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A bound on the superconducting transition temperature

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It is notoriously difficult to make quantitative theoretical predictions of the superconducting transition temperature, T_c , either from first-principles or even from a knowledge of normal state properties. Ultimately, this reflects the fact that the energy scales involved in the superconducting state are extremely small in natural units, and that T_c depends exponentially on a subtle interplay between different interactions so that small uncertainties in microscopic processes can lead to order one effects on T_c . However, in some circumstances, it may be possible to determine (approximate) bounds on T_c . Here we propose such a bound for the conventional phonon-mediated mechanism of pairing with strongly retarded interactions, i.e. in the case in which $\hbar\bar{\omega} \ll E_F$, where $\bar{\omega}$ is an appropriate characteristic phonon frequency and E_F is the Fermi energy. Specifically, drawing on both empirical results (shown in Fig. 2 below) and recent results¹ of determinant quantum Monte Carlo (DQMC) studies of the paradigmatic Holstein model, we propose that $k_B T_c \leq A_{\max} \hbar\bar{\omega}$, where $A_{\max}$ is a dimensionless number of order one that we estimate to be $A_{\max} \approx 1/10$.

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INTRODUCTION

In general, T_c is a function of the phonon spectrum, the electron spectrum, the electron-phonon coupling and the electron-electron interactions. Given that the bare interactions between electrons are repulsive, it is something of a miracle that the effective interactions at low energies can be effectively attractive, i.e. produce pairing. In conventional superconductors, this miracle is a consequence of the retarded character of the phonon-induced interactions, $\hbar\bar{\omega} \ll E_F$. (In unconventional superconductors, it is rather the strong k dependence of the screened but still largely repulsive effective interactions that allows pairing to occur.) As we are focusing here on the case of conventional superconductors, it is reasonable to write a general expression for T_c as the product of a dimensional factor $\hbar\bar{\omega}/k_B$ times a dimensionless function of the various dimensionless parameters that characterize the particular system in question,

$$k_B T_c = \hbar\bar{\omega} A(w, \lambda, \mu, \dots), \quad (1)$$

where $w \equiv \hbar\bar{\omega}/E_F$, λ is the (conventionally defined) dimensionless electron-phonon coupling, μ is the dimensionless electron-electron repulsion, and $\dots$ represents other things, such as the form of the electron dispersion (e.g. the ratio of second to first neighbor hopping matrix elements), the phonon dispersion, etc.

Given that in typical metals, the Fermi energy is large compared to all other energies, it is reasonable to evaluate A in the $w \rightarrow 0$ limit. In this same limit, μ is highly renormalized downward, so that $\mu \rightarrow 0$; we will therefore consider A in the limit $\mu = 0$. Thus, the most significant parametric dependence of A concerns λ .

RESULTS AND DISCUSSION

Various approximate theoretical treatments of this problem based on Migdal-Eliashberg (ME) theory have long served as the basis for the accepted wisdom on this subject. As nominally ME theory is valid so long as $w\lambda \ll 1$, it is generally believed that it can be

applied even to the strong-coupling regime in which $w^{-1} \gg \lambda \gg 1$. Moreover, various approximate evaluations of the resulting self-consistency equations produce an expression for A that is a monotonically increasing function of λ ; if correct, this would imply that, barring other instabilities i.e. lattice instabilities or charge-density wave (CDW) formation, the larger λ the larger T_c .

We have recently shown¹, on the basis of exact DQMC studies of the Holstein model (defined below), that this expectation is incorrect. Specifically, for a given small value of w we find that the ME approximation is extremely accurate for λ smaller than a characteristic value $\lambda^* \sim 1$, while for $\lambda > \lambda^*$ (even if $\lambda \ll w^{-1}$) ME theory is both quantitatively and qualitatively incorrect. In particular, λ^* marks a crossover to a strong-coupling regime characterized by bipolaron formation, growth of commensurate CDW correlations unrelated to Fermi surface nesting, and incipient phase separation.

The Holstein model consists of a single electronic band, and a non-dispersing optical phonon coupled by the most local possible interaction to the on-site electron density. In relating model calculations with experiment, it is important to distinguish “bare parameters” (i.e., the parameters that appear in the model, such as the bare phonon frequency, ω_0 and the bare dimensionless electron-phonon coupling, λ_0) from “physical” quantities, such as the actual phonon dispersion, $\omega_{\vec{q}}$, and the renormalized electron-phonon coupling, λ . The tendency to phonon softening with increasing λ_0 implies that $\omega_{\vec{q}} < \omega_0$ and $\lambda > \lambda_0$. Indeed, in the context of ME theory, λ diverges upon approach to a lattice instability. The breakdown of ME theory we have identified is distinct from any such lattice instability, and occurs when λ and λ_0 are both of order one. The crossover at λ^* is associated with a complete rearrangement of the important low energy degrees of freedom.

To quantify this crossover, we show in Fig. 1 the $T \rightarrow 0$ occupancy of the single particle state at the bottom of the band ($n_{\vec{k}}$ for $\vec{k} = \vec{0}$), measured in DQMC and computed within ME theory. This state is far below the Fermi energy and hence, for non-interacting electrons $n_{\vec{0}} = 2$. On the other hand, in the

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Fig. 1 Occupancy of the $\vec{k} = \vec{0}$ (band bottom) single-particle state as a function of the bare dimensionless electron-phonon coupling λ_0 (lower scale) and the renormalized coupling, λ (upper scale). (The definitions are as given in ref. ¹). Solid dots are from DQMC simulations described in ref. ¹ with $\hbar\omega_0/E_F = 0.1$, and the data shown are at a temperature $T \approx E_F/30$, at which n_0 has reached its asymptotic low T -value. The dashed line is the same quantity computed within ME theory. The inset shows the difference between the DQMC and ME results. The scale on the vertical axis has been chosen such that 0 is the value for non-interacting electrons and 1 is the value in the polaronic limit. ($\rho = 0.8$ is the average electron density per site.)

strong-coupling polaronic limit, electrons are essentially localized on a lattice site, so n_0 approaches the average electron density per site. For $0 < \lambda \ll 1$ the electronic spectrum is perturbatively rearranged and n_0 is slightly depressed. This behavior is apparent in both the ME approximation and from the DQMC results for $\lambda < \lambda^*$. However, for $\lambda > \lambda^*$, the DQMC results show a rapid decrease of n_0 , consistent with a crossover to the polaronic limit. Moreover, even though we are not able to directly compute T_c (due to the difficulty in obtaining convergence of the DQMC results at low temperatures), by a series of indirect arguments, we¹ inferred that T_c is maximal near the point of this crossover, $\lambda = \lambda^*$, and decreases dramatically when λ is either decreased or increased further. This leads us to the conclusion that there is a well-defined maximal value $\text{Max}[A] \equiv A_{\text{max}} = A(0, \lambda^*, 0, \dots)$.

It turns out that a careful numerical evaluation of the full ($\vec{k}$ and ω dependent) self-consistent ME equations also leads to a non-monotonic behavior of A , which leads to a vanishing T_c for $\lambda > \lambda^*$. However, in contrast to what is found in the DQMC, in the ME treatment the depression of T_c for $\lambda > \lambda^*$ is associated with the onset of a competing incommensurate CDW order. This distinction is important, since if it were only the competition with CDW order that prevented high T_c s, one could “engineer” interactions² that suppress CDW order so as to enhance T_c .

Combining the results from the ME theory (where valid) with the DQMC results, we obtained estimates of A_{max} for the Holstein model on the square lattice. For the range of parameters we have explored, the highest value of T_c we have inferred is 0.08 times the bare phonon frequency, but because significant phonon softening occurs for $\lambda \sim \lambda^*$, this value of T_c is 0.12 times the maximal renormalized phonon frequency. Many physically realistic generalizations of this model are possible—either by modifying the lattice structure, the electron band structure (further neighbor hopping matrix elements), the number of phonon modes and their dispersion, and the structure of the electron-phonon coupling—all features represented by the $\dots$ in A . There is no reason that the value of $A_{\text{max}}(\dots)$ obtained by optimizing with respect to λ , should not depend somewhat on these various features, although we have already found it to be relatively insensitive to small changes

Fig. 2 Measured values of T_c and Θ_D for various putatively conventional crystalline superconductors. The dashed line is the proposed bound $T_c = \Theta_D/10$. Data on the various materials were obtained from the following references: elements from refs. ^{19,20} A-15s from ref. ²¹ Skutterudites from refs. ^{22–24} CaC_6 from ref. ²⁵ BKBO from ref. ⁶. In most cases estimates of Θ_D were obtained from low-temperature-specific-heat measurements, in others it was estimated from e.g. low temperature resistivity. This dataset is far from exhaustive and we plan to expand on it in the future

of the band structure. Still, it is an interesting exercise (which we are currently undertaking) to determine what microscopic features of the electron-phonon problem can increase A_{max} .

For now, however, we will adopt an estimate of $A_{\text{max}} \approx 1/10$ as suggested by results for the simple Holstein model, and see how it compares with experiment in real materials.

Experimental determination of $k_B T_c / \hbar \bar{\omega}$

In Fig. 2 we plot the superconducting T_c vs. the Debye temperature, Θ_D for various elemental superconductors and compounds for which data are available. In most of the data shown, Θ_D is computed on the basis of the measured low temperature lattice contribution to the specific heat and the number of atoms per unit cell in the crystal structure, while in others it is inferred from e.g. low temperature resistivity. It thus represents a specific, unambiguously defined (although somewhat crude) estimate of the characteristic maximal phonon frequency $\hbar \bar{\omega} \sim k_B \Theta_D$. Also shown in the figure is the proposed bound $T_c \leq \Theta_D/10$.

Not only do we see that the bound is satisfied by all the data we have found (which is not, unfortunately, an exhaustive set), but in some cases the materials come quite close to saturating the bound, meaning that the bound may have some real significance. Specifically, for Pb ($T_c = 7.2$ K), Nb ($T_c = 9.25$ K), and Hg ($T_c = 4.15$ K), three elemental superconductors known for their relatively strong electron-phonon couplings, T_c/Θ_D takes on the values 0.069, 0.034, and 0.058, respectively. The A-15 family of old fashion “high temperature superconductors,” Nb_3Sn ($T_c = 17.9$ K), Nb_3Ga ($T_c = 19.8$ K), and Nb_3Ge ($T_c = 21.8$ K) have T_c/Θ_D equal to 0.066, 0.071, and 0.072, respectively.

At ambient pressure, the highest temperature superconductivity of a clearly conventional sort (with $w \ll 1$) is MgB_2 , which does not appear in the figure because it has such a high $\Theta_D = 884$ K, and thus has $T_c/\Theta_D = 0.04$.³ This suggests that if a way can be found to increase the value of λ in this material, it could lead to as much as a factor of 2 enhancement of T_c . The highest T_c of all conventional superconductors is $T_c = 203$ K in H_3S at 155 GPa.⁴ As far as we know, the Debye temperature has not been measured; however, if we identify $\bar{\omega}$ with the largest phonon frequencies found in DFT calculations of the phonon band structure we obtain the estimate $\hbar \bar{\omega} = 0.23$ eV.⁵ If we accept this theoretical value,

then $k_B T_c / \hbar \bar{\omega} = 0.08$, i.e. it comes very close to saturating our bound.

An especially interesting material from our perspective is $\text{Ba}_{1-x}\text{K}_x\text{BiO}_3$ (BKBO), which has an optimal $T_c = 32$ K ($T_c/\Theta_D \approx 0.09$) for $x \approx 0.4$.⁶ Various features^{7,8} of BKBO near optimal T_c —softening of an optic phonon mode, diamagnetism above T_c , proximity to a commensurate CDW phase—indicate this material may be especially relevant for studying the crossover from conventional superconductivity to strong-coupling, polaronic physics.

Further remarks

The idea of bounding T_c is not new. For instance, an absolute bound for an electron-phonon mechanism $T_c < 30$ K was proposed in ref. ⁹. The loopholes in this analysis were recently summarized in ref. ¹⁰. Conversely, a remarkable and highly influential analysis¹¹ of ME theory suggested that T_c grows without bound with increasing λ , and can even be larger than $\hbar \bar{\omega} / k_B$. It has long been recognized that this proposal was subject to the caveat that at large λ , a system may be prone to other instabilities, which could compete with superconductivity. It was shown¹⁰ that the effect of phonon softening—still assuming the validity of ME theory—leads to a reduced prefactor in the T_c expression, and thus to a bound on T_c given by the bare phonon frequency, which is approached asymptotically as $\lambda \rightarrow \infty$. Arguments for a bound within the context of ME theory have also been presented in refs. ^{12,13,14}. The breakdown of ME theory due to spontaneous breaking of translation symmetry has also been analyzed.^{15,16}

As the analysis in the present paper shares some features with these earlier studies, there are important ways in which it is different, both conceptually and practically. Our DQMC results show that deviations from the predictions of ME theory occur even in ranges of temperatures and λ in which no other form of order has arisen; in this range, ME theory always over-estimates the superconducting susceptibility. The non-monotonic λ dependence of T_c that leads to our proposed bound is associated with a crossover at $\lambda \sim \lambda^*$ from a regime in which ME theory is extraordinarily accurate to a strong-coupling regime where the ME approximation breaks down entirely. This leads to a sharp drop of T_c , even if the system in question has been carefully engineered to have no competing charge-ordering instabilities. The existence of an optimal λ^* independent of competing instabilities, as far as we know, is inconsistent with all analysis based on ME theory, but not in conflict with any experimental observation.

Recently, it has been found that superconductivity in SrTiO_3 persists to such low electron densities that the Fermi energy is less than the typical phonon frequency, i.e. into a regime in which $w \gg 1$. In this limit, it is far from clear that the effects of a bare repulsion, $\mu > 0$, can still be neglected. However, as a problem in model physics, it is possible to ask whether a more general bound exists on $A(w, \lambda, \mu = 0, \dots)$. In the large w limit, it is possible to integrate out the phonons to obtain an instantaneous attractive interaction with a magnitude proportional to λ . In particular, the Holstein model in the limit $w \rightarrow \infty$ maps onto the negative U Hubbard model with $U \sim -E_F \lambda$. It is well known that this model has an optimal T_c at an intermediate value of $|U| \sim E_F$, where the maximal T_c is bounded by a scale that is a fraction of E_F .¹⁷ Thus, at least in the artificial limit $\mu = 0$, there exists a more general bound of the form $A(w, \lambda, \mu = 0, \dots) \leq A(w, \lambda^*(w), \mu = 0, \dots)$ where $A(w, \lambda^*(w), \mu = 0, \dots) \sim 1/w$ as $w \rightarrow \infty$.

There is another class of bounds on T_c that can be inferred in a different manner; rather than taking normal state data, one can start with measured properties of the superconducting ground-state, from which one can attempt to bound the actual T_c . Ideally, these bounds should apply to both conventional and unconventional superconductors.

For a simple BCS s -wave superconductor in the weak coupling limit, $T_c = B \Delta_0$ where Δ_0 is the zero-temperature gap and $B = e^\gamma /$

$\pi \approx 0.567$. Strong-coupling effects, even in the context of BCS mean-field theory, have a tendency to decrease the value of B , and certainly fluctuational effects beyond mean-field theory will likewise decrease the value of B . Thus, taking into account the fact that the gap function can vary along the Fermi surface, one would generally expect that

$$k_B T_c \leq B |\Delta_{\max}|, \quad (2)$$

where (with the case of unconventional superconductors in mind) $\Delta_{\max}$ is the largest value of the $T = 0$ gap on the Fermi surface. As far as we know, this inequality is satisfied (and often very nearly saturated) by all known crystalline superconductors. (In the presence of disorder it is, of course, possible to have gapless superconductors.)

In a similar vein, a bound was proposed in ref. ¹⁸ based on the measured value of the zero-temperature superfluid stiffness, $\rho_s(T = 0)/m^*$ (or equivalently from the zero-temperature value of the London penetration depth)

$$k_B T_c \leq C \frac{\hbar^2 \rho_s(0) a}{2m^*}, \quad (3)$$

where in a layered (quasi-2D) superconductor, a is the inter-layer separation while in a 3D superconductor, $a = \sqrt{\pi} \xi_0$, where ξ_0 is the zero-temperature coherence length, and $C \approx 2.2$. (2.2 is the ratio of T_c to the zero-temperature phase stiffness of the 3D XY model on a cubic lattice.) Most superconductors satisfy this inequality but come nowhere near saturating it. However, certain high temperature superconductors, especially hole-doped cuprates, come within a factor of two or three of saturating this inequality.

DATA AVAILABILITY

The data that support the findings of this study are available from the corresponding author upon reasonable request.

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AUTHOR CONTRIBUTIONS

All three authors have contributed equally to the development of the ideas in this work and to the writing of the paper.

ADDITIONAL INFORMATION

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