Electronic mechanism of superconductivity in the cuprates, C_{60}, and polyacenes

Sudip Chakravarty and Steven A. Kivelson

Department of Physics and Astronomy, University of California Los Angeles, Los Angeles, California 90095-1547

On the basis of an analysis of theoretical and numerical studies of model systems and of experiments on superconductivity in doped C_{60}, polyacenes, and the cuprate high-temperature superconductors, we propose that a purely electronic mechanism of superconductivity requires structures at an intermediate scale or mesoscale. Specifically, we address the crucial question of how high-temperature superconducting pairing on the mesoscale can arise from purely repulsive electronic interactions.

I. INTRODUCTION

Induced attractions between electrons, such as are mediated by phonons in conventional superconductors, are typically weak while the direct repulsive interactions between electrons are strong. It has therefore long been felt that the key to high-temperature superconductivity is a purely electronic mechanism that directly exploits the repulsive interaction to produce pairing.

After the discovery of high-temperature superconductivity in cuprates by Bednorz and Müller,[1] an idea for how this could be achieved was proposed.[2] It was suggested that an antiferromagnet disordered by quantum fluctuations and characterized by resonating singlet pairs of spins could be viewed as a state in which superconducting pairing occurs, even though the system is an insulator with one electron per site and zero superfluid density. In this case, when doped so that charge motion is allowed, the system will automatically become a superconductor. A related idea is that singlet pair formation in the insulating state produces a gap in the spin excitation spectra,[3,4] which evolves into the superconducting pairing gap upon doping.

A fundamental flaw with this approach soon became clear; in the relevant two-dimensional spin-1/2 antiferromagnet on a square lattice, the ground state is magnetically ordered[5] and indeed so strongly that the elementary excitations about the ordered state, spin waves, give a quantitatively accurate description of many quantities. Needless to say, the magnetically ordered state bears no resemblance to a superconductor, even locally.

Yet intuition that the high-energy scale of high-temperature superconductors must have its origin in repulsive interactions remained. The discovery by Hebard *et al.*[6] of high-temperature superconductivity in alkali-doped C_{60} was another milestone. It illuminated a path, in the clearest terms, that the missing element in the above revolutionary argument is the existence of a mesoscale structure. The C_{60} molecule itself plays the role of this structure, permitting electronic pairing, which would disappear if the molecule were expanded to the macroscopic scale. We were thus led to propose a mechanism[7−9] of superconductivity in which attraction arises from repulsion. Later it was suggested that a similar pairing mechanism may apply in the cuprate high-temperature superconductors,[10,11] where the relevant mesoscopic structures are self-organized stripes.

Here, we present evidence, which we consider to be exceedingly strong, that this set of ideas underlies the occurrence of high-temperature superconductivity in diverse materials. It is shown that local singlet formation as a driving mechanism for ''pairing'' is correct, but only on a mesoscopic scale. The pairing tendencies are either much weaker or nonexistent in extended systems.

There are also a number of remarkable recent experiments on doped C_{60} (Refs. 12 and 13) and polyacene crystalline films[14] which encourage the view that these are electronically driven true high-temperature superconductors in disguise. Although the authors of these papers ascribe the superconductivity of these materials to the electron-phonon interaction, we feel that the experimental facts, including the high value of T_c itself (presently up to 52 K), rather indicate that these materials are true ''high-temperature superconductors,'' in which correlation effects play a dominant role both in the normal state and in the mechanism of superconductivity. We shall briefly discuss this issue in the final section.

It is important to stress the distinction between *possible* and *necessary* consequences of the existence of mesoscale structures — surely not all forms of repulsive interactions on any given cluster will lead to pair binding. Additionally, there are strong reasons[15,16] to expect the same mesoscale physics to lead to competing orders. Indeed, we propose that the existence of a complex phase diagram with a variety of broken symmetry phases, including high-temperature superconductivity, is a characteristic feature of a material with an electronic mechanism of pairing on the mesoscale. It may not generally be clear, however, whether competing orders cause or are induced by mesoscale structure.

II. MESOSCALE PAIR BINDING

At atomic scales, the Hamiltonian is simple (although strongly interacting) and the dominant Coulomb interactions are readily identified. At the macroscopic scale, the physics is again simple and is governed by the universal properties of the attractive fixed points of the renormalization group theory. However, as the high-energy degrees of freedom are integrated out, beginning with the microscopic scale, every imaginable multiparticle interaction is generated, so that the effective Hamiltonian becomes complicated and the dominant physics can be obscure. Thus, it is necessary to first determine whether there is any robust and predictable behav-

ior at all. We argue that on certain finite clusters quantum fluctuations of the spins can produce a disordered ground state with a large gap in the spin excitation spectrum and a robust pair binding of holes or electrons.

In each case, we start with a "neutral" cluster with N sites and one electron per site. For all the systems studied, the neutral cluster has a unique, spin-singlet groundstate. We define $E(Q,S)$ to be the lowest-energy eigenvalue of the cluster with total spin S and "charge" Q or, equivalently, a total of $N+Q$ electrons. Whenever the ground state is a spin singlet, we can define the spin gap Δ_s to be

$$\Delta_s(Q) = E(Q,1) - E(Q,0). \tag{1}$$

The pair-binding energy is defined as

$$E_p(Q) = 2E(Q+1) - E(Q+2) - E(Q), \tag{2}$$

where $E(Q)$ signifies the minimum over S of $E(Q,S)$. Clearly, a positive pair-binding energy signifies an effective attraction between electrons, in the sense that given $2(N+Q+1)$ electrons and two clusters, it is energetically preferable to place $N+Q+2$ electrons on one cluster and $N+Q$ on the other than to put $N+Q+1$ electrons on each of the clusters.

We illustrate the origin of these effects, the relation between Δ_s and E_p, and the importance of intermediate scales to the occurrence of such "attraction from repulsion" by analyzing a variety of models. We defer to the following section any discussion of the relation between spin-gap formation and pair binding with the occurrence of superconducting or other long-range order in extended systems.

A. Hubbard rings

As a first example consider Hubbard rings with N sites, where N is even. The Hamiltonian is

$$H = -t\sum_{i\sigma} (c_{i\sigma}^{\dagger}c_{i+1\sigma} + \text{H.c.}) + \frac{U}{2}\sum_{i\sigma} n_{i\sigma}n_{i-\sigma}, \tag{3}$$

with the implied periodic boundary condition. The fermion operator $c_{i\sigma}^{\dagger}$ creates an electron with spin σ on site i, and $n_{i\sigma} = c_{i\sigma}^{\dagger}c_{i\sigma}$ is the density of electrons of spin σ on site i.

The energies $E(Q,S)$ can be calculated exactly from the Bethe ansatz.[17] We have extended existing results for the pair-binding energy E_p by numerically evaluating the Bethe-ansatz equations for a wide range of system sizes as large as 1024 sites and by calculating the spin gaps Δ_s. The exact particle-hole symmetry of the Hubbard model on a bipartite lattice implies that electron doping, $Q>0$, and hole doping, $Q<0$, are equivalent. As can be seen in Fig. 1 pair binding occurs for electrons added to the neutral molecule, $E_p(0)>0$, whenever $N=4n$, but does not occur when $N=4n+2$, where n is a positive integer. The difference between these two cases can be readily understood from low-order perturbation theory in U/t as discussed in the Appendix.

The role of intermediate scales can be seen directly from Fig. 1; the pair-binding energy vanishes for large N and is maximum at an intermediate value of N. Moreover, in Fig. 2 we show E_p for fixed N as a function of U, from which it is
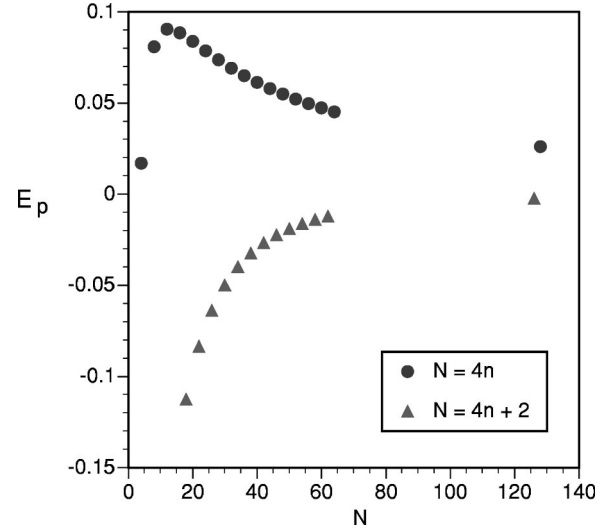

FIG. 1. Pair-binding energy E_p of $N=4n$ and $N=4n+2$ site Hubbard rings with $t=1$ and $U=4$.

clear that it is maximal for intermediate interaction strengths as well. Indeed, we have proved a rigorous theorem,[18] that for the standard Hubbard model on any finite lattice and with positive hopping matrix elements, $E_p \leq 0$ for $U\to\infty$. (Trivially, $E_p \leq 0$ for $U=0$.)

The crucial question is, what is the mechanism of pair binding? We can gain some insight into this question in the large-N limit from bosonization.[19] We show that pair binding is closely related to the phenomenon of spin-gap formation. It is well known that at long wavelength, spin-charge separation occurs in one-dimensional (1D) Hubbard rings. Therefore, all energies can be written as a sum of a spin contribution and a charge contribution. The result is that, for $N=4n\gg 1$,

$$\Delta_s = \frac{v_s}{N}[B_1\ln^{1/2}(N) + B_2] + \cdots, \tag{4}$$
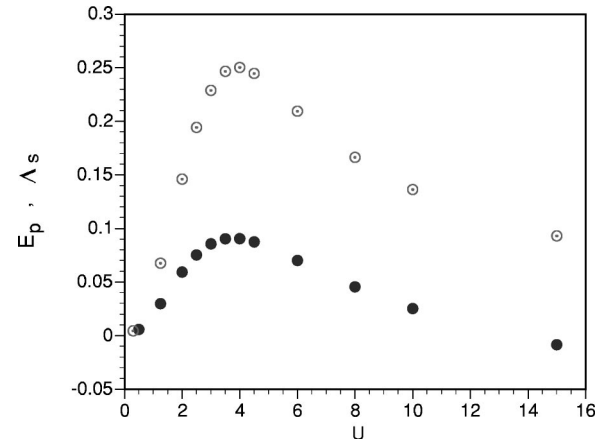

FIG. 2. Pair-binding energy E_p (solid symbols) and spin gap Δ_s (open symbols) of a 12-site Hubbard ring as a function of U in units of $t=1$.
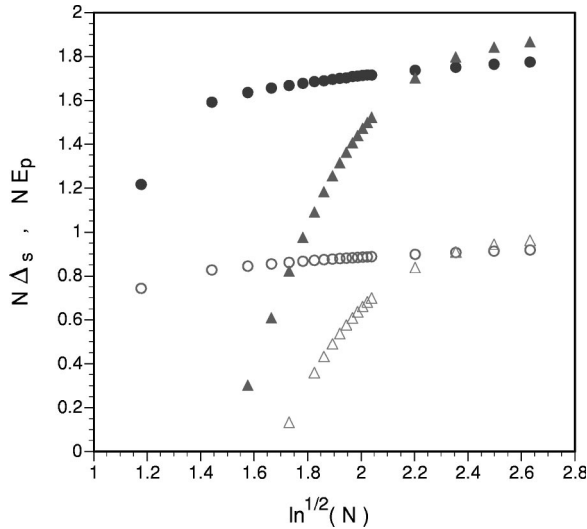
FIG. 3. The large $N=4n$ scaling of the pair-binding energy E_p (triangles) and spin gap Δ_s (circles) of Hubbard rings in units of t $=1$. All energies are scaled by an explicit factor of N to remove the dominant $1/N$ dependence, revealing the logarithmic dependence predicted in Eq. (4). Solid symbols are for $U=10$ and open symbols are for $U=20$.

$$E_p = \Delta_s + B_3 \frac{v_s}{N} - \frac{B_4}{N^2}\left[\frac{v_c^2}{\Delta_c}\right] + \cdots . \qquad (5)$$

Here, v_s and v_c are the spin and charge velocities, respectively (in units in which the lattice constant is unity) and Δ_c is the charge gap in the $N\rightarrow\infty$ limit. The constants B_j are numbers of order unity, which we have not evaluated. The large-N behavior of these quantities computed from the Bethe ansatz are shown in Fig. 3 and appears, from the similarities of slopes, to be in good agreement with these expressions.

Because of the relevance of umklapp scattering, the charge degrees of freedom are described by a sine-Gordon field theory. Dilute doping results in a dilute gas of spin-0 charge $\pm e$ solitons (holons or eons[8]) with a gapped spectrum. These solitons can, in turn, be mapped onto massive Dirac fermions. Consequently, the finite-size level spacings are those of a nonrelativistic particle in a box, which gives rise to the third term in Eq. (5). However, in making a spin excitation in the neutral molecule, no charge is added, so the spin gap is independent of the charge dynamics.

It has been previously observed[20,21] that, because the spin system is quantum critical, the spin correlation functions are conformally invariant, so that the spin gap must scale with v_s/N. The slow renormalization group flow associated with a marginally irrelevant operator at the fixed point invalidates this finite-size scaling behavior, however. A consequence[22] of this for the infinite system is that the spin-spin correlation function falls with distance r as $(\ln^{1/2}r)/r$. We conjecture that a similar logarithmic correction occurs in the finite-size scaling behavior, hence the logarithmic term in Eq. (4). As can be seen from the large-N behavior of the Bethe ansatz solution in Fig. 3, just such a logarithmic term appears in the data. In terms of the elementary spinon excitations of the
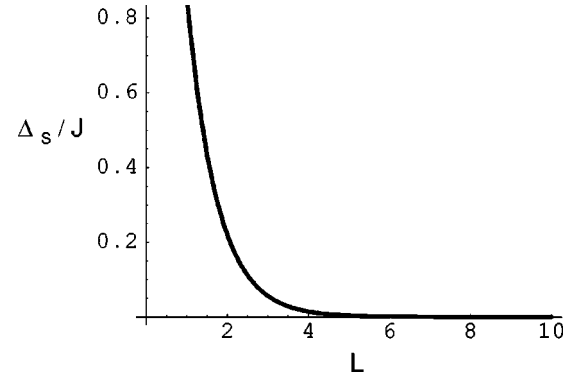

FIG. 4. The spin gap in $S=1/2$ Heisenberg ladders of width $2L$.

spin-1/2 Heisenberg model, Δ_s is interpreted as the energy of a two-spinon state, while $\Delta_s + B_3 v_s/N$ is twice the single-spinon energy; $-B_3 v_s/N$ thus has the interpretation of an effective spinon-spinon interaction.

An important lesson of this analysis is that, for large N, $E_p \approx \Delta_s$. This relation, originally proposed by us in the context of pair binding on a C_{60} molecule,[8] is in this case a consequence of the quantum critical character of the 1D Hubbard model. Moreover, since both the separation of charge and spin, and the quantum critical nature of the spin correlations, are robust features of the one-dimensional electron gas, they are not limited to the integrable Hubbard model, but would be expected to survive the inclusion of second- and further-neighbor Coulomb repulsions as well.

B. t-J ladders

Hubbard or t-J chains have no spin gap in the limit $N \rightarrow \infty$ and, in addition, have small superconducting susceptibilities irrespective of the doping level. In contrast, ladder systems, that is, quasi-one-dimensional systems of finite width, can exhibit both a spin gap and strong tendencies toward superconducting order, even in this limit. While these systems are infinite in extent, the mesoscopic physics comes in through the finiteness of the transverse dimension. Because so much is known theoretically about one-dimensional quantum systems, such ladders are also an excellent laboratory for exploring the general physical principals set forth in the Introduction.

The Hamiltonian of a spin-1/2 Heisenberg ladder, as shown in Fig. 4, is

$$H_J = J \sum_{\langle ij \rangle} [\mathbf{S}_i \cdot \mathbf{S}_j - (1/4)n_i n_j], \qquad (6)$$

where $\mathbf{S}_i$ is a spin-1/2 operator, J is the antiferromagnetic exchange interaction, and $\langle ij \rangle$ signifies nearest-neighbor sites, of spacing a, on the ladder. For a Heisenberg ladder, the site occupation numbers n_i are constants of motion and are unity. So the second term in the Hamiltonian is simply an irrelevant constant; this term will become important for the t-J ladder to be discussed later. For an even-leg ladder of width $W/a=2L=2$, the spin gap is known numerically[23] to be $\Delta_s \approx J/2$, but this gap vanishes exponentially,[24] as $\Delta_s \sim 3.35J \exp[-0.682(W/a)]$, for wider ladders, $L=2,3,\ldots,$

as shown in Fig. 4. In contrast, for odd-leg ladders, $W/a = 2L+1$, H_J has gapless spinon excitations, but here, too, there is an important energy scale, with the same functional dependence on L as Δ_s, below which the physics is dominated by spinons, as for a spin-1/2 Heisenberg chain. Since, once again, the spin-gap formation is related to superconductivity, as we shall show below, this implies that only rather narrow ladders (two or three legs) are good candidates for the mesoscopic building blocks of a high-temperature superconductor.

For a doped system, we cannot only ask about the dependence $\Delta_s(x)$ of the spin gap and of the pair-binding energy $E_p(x)$ on the concentration of added charge x, but we can also ask about the superconducting susceptibility. To be concrete, we consider results for the t-J model,

$$H_{tJ} = -t \sum_{\langle i,j \rangle, \sigma} [c_{i,\sigma}^\dagger c_{j,\sigma}^\dagger + \text{H.c.}] + H_J, \qquad (7)$$

which is defined on the space of no doubly occupied sites, and can be viewed as the large-U limit of the Hubbard model as long as $J = 4t^2/U \ll t$.

Numerical studies[25] on the two-leg t-J ladder with $J = 0.35t$ show that the spin gap is roughly the same magnitude as in the undoped two-leg ladder for a range of x between 0 and 0.15 and so is the pair-binding energy. The three-leg ladder[26] is more interesting — the spin gap is 0 for $x \lesssim 0.05$, then rises to a value comparable to the spin gap in the two-leg Heisenberg ladder for $x \sim 0.15$, and then becomes small or possibly zero as x gets to be 0.2 or larger. This behavior can be readily understood (and was to a large extent anticipated) from both perturbative renormalization group analyses[27,28] and from strong coupling bosonization[11,28] methods.

Because continuous symmetries cannot be broken in one dimension, the ladders can never be truly superconducting. However, their tendency to superconduct can clearly be seen in the superconducting susceptibility $\chi_{sc}(T)$; for instance, in a quasi-one-dimensional array of ladders, one can estimate the superconducting T_c from the mean-field equation $z\mathcal{J}\chi_{sc}(T_c) = 1$, where z is the number of nearest-neighbor ladders, and $\mathcal{J}$ is the interladder Josephson coupling. For a one-dimensional system with a spin gap, the superconducting susceptibility[11,15] is

$$\chi_{sc} \sim \Delta_s T^{1/K_c - 2}, \qquad (8)$$

where K_c is the charge Luttinger exponent. This expression reveals a direct relation between spin gap and enhanced superconducting fluctuations. A related result, which can be more easily compared to the results of numerical experiments, is the pair-field–pair-field correlator, $D(r)$, given by

$$D(r) \sim \Delta_s |r|^{-1/K_c}. \qquad (9)$$

For the purpose of understanding the competition between order parameters, discussed below, it is worth noting that the susceptibility to $2k_F$ charge-density wave (CDW) is

$$\chi_{CDW} \sim \Delta_s T^{K_c - 2}. \qquad (10)$$

A spin gap enhances both the CDW and superconducting susceptibilities. Indeed, it is tempting, and sometimes useful, to think of the spin gap as a superconducting gap, which exists in the absence of superconducting long-range order due to violent phase fluctuations characteristic of a one-dimensional system. But Eq. (10) makes it clear that the spin gap can be equally well thought of as a CDW gap, where true CDW order has been suppressed due to the divergent fluctuations of the acoustic phonons in the CDW state.

The charge Luttinger exponent K_c is a nonuniversal function of doping, x, and depends on the nature of the interactions. As long as $K_c > 1/2$, the χ_{sc} is divergent, but not as strongly divergent as the χ_{CDW}, unless $K_c > 1$. For a Hubbard chain, it is well known that $K_c < 1$, but this is not a strict physical bound. For instance, by comparing the expression in Eq. (9) with numerical experiments on the two-leg Hubbard ladder,[29] one can see that $K_c > 1/2$ for a very wide range of parameters, and that for some ranges of parameters, $K_c > 1$. For instance, for $x = 0.0625$, $K_c > 1$ for $5 \lesssim U/t \lesssim 15$, that is, for intermediate values of U.

C. Hubbard molecules

In the past we have examined a number of small Hubbard molecules[30] by exact diagonalization and found pair binding to operate in all cases. These were the 4×4 torus, the 8-site cube, and the 12-site truncated tetrahedron. In all cases, the degeneracy of the state in which doping takes place is important, and in all cases studied, second-order perturbation theory captures qualitatively all the aspects of the phenomenon for what appears to be large values of U. This is not so surprising in a finite system with finite energy denominators; hence, perturbation theory is an effective tool[8,31] in studying large molecules such as C_{60}, where exact diagonalization methods are prohibitive.

We have also demonstrated that nearest-neighbor repulsive interactions for the truncated tetrahedron is harmful for pair binding. In contrast, pair binding in t-J ladders remains robust[32] for nearest-neighbor repulsion V as large as $4J$. Similarly, the realistic frequency-dependent screened potential for doped C_{60} leaves the results essentially unchanged from the pure Hubbard model.[33] This we could only demonstrate in second-order perturbation theory.

The conclusion to draw is that in spite of the complexities at the mesoscopic scale, which surely exist, it is well established that certain mesoscopic clusters have positive pair-binding energies $E_p > 0$. Moreover, E_p can be of order the spin gap, which is an intrinsically large electronic energy scale. There still remains the question as to whether this mesoscopic pairing tendency leads to global superconductivity.

D. Two-dimensional t-J model

Superconductivity in the two-dimensional t-J or Hubbard models on a square lattice remains controversial—no exact analytic results exist and numerical studies are confined to rather small systems or high temperatures. However, a few things are clear. The undoped system is an ordered antiferromagnet, and therefore $\Delta_s = 0$. Moreover, while the pair-

binding energy for two doped holes is positive on finite-size molecules, in the physically relevant limit of small t/J <0.4, E_p decreases with system size, and appears[34] to approach 0 in the thermodynamic limit.

It is plausible, even likely, that on a sufficiently frustrated lattice, the spin-1/2 Heisenberg antiferromagnet (the "undoped system") can have a quantum-disordered ground state with a spin gap.[35] Such a system, when doped, might also become a high-temperature superconductor. However, whereas pairing on the mesoscale appears to be a very robust phenomenon, finding magnetic systems with sufficient frustration to produce a significant spin gap is not simple in dimension greater than 1. So while doping such a homogeneously frustrated antiferromagnet may provide a mechanism for high-temperature superconductivity, we find pairing on mesoscale structures to be a more common (and hence more natural) mechanism.

III. EFFECTIVE INTERACTIONS, COMPETING ORDERS, AND SUPERCONDUCTIVITY

Since a finite cluster cannot be a superconductor and even an extended ladder cannot exhibit a finite-temperature superconducting state, the understanding of this mesoscale physics simply serves to define a new, simpler effective Hamiltonian, which governs the physics on longer length scales.

A. Long-range order in molecular crystals

When the extended system can be thought of as a molecular crystal composed of finite clusters, the effective Hamiltonian is obtained by integrating out all the molecular orbitals other than those at the Fermi level. Where there are several degenerate orbitals at the Fermi energy, the resulting effective Hamiltonian will have more than one molecular orbital per site. To be concrete, we will use as an example the case of a C_{60}-like crystal doped with x added electrons per molecule, with $0<x<6$, and vary the intramolecular and the intermolecular couplings to examine its properties.

The effective Hamiltonian is thus of the form

$$H = \sum_j V(\mathbf{S}_j^2, \mathbf{L}_j^2, \Delta N_j) + \sum_{\langle ij \rangle} H_{ij}, \qquad (11)$$

where the effective interaction V on the jth molecule depends on the total number of added electrons, ΔN_j; the square of the total spin, $\mathbf{S}_j^2$; and the square of the total orbital angular momentum, $\mathbf{L}_j^2$ (or, more precisely, the equivalent Casimir operators of the ichosohedral group), and H_{ij} is the intermolecular interaction. In the simplest case, H_{ij} can be taken to consist of a sum of intermolecular hopping operators, which transfer a single electron between molecules i and j, but it can also contain additional terms, such as assisted hopping and Coulomb interactions.

Where E_p is positive on the cluster, V can be thought of as an effective attraction between pairs of electrons on a given molecule. The ratio of E_p to the intermolecular bandwidth W is an important parameter in the problem.

1. Strong-coupling limit

If the typical magnitude of V is large compared to W, we can further thin the low-energy Hilbert space by integrating out all states other than the molecular ground states in each charge sector. In most cases, this limit is unphysical, but because it is easily analyzed, it is worth considering for pedagogic purposes. In particular, if $E_p>0$, we can eliminate all states with an odd number of electrons per site, while for $E_p<0$, we can eliminate all states with an even number of electrons. The resulting effective Hamiltonian has no remaining fermionic degrees of freedom; the states are specified entirely by the number of electrons, and possibly the spin and the orbital moment of each molecule. Under appropriate circumstances, we are led to spin or orbital effective Heisenberg models and even to a bosonic version of the t-J model.

Depending on details of the interactions, such effective Hamiltonians can easily lead to a rich variety of ordered phases, including ferromagnets or antiferromagnets, orbital ferromagnets or antiferromagnets, spin or orbital[36] nematics, modulated (incommensurate or high-order commensurate) versions of any of these states coexisting with charge-density wave order, etc. This is, of course, both exciting and discouraging. It suggests that in the presence of strong interactions in systems with mesoscale structure, there should appear an enormous variety of ordered phases, some of them being new states of matter that have never before been documented. While it invites us to exercise our imagination, the prospects of predicting the ultimate form of order from microscopic considerations in any such system becomes a difficult task, if not impossible.

To take the simplest case, let us imagine that the effective interactions favor an even number of electrons per molecule ($E_P>0$) and disfavor molecular states with nonzero spin or orbital moment. In this case, the low-energy physics of the molecular crystal reduces to that of interacting bosons (electron pairs) on the molecular lattice:

$$H^{eff} = \sum_j [\mu_b b_j^\dagger b_j + V(b_j^\dagger b_j)] - \sum_{\langle ij \rangle} t_{\text{pair}}[b_j^\dagger b_i + b_i^\dagger b_j + \cdots]. \qquad (12)$$

Here, $b_j^\dagger$ is a charge-$2e$ bosonic creation operator, μ_b is 1/2 the electron chemical potential, V is the repulsion between pairs on the same molecule and includes a hard-core interaction that forbids more than three bosons on the same molecule, t_{pair} is the pair-hopping term which is second order in the electron-hopping matrix element, and the ellipsis signifies additional interactions between bosons on neighboring molecules. Of course, even here, the ground-state phases of the system will depend on the precise balance between these residual interactions, as well as on the mean boson density.

Typically, if the electronic charge per molecule is $x=2$ or 4, the ground state will be insulating, with essentially a fixed number of electron pairs on each molecule. This state has no broken symmetry, but is a Mott insulator, in the sense that in the noninteracting limit the system would be metallic. For other mean-charge densities, this system will either form a pair-density wave (presumably insulating) or a superfluid. In the latter case, the pairing scale is intramolecular, and hence

large, while the superfluid density, and hence the global phase ordering temperature T_c, will be smaller, determined by the intermolecular bandwidth. Moreover, in this case, pairing should produce a pseudogap which survives at temperatures well above T_c. In this limit, because the effective boson kinetic energy is proportional to the square of the intermolecular hopping matrix elements, one would expect T_c to be a decreasing function of lattice parameter or an increasing function of pressure.

2. Weak-coupling limit

If the typical scale of interactions, V, is small compared to W and if the molecular crystal is three dimensional, it is reasonable to treat the effective Hamiltonian in a mean-field approximation, that is, by variational ground states, in the spirit of the BCS state, by solving the noninteracting problem in the presence of a symmetry-breaking mean field. Because of the narrowness of the bands in typical molecular solids, it is equally unclear whether this limit is actually realized in real materials. But it is at least another limit in which controlled theoretical results can be obtained. It is probably closer to reality than the strong-coupling limit, at least in relatively metallic materials, such as alkali-doped C_{60}.

In this limit, the various charge, spin, and orbital moment density-wave states are unlikely, unless there are particular nesting wave vectors of the relevant Fermi surface. Thus, except at certain commensurate values of x, they can be safely ignored.

For positive E_p, a BCS instability to a superconducting state is still generic with a superconducting transition temperature

$$T_c \sim W \Theta(V^{\text{eff}}) \exp[-1/\rho(E_F)V^{\text{eff}}(x)], \quad (13)$$

where Θ is the Heaviside function and

$$\rho(E_F) \propto 1/W \quad (14)$$

is the density of states at the Fermi energy of the noninteracting band structure. The quantity

$$V^{\text{eff}}(x) = \sum_{Q,S} P_x(Q,S)E_p(Q,S) \quad (15)$$

is the average of the pair-binding energy for the various charge states of the molecule averaged over the appropriate probability distribution $[\Sigma_{Q,S}P_x(Q,S)=1]$ of charge and spin states of the molecule. Here, T_c would be expected to be a strongly increasing function of lattice parameter (decreasing function of pressure) since it varies with the inverse exponential of $1/W$.

While it might seem at first that this BCS expression for T_c is generic to any mechanism of superconductivity with an intramolecular pairing force (for instance, one generated by coupling to the intramolecular optical phonons), the strong x dependence of V^{eff} implied by the electronic mechanism discussed here is very pronounced and unique. For instance, from the perturbative results for the Hubbard model on a C_{60} cluster described above,[8] one might expect that for interme-
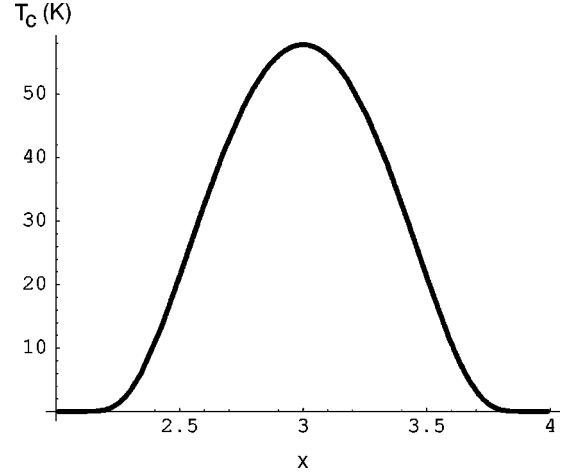

FIG. 5. T_c as a function of electron concentration x, for the simple, weak-coupling model of correlation-induced pairing in C_{60} described in Eqs. (13) and (16).

diate U, V^{eff} is positive (attractive) for $x=3$ and negative (repulsive) for $x=2$ or $x=4$. Crudely, this leads to a doping-dependent effective attraction of the general form

$$V^{\text{eff}} = V_0(x-x_0)(x_1-x), \quad (16)$$

with $2<x_0<3<x_1<4$. This leads to a large T_c only in a constrained region about $x=3$ and to $T_c=0$ for $x<x_0$ or $x>x_1$. This is illustrated in Fig. 5, where, to make a crude comparison with experiments, we have taken $W=0.1$ eV, $\rho(E_F)V_0=1/3$, $x_0=2$, and $x_1=4$.

B. Long-range order in arrays of ladders

Long-range order in an array of ladders is related to the general problem of order in quasi-one-dimensional electronic systems and has been studied for many years;[37] this is theoretically one of the best understood cases of competing orders. In particular, the occurrence of a spin gap enhances the tendency for both CDW and superconducting order in a way that does not distinguish between them.

Even in this case, the competition plays out in a manner that was not previously recognized. It is not sufficient to simply identify the most divergent susceptibility of the isolated ladder in order to determine which type of long-range order will win out. There are, in addition, a variety of marginal interladder forward-scattering interactions which can affect the balance or whether or not there is an ordered ground state at all.[38] A cautious, but an optimistic conclusion from the mesoscale calculations is that the spin gap, which can be large on narrow ladders, permits the *possibility* of high-temperature superconductivity, but it can also lead to a variety of alternative insulating or metallic phases.

IV. FINAL REMARKS

Superconductivity in simple metals is well understood in terms of the BCS mechanism — the normal state is well approximated as a Fermi liquid, and the effective attraction between electrons is mediated by phonons. The effects of

electron-electron interactions appear in this description in the form of a few Fermi-liquid parameters (which are typically small) and in the Coulomb pseudopotential μ^*. The Fermi-liquid character of simple metals is exceedingly robust—in the absence of special nesting conditions of the Fermi surface or very strong interactions, the *only* instability of the metallic state is the BCS instability. A conventional superconductor, when driven normal by suitable alloying, by weak disorder (magnetic impurities), increasing temperature, or magnetic field, remains a highly conducting metal.

In both the cuprates and organic superconductors, including doped C_{60}, there is strong reason to doubt the accuracy of the Fermi-liquid description of the normal state. Screening is generally poor, and the typical magnitude of Coulomb energies is large compared to the valence-electron bandwidth. And, indeed, the materials are not robustly metallic—resistances greater than the quantum of resistance (often accompanied by "insulating" negative values of $d\rho/dT$) are frequently found in these materials when the superconducting state is destroyed. Even when the resistance has a metallic temperature dependence (positive $d\rho/dT$), as it does in doped C_{60} in the "normal" state, the resistance is too large to correspond to any sort of freely propagating quasiparticle. In electron-doped C_{60}, the room-temperature resistance[39,13] is 2–5 mΩ cm, which were it interpreted in terms of a Drude conductivity would correspond to a mean free path of 1–2 Å; in hole-doped C_{60}, the room-temperature resistance[13] is almost 20 mΩ cm, which at face value would correspond to a mean free path of order 0.1 Å. Finally, in addition to superconducting order, evidence of a variety of competing orders abounds.

Given the striking evidence of strong correlation effects in these materials, we suppose that they are fundamental to the mechanism of their unprecedentedly high T_c's. However, we suggest that such a mechanism is robust only if the pairing originates on mesoscale structures. Therefore, it is not accidental that the materials in question are either molecular crystals, with reasonably large molecular building blocks, or materials which exhibit self-organized mesoscale structures.

A. Electron-phonon coupling

Electron-phonon interactions are reasonably strong in all the high-temperature superconductors. In particular, the phonon frequencies in C_{60} are much higher than in conventional metals. In spite of this, we very much doubt that superconductivity is driven principally by electron-phonon interactions. That T_c exhibits isotope effect cannot be an argument as it can be explained by the electronic mechanism as well.[40]

In the first place, the pairing induced by strong repulsive interactions on all the clusters that have been studied to date have d-wave character, for reasons that are by now well understood. Phonons typically produce s-wave attraction and are often pair breaking in other channels. Indeed, when we[41] analyzed the effects of electron-phonon couplings on an assumed electronic mechanism of pairing on a C_{60} molecule, we found that most, but not all, of the high-energy phonons are pair breaking. Note that local d-wave character may or may not imply that the global order has d-wave symmetry —

for instance, we have found[7,8] that the superconducting order in electron-doped C_{60} is globally s wave.

In the second place, the strong electron-phonon interaction, presumably responsible for high T_c, is always accompanied by self-trapping or bipolaron formation. The result is a large exponential Frank-Condon reduction of the energy scale for coherent motion of charge, inevitably leading to an insulating state.

In the weak-coupling limit, the usual BCS result applies with an exponentially small pairing scale, and the retarded nature of the electron-phonon coupling plays an essential role — the Coulomb interaction between electrons is reduced due to the fact that they do not have to be at the same place at the same time. However, in the cuprates and even more clearly in doped C_{60}, the phonon frequencies are comparable to the electron bandwidth, so retardation does not lead[42] to any reduction of μ^*.

B. Superconductivity in the polyacenes

Superconductivity has been recently discovered in a surface layer of electrostatically doped crystals of anthracene, tetracene, and pentacene.[14] These molecules can be viewed as segments of a two-leg ladder with every other rung weakened. Thus, we believe that the basic mechanism of superconducting pairing is the same as the one discussed previously for the two-leg t-J and Hubbard ladders. As a consequence, we are led to expect that the superconducting order will have a d-wave-like symmetry, the order parameter changing sign under 90° rotation. However, because of the quasi-one-dimensional geometry, it is possible that there are no gapless "nodal" quasiparticles in this system, despite this.[43]

We note that a number of features of the experiment are consistent with this suggestion. In the first place, T_c is maximal when there is approximately an odd number of electrons per molecule. Moreover, the fact that the optimal T_c decreases with increasing size of the molecule is consistent with a mesoscopic origin of the pairing.

C. C_{60}

Narrow bands in C_{60} make superconductivity at high temperatures (presently 52 K) difficult unless the molecule itself is in some sense superconducting. The same difficulty holds for all narrow-band materials[44] for the following reasons.

First, the net interaction at $\omega = 0$ must be repulsive; otherwise, we will get a CDW—that is, the interaction is

$$V_{\text{eff}}(q,\omega) = \frac{4\pi e^2}{q^2 \epsilon(q,\omega)}, \quad \epsilon(q,\omega=0) > 0. \quad (17)$$

Typically, a peaked density of states implies that only a single band is relevant, corresponding precisely to the band in which the peak in the density of states is situated. Thus, if only one band is relevant, no local field effects are possible, and the ions will see the same ϵ as the electrons.

The second reason is that the retardation of the electron-phonon interaction in BCS superconductors (which is so crucial for the existence of a net electron-electron attraction

through the reduction of the Coulomb pseudopotential) is no longer operative. This is because the Coulomb pseudopotential μ^* is given by

$$\mu^* = \frac{\mu}{1 + \mu \ln(W/\omega_0)}, \qquad (18)$$

where μ is the Coulomb matrix element at the bare high-energy scale, W is the bandwidth, and ω_0 is the typical phonon scale. But if W is not much larger than ω_0, which is manifestly the case in C_{60}, we get little reduction in μ^*.

In contrast, in a molecular crystal, the existence of a structure at an intermediate scale implies atomic energy scales much larger than intramolecular-energy scales, which in turn are larger than the intermolecular scales of the solid. This clear separation of scales allows us to solve first the problem of a single C_{60} molecule alone and then incorporate the coupling between the molecules. This approach leads to the by-now well-substantiated phenomenon of attraction from repulsion that has been the cornerstone of our approach. Even issues concerning the proper screening of the longer-range pieces of the Coulomb interaction can be reliably analyzed,[33] taking advantage of this hierarchy of energy scales.

We conclude with a few observations regarding the present experiments[12,13] on C_{60} field effect transistors (FET's). It is clear that a high density of states cannot be the principal feature responsible for the high-temperature superconductivity in hole-doped C_{60} as T_c is clearly not peaked at the same charge per molecule as the density of states. Moreover, the T_c profile as a function of doping does not presently have any natural explanation in the electron-phonon theory of a BCS superconductor; there appears to be no reason for the electron-phonon coupling to show such a strong dependence on the band filling. In the electron-doped case,[12] the onset of superconductivity is very sharp. This is consistent with our theory in which T_c is highest at a doping corresponding to an odd number of added electrons or holes, where the pair binding on a single molecule is largest, but then vanishes for doping corresponding to an even number of added electrons or holes.[8] A crude model is shown in Fig. 5. Of course, sample inhomogeneity and disorder can broaden the doping profile, which one should be able to better address in the near future as the sample quality improves further. Moreover, relatively *low-temperature tails* in T_c vs x could result from residual electron-phonon interactions.

If the explanation of superconductivity lies in the electronic correlation effects on the mesoscopic scale, there is no reason why T_c could not be raised further (>52 K) in the near future. Such high values of T_c will constitute a strong argument against the electron-phonon mechanism of superconductivity in these materials.

APPENDIX: PERTURBATION THEORY FOR A HUBBARD CHAIN

First-order perturbation theory leads to the conclusion, which turns out to be exact[45] for all U/t, that for $N = 4n$, the ground state is a spin singlet for $Q = 0$ and $Q = \pm 2$ and a doublet for $Q = \pm 1$, while for $N = 4n+2$ the ground state is a singlet for $Q = 0$, a doublet for $Q = \pm 1$, and a triplet for $Q = \pm 2$. As a consequence,

$$E_p(0) = \frac{A_2(N)}{N} \frac{U^2}{t} + \mathcal{O}(U^4/t^3), \qquad (A1)$$

where A_2, a number of order unity, is positive for $N = 4n$ and negative for $N = 4n+2$, reflecting the difference in spin of the doubly charged state.

For $N = 4n+2$ and $U = 0$, the ground state with $Q = 0$ is a unique spin singlet with a gap; for $Q = \pm 1$, the ground state is still unique up to symmetry — it has spin 1/2 and nonzero crystal momentum; however, for $Q = \pm 2$, there are three singlet and one spin-triplet states that are degenerate. In first order in U/t, the degeneracy of the doubly charged system is lifted and, as required by Hund's rule, the spin-1 state is selected as the ground state. In the Hubbard model, there is no direct interaction between electrons of like spin, so a consequence of the triplet character of the doubly charged state is that there is no first-order contribution to the pair-binding energy. However, mainly because of the unfavorable ferromagnetic correlations in the doubly charged state, it turns out that $A_2(4n+2)$ is negative — there is pair repulsion.

For $N = 4n$, there are two degenerate orbitals at the Fermi level of the noninteracting neutral molecule resulting in accidental degeneracies. To first order in U/t, the energies of two of the singlet states of the neutral molecule are elevated, but one singlet state remains degenerate with the triplet state. This miracle is due to an umklapp process which allows a singlet pair of electrons, each with crystal momentum $\pi/2$, to scatter into the state in which each electron has crystal momentum $-\pi/2$. The final degeneracy for $Q = 0$ is then lifted in second-order perturbation theory, in which the antiferromagnetic correlations of the singlet state are preferred over the ferromagnetic (triplet) state. This violation of Hund's rule is peculiar to the case of $N = 4n$ and $Q = 0$. By the same token, the antiferromagnetic correlations of the neutral molecule lead to anomalous stability of the neutral state and, hence, a negative $A_2(4n)$ — there is pair binding. It is worth noting that, although for large U/t the perturbative results are, of course, quantitatively poor, as there are[45] no ground-state level crossings as a function of U/t, perturbation theory gives correct results for the ground-state quantum numbers of all these states.

[1] J. G. Bednorz and K. A. Müller, Z. Phys. B **64**, 189 (1986).

[2] P. W. Anderson, Science **235**, 1196 (1987).

[3] S. A. Kivelson, D. S. Rokhsar, and J. P. Sethna, Phys. Rev. B **35**, 8865 (1987).

[4] R. B. Laughlin, Phys. Rev. Lett. **60**, 2677 (1988).

[5] S. Chakravarty, B. I. Halperin, and D. Nelson, Phys. Rev. Lett. **60**, 1057 (1988); Phys. Rev. B **39**, 2344 (1989).

[6] A. F. Hebard *et al.*, Nature (London) **350**, 360 (1991).

[7] S. Chakravarty and S. Kivelson, Europhys. Lett. **16**, 751 (1991).

[8] S. Chakravarty, M. Gelfand, and S. Kivelson, Science **254**, 970 (1991).

[9] G. Baskaran and E. Tosatti, Curr. Sci. **61**, 33 (1991).

[10] V. J. Emery and S. A. Kivelson, Physica C **209**, 597 (1993); S. A. Kivelson and V. J. Emery, in *Strongly Correlated Electronic Materials: The Los Alamos Symposium 1993*, edited by K. S. Bedell *et al.* (Addison Wesley, Reading, MA, 1994), p. 619.

[11] V. J. Emery, S. A. Kivelson, and O. Zachar, Phys. Rev. B **56**, 6120 (1997).

[12] J. H. Schön, Ch. Kloc, R. C. Haddon, and B. Batlogg, Science **288**, 656 (2000).

[13] J. H. Schön, Ch. Kloc, and B. Batlogg, Nature (London) **408**, 549 (2000).

[14] J. H. Schön, Ch. Kloc, and B. Batlogg, Nature (London) **406**, 702 (2000).

[15] S. Kivelson, E. Fradkin, and V. Emery, Nature (London) **393**, 550 (1998).

[16] S. Chakravarty, R. B. Laughlin, D. K. Morr, and C. Nayak, Phys. Rev. B **63**, 094503 (2001).

[17] R. M. Fye, M. J. Martins, and R. T. Scalettar, Phys. Rev. B **42**, 6809 (1990).

[18] S. Chakravarty, L. Chayes, and S. Kivelson, Lett. Math. Phys. **23**, 265 (1991).

[19] See V. J. Emery, in *Highly Conducting 1D Solids*, edited by J. T. Devreese *et al.* (Plenum, New York, 1979).

[20] F. Woynarovic, J. Phys. A **22**, 4243 (1989).

[21] H. Frahm and V. E. Korepin, Phys. Rev. B **42**, 10 553 (1990).

[22] I. Affleck, J. Phys. A **31**, 4573 (1998).

[23] S. R. White *et al.*, Phys. Rev. Lett. **73**, 886 (1994).

[24] S. Chakravarty, Phys. Rev. Lett. **77**, 4446 (1996).

[25] E. Jeckelmann *et al.*, Phys. Rev. B **58**, 9492 (1998).

[26] S. R. White and D. J. Scalapino, Phys. Rev. B **57**, 3031 (1998).

[27] H.-H. Lin, L. Balents, and M. P. A. Fisher, Phys. Rev. B **56**, 6569 (1997); L. Balents and M. P. A. Fisher, *ibid.* **53**, 12 133 (1996).

[28] V. J. Emery, S. A. Kivelson, and O. Zachar, Phys. Rev. B **59**, 15 641 (1999).

[29] R. M. Noack *et al.*, Phys. Rev. B **56**, 7162 (1997).

[30] S. R. White, S. Chakravarty, M. P. Gelfand, and S. Kivelson, Phys. Rev. B **45**, 5062 (1992).

[31] A. Auerbach and G. Murthy, Europhys. Lett. **19**, 103 (1992); G. Murthy and A. Auerbach, Phys. Rev. B **46**, 331 (1992); T. Tokuyasu, M. Kamal, and G. Murthy, Phys. Rev. Lett. **71**, 4202 (1993); N. Berdenis and G. Murthy, Phys. Rev. B **52**, 3083 (1995).

[32] C. Gazza, G. B. Martins, J. Riera, and E. Dagotto, Phys. Rev. B **59**, R709 (1998).

[33] P. E. Lammert, D. S. Rokhsar, S. Chakravarty, and S. Kivelson, Phys. Rev. Lett. **74**, 996 (1995).

[34] M. Boninsegni and E. Manousakis, Phys. Rev. B **47**, 11 897 (1993).

[35] R. Moessner and S. L. Sondhi, Phys. Rev. Lett. **86**, 1881 (2001).

[36] A. Auerbach, Phys. Rev. Lett. **72**, 2931 (1994).

[37] For a review, see C. Bourbonnais, and L. G. Caron, Int. J. Mod. Phys. B **5**, 1033 (1991).

[38] V. J. Emery, E. Fradkin, S. A. Kivelson, and T. Lubensky, Phys. Rev. Lett. **85**, 2160 (2000).

[39] A. F. Hebard *et al.*, Phys. Rev. B **48**, 9945 (1993).

[40] S. Chakravarty, S. A. Kivelson, M. I. Salkola, and S. Tewari, Science **256**, 1306 (1992).

[41] M. Salkola, S. Chakravarty, and S. Kivelson, Int. J. Mod. Phys. B **7**, 2859 (1993).

[42] S. Chakravarty, S. Khlebnikov, and S. A. Kivelson, Phys. Rev. Lett. **69**, 212 (1992).

[43] M. Granath, V. Oganesyan, S. A. Kivelson, E. Fradkin, and V. J. Emery, cond-mat/0010350 (unpublished).

[44] These arguments are essentially due to P. W. Anderson; see also, Ref. 42.

[45] M. Ogata and H. Shiba, Phys. Rev. B **41**, 2326 (1990).