, in order to get an analogous BCS expression for anharmonic phonons as in Equation (7):

(7) $$k \cdot T(c) = 1.14 \cdot (h\omega_{(D)} - (h\omega_{(D)})^2/4D_{(e)}) \cdot \exp(-1/\lambda)$$

In (7) we have thus introduced the effect of the bond strength $D_{(e)}$ into the BCS theory of superconductivity.

And from the point of view of Badger's relation[5], a correlation between bond force constant, k, and bond distance, $r_{(e)}$, developed in the 1930's to relate together various spectroscopic information across the Periodic Table as, $k = a(r_{(e)} - b)^{-3}$ where k and $r_{(e)}$ have their usual definitions, and "a" and "b" are empirical fitting constants of the appropriate dimensions, which is the Badger's relation, and one can look again to the BCS expression, this time to Equation (8) for the electron-phonon coupling constant[6]:

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[4] L. Pauling, The Nature of the Chemical Bond, 3rd edition, Cornell University Press, Ithaca, NY, 1960, p.594.

[5] Ibid (4), p.231

[6] Ibid (2)

(8) $$\lambda = ((N(0) \cdot C)/\langle\omega^2\rangle)$$

And one can replace the term in ω by recognizing the relationship $\omega = \sqrt{(k/\mu)} = \sqrt{(a(r_{(e)} - b)^{-3}/\mu)}$ where μ is the reduced mass of the chemical bond of interest in the electron-phonon coupling phenomena.

Therefore, upon squaring the latter expression for the phonon frequency, in terms of $\omega^2 = (k/\mu) = (a(r_{(e)} - b)^{-3}/\mu)$, we get the following result for the electron-phonon coupling parameter from the BCS theory:

(9) $$\lambda = ((N(0) \cdot C)/(a(r_{(e)} - b)^{-3}/\mu))$$

Where the electron-phonon coupling constant is in terms of the variables in N(0), the density of states at the Fermi level, the Badger chemical bond parameters a and b, the equilibrium internuclear distance of interest $r_{(e)}$, the reduced mass, μ, of the bond of interest and the electron-phonon coupling constant C.

If we thus introduce all of the changes made above into Equation (6), we would have a BCS expression that introduces both the phonon bond dissociation energy, $D_{(e)}$, and the phonon equilibrium internuclear distance, $r_{(e)}$, explicitly into the overall BCS picture of superconductivity as in Equation (10):

(10) $$k \cdot T(c) = 1.14 \cdot (h\omega_{(D)} - (h\omega_{(D)})^2/4D_{(e)}) \cdot \exp\text{-}(1/((N(0) \cdot C)/ (a(r_{(e)} - b)^{-3}/\mu)))$$

Thus one has effectively transformed the BCS expression, in terms of phonon frequencies, $\omega_{(D)}$, into an equivalent, viable expression in terms of phonon properties of dissociation energy, $D_{(e)}$ and equilibrium bond length, $r_{(e)}$, that are in fact more

intuitive quantities to deal with and that have been determined spectroscopically quite accurately across the Periodic Table.

Equation (10), and the effects of chemical bond length, $r_{(e)}$, and chemical bond strength $D_{(e)}$, can thus be simply interpreted for the chemical bond that has given rise to the phonon of interest in the given superconductivity mechanism, by making some obvious assumptions. Thus by assuming that the given maximum values for the associated density of states of the material at the Fermi energy, N(0), and simultaneously a maximum in the electron-phonon coupling constant C hold for the purposes of testing out the effect of these chemical bond parameters on the overall critical temperature, $T_{(c)}$, of various superconducting compositions, one would analyze Equation (10) to find that as $r_{(e)}$ gets larger, to a power of 3, the corresponding critical transition temperature gets larger, $T_{(c)}$. By an analogous algebraic analysis, one can see that as $D_{(e)}$ gets larger, similarly $T_{(c)}$ gets larger as well. So one would like to maximize both these chemical bond parameters, r(e) and D(e), in order to maximize the critical superconducting temperature in a given composition. The approach one would take, in such a case, would be of course to scan the spectroscopic data across the Periodic Table, and see which diatomic chemical bond potentials maximize the product function given in Equation (11) below:

(10) $$r_{(e)} \cdot D_{(e)} = \text{“critical temperature constant”}$$

It seems to be the case, in this connection, that such expressions as Equation (10) & Equation (11) lead to a more chemically intuitive understanding of the phonons involved in the superconductivity mechanism. One can thus use (10) & (11) to get a more predictive handle on the superconductivity transition temperature, a central result emerging out of the BCS theory, using chemically intuitive concepts such as the

spectroscopic chemical bond parameters given by $r_{(e)}$, and $D_{(e)}$.