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Phonon-mediated attraction between large bipolarons: Condensation to a liquid

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The self-trapped carriers of large (multisite) bipolarons redistribute themselves among the sites of their molecular orbitals as their self-trapping potential wells are altered by changing atomic positions. Through this polarizability, large bipolarons reduce the phonon frequencies. The dependence of the lowering of the zero-point vibrational energy on the spatial distribution of large bipolarons produces an intermediate-ranged phonon-mediated attraction between large bipolarons that is comparable to a phonon energy. Coulomb repulsions that oppose the phonon-mediated attractions tend to be suppressed by the large static dielectric constants associated with large-bipolaron formation. However, a strong short-range repulsion between bipolarons, analogous to the hard-core repulsion between helium atoms, persists. With the dominance of the medium-range phonon-mediated attraction and the short-range repulsion, large bipolarons can condense into a liquid. The bipolaronic liquid might be the condensed fluid phase that has been suggested as a precursor to superconductivity in cuprates.

I. INTRODUCTION

In multidimensional electronic systems two distinct types of polaronic state can form.[1,2] A large polaron can form when the electron-lattice interactions due to the long-range Coulombic interactions between an electronic carrier and a solid's ions are of paramount importance. Competing effects then determine a radius that generally exceeds an interatomic separation.[1-3] Because such self-trapped states extend over multiple sites, the self-trapped carrier can continuously adjust to alterations of the atomic positions and thereby move "coherently."

By contrast, a small polaron typically forms when a short-range electron-lattice interaction, such as the deformation-potential interaction, is dominant.[1,2,4] Then the small-polaron's self-trapped carrier shrinks without limit until it is confined to a single site. As a result of this severe confinement, "coherent" small-polaronic motion is generally suppressed. Small-polaronic motion then proceeds by a succession of "incoherent events," thermally assisted hops.

If the electron-lattice interaction is sufficiently strong, carriers can form bipolarons. Then the increased polaronic binding that occurs when two carriers occupy a common site exceeds these carriers' Coulomb repulsion. The existence of a large-bipolaronic bound state requires that $\varepsilon_0 > 2\varepsilon_\infty$, where ε_0 and ε_∞ are the static and optical dielectric constants, respectively.[5] The energy of this large bipolaron exceeds the energy of two separated large polarons by at most the Coulomb energy $e^2/\varepsilon_0 R$, where R is the radius of the hydrogenic self-trapped state. Stabilization of a large bipolaron with respect to separation into two separate large polarons can occur with the addition of only a modest short-range electron-lattice interaction.[5] Since unusually large values of $\varepsilon_0/\varepsilon_\infty$ characterize the insulating parents of oxide superconductors, one is led to consider the possibility that charge carriers added to them are bipolaronic.[6]

Evidence suggestive of polaronic carriers in cuprate semiconductors and superconductors has been found. Carrier-induced infrared-absorption bands expected of polaronic carriers are reported in cuprate semiconductors and superconductors.[7-10] Polaronic absorption bands arise from exciting carriers from the self-trapping potential well within which they are bound. The shapes and temperature dependences of polaronic absorption bands distinguishes between those of large- and small-polaronic carriers.[11] The temperature-independent asymmetric shapes of these carrier-induced absorption bands are similar to expectations of large-polaronic carriers.[11] In addition, neutron-diffraction experiments find that doping introduces dynamic regions of displaced atoms that are consistent with the presence of large-polaronic carriers.[12]

Indications that the carriers in the cuprates are singlet pairs also exist. The independence of the Seebeck coefficient of an applied magnetic field implies that the carriers have no spin degree of freedom.[13] In addition, carriers in doped La_2CuO_4 induce a structural transformation to a tetragonal insulating state (with a square geometry in the CuO_2 layers) when there is $\frac{1}{8}$ hole per unit cell.[14,15] This result is consistent with bipolaronic carriers condensing into a state commensurate with the lattice geometry. In this view, there is one bipolaron for each 4×4 superlattice unit, $\frac{1}{8}=2/4^2$.

Changes in the atomic vibrational motions indicating collective behavior are observed with the onset of superconductivity in cuprate superconductors.[12,16,17] Since superconductivity is generally understood to be a cooperative property of carriers, these changes in the vibrational motions suggest collective polaronic effects. To address superconductivity of bipolarons one must consider the interactions between them. Recent intriguing reports argue that carriers in cuprates coalesce into a condensed fluid state prior to their manifesting superconductivity.[18,19] This finding, implies an attraction between carriers.

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Here interactions between bipolarons are considered. Consistent with the carriers being self-trapped, interactions between bipolarons are treated within the adiabatic approach. That is, the electronic carriers are presumed to adjust to the instantaneous atomic positions.

There are several different interactions between bipolarons. Of course, bipolarons repel one another through their Coulomb interaction. However, the Coulomb repulsion between them is reduced by the static dielectric constant. An additional repulsion arises because singlet bipolarons are stable against coalescing to form "grander" polarons since the Pauli principle forces additional carriers to occupy excited states of the self-trapping well.[20] This effect produces a short-range repulsion between bipolarons analogous to the hard-core repulsion between helium atoms.

Another interaction between bipolarons arises because the adjusting of self-trapped carriers to changing atomic positions lowers a solid's vibrational frequencies.[21] The dependence of a solid's vibrational energy on the relative positions of large bipolarons is herein shown to constitute a (phonon-mediated) medium-range *attraction* between them. Through this attraction a gas of large bipolarons can condense into a liquid.

This paper is organized as follows. The adiabatic formalism is introduced in Sec. II. The repulsive interactions between bipolarons are also described in this section. In Sec. III the effect of bipolarons on the vibrational frequencies is addressed. In Sec. IV the dependence of the lowering of the zero-point vibrational energy on the spatial distribution of large bipolarons is considered. This dependence results in a phonon-mediated attraction between large bipolarons. The phase diagram for the condensation of large bipolarons into a liquid is discussed in Sec. V. The possible relationship between the formation of a large-bipolaronic liquid and superconductivity is discussed in Sec. VI. The primary arguments of the paper are summarized in Sec. VII.

II. ADIABATIC ENERGY OF *n* BIPOLARONS

To begin, consider the formation of a large polaron. Within the adiabatic approach the potential energy for atomic motion is the sum of the potential energy arising from direct interactions between atoms, V_S, and the carrier's electronic energy, itself a function of atomic positions, E_{el}. Beyond the electronic kinetic energy, a carrier's electron energy contains the potential energy resulting from the electron-lattice interaction:

$$E_{el}=\int d\mathbf{r}\frac{\hbar^2|\nabla\Psi|^2}{2m}+\int d\mathbf{r}|\Psi|^2V(\mathbf{r}) \ . \tag{1}$$

Here $V(\mathbf{r})$ denotes the potential experienced by an electronic carrier at position $\mathbf{r}$ as a result of atomic displacements. Modeling atomic displacements centered at position $\mathbf{u}$ by the scalar parameter $\Delta(\mathbf{u})$ yields:[2]

$$V(\mathbf{r})\equiv\int d\mathbf{u}\, Z(\mathbf{r}-\mathbf{u})\Delta(\mathbf{u}) \ , \tag{2}$$

where $Z(\mathbf{r}-\mathbf{u})$ describes the electron-lattice interaction. The strain energy resulting from direct interatomic interactions is $V_S\equiv S\int d\mathbf{u}\,\Delta^2(\mathbf{u})/2$, where $S\equiv k/a^3$ is the stiffness constant k per unit volume and a is the lattice constant.

The first and second derivatives of $\varepsilon(\mathbf{u})\equiv E_{el}+V_S$ with respect to variations of $\Delta(\mathbf{u})$ are

$$\frac{\partial\varepsilon(\mathbf{u})}{\partial\Delta(\mathbf{u})}=S\Delta(\mathbf{u})+\int d\mathbf{r}|\Psi|^2Z(\mathbf{r}-\mathbf{u}) \ , \tag{3}$$

and

$$\frac{\partial^2\varepsilon(\mathbf{u})}{\partial\Delta(u)\partial\Delta(\mathbf{u}')}=S\delta(\mathbf{u}-\mathbf{u}')+\int d\mathbf{r}\frac{\partial|\Psi|^2}{\partial\Delta(\mathbf{u}')}Z(\mathbf{r}-\mathbf{u}) \ . \tag{4}$$

In obtaining these results the normalization of $|\Psi|^2$ is used to eliminate derivatives of the electronic wave function with respect to $\Delta(\mathbf{u})$ from Eq. (3).

The carrier-induced shifts of the equilibrium dilations from $\Delta(\mathbf{u})=0$ to $\Delta(\mathbf{u})=\Delta_0(\mathbf{u})$ are determined by setting the right-hand side of Eq. (3) to zero. When atoms are constrained to these equilibrium positions, the energy of the system is lowered by $E_p\equiv -S\int d\mathbf{u}[\Delta_0(\mathbf{u})]^2/2$.[2] As described by Eq. (4), the carrier's presence also shifts the stiffness constant from its carrier-free value S. Thus, the adiabatic Hamiltonian may be written as $H_{ad}=E_0+T_L+V_L$, where E_0 is the system's energy when the atoms are at the equilibrium they assume in the presence of charge carriers. Vibrations of the atoms about these positions are described by the sum of the atomic kinetic energy, T_L, and quadratic displacements of the adiabatic potential from these equilibrium positions, V_L.

In Ref. (5) the energy minima E_0 associated with polaron and bipolaron formation were studied. The analysis of Ref. (5) can be readily generalized to obtain E_0 when there are multiple large bipolarons that interact with one another. For a system of n large bipolarons that each have a binding energy of E_{bi}:

$$E_0=-nE_{bi}+\tfrac{1}{2}\int d\mathbf{r}\,\rho(\mathbf{r})\int d\mathbf{s}[\rho(\mathbf{r}+\mathbf{s})-\delta(\mathbf{s})]\varepsilon_R(\mathbf{s}) \ , \tag{5}$$

where $\rho(\mathbf{r})$ is the density of bipolarons centered at the position $\mathbf{r}$ and $\varepsilon_R(\mathbf{s})$ is the interaction energy of two bipolarons separated by the distance $\mathbf{s}$. For n particles there are n single-particle and $n(n-1)/2$ distinct two-particle contributions to the energy of Eq. (5). The delta function in Eq. (5) eliminates counting a particle's interaction with itself.

The prime interactions are repulsions described by

$$\varepsilon_R(\mathbf{s})\equiv(2e)^2/\varepsilon_0(|\mathbf{s}|+R)+C_1E_p\exp(-C_2|\mathbf{s}|/R) \ , \tag{6}$$

where C_1 and C_2 are numerical constants. The first of the terms in Eq. (6) represents the Coulomb interactions between bipolarons of radius R. Since the carriers adiabatically follow the atomic motion, the Coulomb interactions between bipolarons are reduced by the static dielectric constant.[5] This repulsion becomes the dominant term in Eq. (6) at sufficiently large separations, $|\mathbf{s}|\gg R$. Then, this Coulomb repulsion approaches that of static point charges separated by $\mathbf{s}$. The exceptionally large static dielectric constant required for bipolaron formation also tends to suppress the long-range Coulomb repulsions between bipolarons.[5]

The second term in Eq. (6) describes the repulsion between large bipolarons that occurs when the wave functions of the self-trapped carriers of different large bipolarons overlap one another. This repulsion occurs because the Pauli principle forces two of the four electronic carriers of two bipolarons into excited electronic states of the self-trapping potential well as two bipolarons are brought together. This short-range repulsion occurs for large bipolarons but not for large polarons. Thus, even though large polarons may find it energetically favorable to merge into large bipolarons, large bipolarons are presumed not to coalesce into grander polarons such as quadpolarons.

As detailed in Appendix A, if the self-trapped electronic states of a large bipolaron are hydrogenic, the electronic energy is $-3E_p$ and the energy from the ground state to the first excited state is three-quarters of $3E_p$. Then, when $\mathbf{s}=0$ the repulsive energy is $\approx 9E_p/4$; that is, $C_1 \approx \frac{9}{4}$ in Eq. (6). As in the case of the repulsion between helium atoms, the repulsion depends exponentially on electronic overlap between different large bipolarons. This repulsive interaction is one reason why large bipolarons are destabilized if they are packed in too high a density. In addition, beyond a critical density neither large polarons nor large bipolarons can form since the atomic displacements required for the self-trapping of different carriers interfere with one another.

III. INTERACTION OF LARGE-BIPOLARONS' POLARIZABILITY WITH PHONONS

The carrier-induced change of the stiffness tensor, the second term contained on the right-hand side of Eq. (4), is now studied. Calculating this term requires considering the derivative of the electronic probability with respect to atomic displacements: $\partial|\Psi|^2/\partial\Delta(\mathbf{u}')=\Psi^*\partial\Psi/\partial\Delta(\mathbf{u}')+\Psi\partial\Psi^*/\partial\Delta(\mathbf{u}')$. To evaluate this factor, the wave function of a self-trapped carrier is expanded about its value when the atomic displacement pattern is an equilibrium configuration, $\Delta(\mathbf{u})=\Delta_0(\mathbf{u})$. For ease of notation of bra and ket notation is adopted in which the electronic ground state corresponding to a polaron's atomic equilibrium configuration is denoted as $|\mathbf{g},0\rangle$ where the position vector $\mathbf{g}$ designates the centroid of the self-trapped state. The excited electronic states for this potential are labeled by the index n and are denoted by $|\mathbf{g},n\rangle$. As the dilation changes by $\delta\Delta(\mathbf{u}')$ from $\Delta_0(\mathbf{u})$, the electronic wave function is altered. To lowest order the perturbed electronic wave function may be expressed as a superposition of the $|\mathbf{g},n\rangle$:

$$\delta\Psi=-\delta\Delta(\mathbf{u}')\frac{\sum\limits_{n\neq 0}|\mathbf{g},n\rangle\langle\mathbf{g},n|Z(\mathbf{r}-\mathbf{u}')|\mathbf{g},0\rangle}{(E_n-E_0)}\ , \tag{7}$$

where the matrix element represents an integration over the electronic position coordinate contained within it, $\mathbf{r}$. Thus, to lowest nonvanishing order in the deviations of the atomic displacement pattern from equilibrium,

$$\begin{aligned}\int d\mathbf{r}\frac{\partial|\Psi|^2}{\partial\Delta(\mathbf{u}')}Z(\mathbf{r}-\mathbf{u})\\ =-2\frac{\sum\limits_{n\neq 0}\langle\mathbf{g},0|Z(\mathbf{r}-\mathbf{u})|\mathbf{g},n\rangle\langle\mathbf{g},n|Z(\mathbf{r}-\mathbf{u}')|\mathbf{g},0\rangle}{(E_n-E_0)}\ .\end{aligned} \tag{8}$$

The electron-lattice interaction function that appears within the matrix elements of Eq. (8) is now expanded about its value at the polaron's centroid, $\mathbf{g}$: $Z(\mathbf{r}-\mathbf{u})\approx\partial Z(\mathbf{g}-\mathbf{u})/\partial\mathbf{g}\cdot(\mathbf{r}-\mathbf{g})$. With this approximation the tensor of Eq. (8) becomes

$$\begin{aligned}\int d\mathbf{r}\frac{\partial|\Psi|^2}{\partial\Delta(\mathbf{u}')}Z(\mathbf{r}-\mathbf{u})\\ =-2P_{\mathbf{g}}[\partial Z(\mathbf{g}-\mathbf{u})/\partial\mathbf{g}][\partial Z(\mathbf{g}-\mathbf{u}')/\partial\mathbf{g}]\ ,\end{aligned} \tag{9}$$

where the polarizability of a self-trapped carrier centered at $\mathbf{g}$ is defined by

$$P_{\mathbf{g}}\equiv\frac{\sum\limits_{n\neq 0}\langle\mathbf{g},0|(\mathbf{r}-\mathbf{g})|\mathbf{g},n\rangle\langle\mathbf{g},n|(\mathbf{r}-\mathbf{g})|\mathbf{g},0\rangle}{(E_n-E_0)}\ . \tag{10}$$

For polarons that are equivalent to one another the subscript denoting the polaron's position may be dropped, $P_{\mathbf{g}}=P$.

This polarizability arises from the redistribution of the self-trapped charge among different sites of the polaron's molecular orbital. A large polaron's polarizability is essentially the square of the radius of the self-trapped carrier divided by its binding energy, $\approx 3E_p$ for a large polaron.[11] For a single-site (small) polaron $P=0$, since the self-trapped charge is restricted to a single site. In recognition of a large bipolaron's containing two self-trapped carriers, its polarizability is denoted as $2P$.

For a collection of n large bipolarons, the carrier-induced softening term in Eq. (8) is summed over the site index $\mathbf{g}$ that denotes the centroids of the bipolarons. The potential energy produced by shifting the atoms from their equilibrium values by $d(\mathbf{u})\equiv\Delta(\mathbf{u})-\Delta_0(\mathbf{u})$ is then $V_L\equiv S\int d\mathbf{u}\, d^2(\mathbf{u})/2+V_{\text{pol}}$, where

$$\begin{aligned}V_{\text{pol}}&\equiv-2P\sum_{\mathbf{g}}\int d\mathbf{u}\int d\mathbf{u}'[\partial Z(\mathbf{g}-\mathbf{u})/\partial\mathbf{g}]\cdot[\partial Z(\mathbf{g}-\mathbf{u}')/\partial\mathbf{g}]d(\mathbf{u})d(\mathbf{u}')\\ &=-2P\sum_{\mathbf{g}}\int d\mathbf{u}\int d\mathbf{u}'[\partial Z(\mathbf{g}-\mathbf{u})/\partial\mathbf{u}]\cdot[\partial Z(\mathbf{g}-\mathbf{u}')/\partial\mathbf{u}']d(\mathbf{u})d(\mathbf{u}')\\ &=-2P\sum_{\mathbf{g}}\int d\mathbf{u}\int d\mathbf{u}'Z(\mathbf{g}-\mathbf{u})Z(\mathbf{g}-\mathbf{u}')[\partial d(\mathbf{u})/\partial\mathbf{u}]\cdot[\partial d(\mathbf{u}')/\partial\mathbf{u}']\ .\end{aligned} \tag{11}$$

The third equality of Eq. (11) follows an integration by parts.

The atomic displacement parameters are now expressed in terms of phonons through the transformation

$$d(\mathbf{u})=\sum_{\mathbf{q}}\sqrt{\hbar/2MN\omega_{\mathbf{q}}}[e^{i\mathbf{q}\cdot\mathbf{u}}b_{\mathbf{q}}+e^{-i\mathbf{q}\cdot\mathbf{u}}(b_{\mathbf{q}})^*] \ . \tag{12}$$

where $b_{\mathbf{q}}$ and $(b_{\mathbf{q}})^*$ are the operators that respectively destroy and create phonons of wavevector **q** and frequency $\omega_{\mathbf{q}}$. These are the solid's phonons prior to consideration of carrier-induced changes of the stiffness. M and N represent the reduced atomic mass appropriate to the vibrations and the number of unit cells in the solid, respectively. Introducing Eq. (12) into Eq. (11) then yields

$$V_{\text{pol}}=-PN^{-1}\sum_{\mathbf{q}}\sum_{\mathbf{q}'}B(\mathbf{q})B(\mathbf{q}')\cos\theta_{\mathbf{q},\mathbf{q}'}\{[n_{\mathbf{q}-\mathbf{q}'}b_{\mathbf{q}}(b_{\mathbf{q}'})^*+n_{-\mathbf{q}+\mathbf{q}'}(b_{\mathbf{q}})^*b_{\mathbf{q}'}]-[n_{\mathbf{q}+\mathbf{q}'}b_{\mathbf{q}}b_{\mathbf{q}'}+n_{-\mathbf{q}-\mathbf{q}'}(b_{\mathbf{q}})^*(b_{\mathbf{q}'})^*]\} \ , \tag{13}$$

where

$$B(\mathbf{q})\equiv q\sqrt{\hbar/M\omega_{\mathbf{q}}}A(\mathbf{q}) \ . \tag{14}$$

Here $q\equiv|\mathbf{q}|$, $\cos\theta_{\mathbf{q},\mathbf{q}'}$ is the cosine of the angle between **q** and **q**′, and

$$n_{\mathbf{k}}\equiv\sum_{\mathbf{g}}e^{i\mathbf{k}\cdot\mathbf{g}}=\int d\mathbf{r}\,e^{i\mathbf{k}\cdot\mathbf{r}}\sum_{\mathbf{g}}\delta(\mathbf{r}-\mathbf{g})$$
$$=\int d\mathbf{r}\,e^{i\mathbf{k}\cdot\mathbf{r}}\rho(\mathbf{r}) \ , \tag{15}$$

is the Fourier transform of the carrier density $\rho(\mathbf{r})$. The number of bipolarons is $n_0\equiv n$. Since polarons are primarily polarized by phonons for which $qR<1$,[22] the **q** summations should only be carried out up to a maximum value $\approx 1/R$.

The range of the electron-lattice interaction determines the **q** dependence of $A(\mathbf{q})\equiv\int d\mathbf{v}\,Z(\mathbf{v})\cos(\mathbf{q}\cdot\mathbf{v})$, where $A(\mathbf{q})=A(-\mathbf{q})$ since $Z(\mathbf{v})=Z(-\mathbf{v})$. $A(\mathbf{q})$ and $B(\mathbf{q})$ are generally the sum of contributions since $Z(\mathbf{r}-\mathbf{u})$ is the sum of contributions.

The Coulomb interactions of a carrier with the ions of an ionic solid produce the long-range Fröhlich interaction: $Z(\mathbf{r}-\mathbf{u})=(\beta e^2k/a^3\pi^3)^{1/2}/|\mathbf{r}-\mathbf{u}|^2$, where a is the lattice constant and $\beta\equiv 1/\varepsilon_\infty-1/\varepsilon_0$ with ε_∞ and ε_0 being the optical and static dielectric constants, respectively.[23] The transform of this interaction is $A(\mathbf{q})\equiv 2(\beta e^2k\pi/a^3)^{1/2}/q$.[23] Hence, for the long-range interaction with optic phonons $B(\mathbf{q})$ is independent of **q**, apart from the **q** dependence of the vibrational frequencies: $B(\mathbf{q})\equiv 2(\beta e^2\hbar\omega_{\mathbf{q}}\pi/a^3)^{1/2}$. These long-range electron-lattice interactions provide the dominant contribution to the polaronic binding energy when a large polaron or bipolaron forms in a multidimensional electronic system.[1,2,5]

Short-range electron-lattice interactions (the deformation-potential interaction and Holstein interaction) are common to all materials, $Z(\mathbf{r}-\mathbf{u})=A\delta(\mathbf{r}-\mathbf{u})$. The transform of this interaction is $A(\mathbf{q})\equiv A$. Hence, for short-range electron-lattice interactions, $B(\mathbf{q})$, Eq. (14), is explicitly proportional to **q** and also contains the implicit **q** dependence derived from its dependence on $\omega_{\mathbf{q}}$.[5]

Now consider V_{pol} as a perturbation on those carrier-free vibrations for which $qR<1$. The first-order correction to the system's energy is $-nE_{\text{bil}}$, where,

$$E_{\text{bil}}=2PN^{-1}\sum_{\mathbf{q}}B^2(\mathbf{q})[N_{\mathbf{q}}+\tfrac{1}{2}] \ , \tag{16}$$

and $N_{\mathbf{q}}$ is the phonon population of the **q**th vibrational mode. Combined with the vibrational energy of the unperturbed system, E_v, the first-order energy shift has the effect of reducing each phonon's energy from $\hbar\omega_{\mathbf{q}}$ to $\hbar\Omega_{\mathbf{q}}\equiv\hbar\omega_{\mathbf{q}}-2(n/N)PB^2(\mathbf{q})$. That is, $E_v-nE_{\text{bil}}=\sum_{\mathbf{q}}\hbar\Omega_{\mathbf{q}}(N_{\mathbf{q}}+\frac{1}{2})$. Since $P\approx R^2/(\beta e^2/R)$ for a large bipolaron's self-trapped carriers, for the Fröhlich interaction $PB^2(\mathbf{q})$ is proportional to and comparable to $\hbar\omega_{\mathbf{q}}(R/a)^3$. Thus, n bipolarons lower the energy of each long-wavelength phonon by the fraction $(n/N)(R/a)^3$. In other words, the bipolarons produce a perturbatively small effect on the atomic vibrations if the density of bipolarons is small enough so that they do not overlap appreciably with one another: $n/N<(a/R)^3$. Indeed, it is only within this regime that it is even reasonable to speak of bipolarons.

IV. PHONON-MEDIATED ATTRACTION BETWEEN LARGE BIPOLARONS

Phonon-mediated interactions between large bipolarons enter through the second-order correction to the system's energy, E_2. Treating V_{pol}, Eq. (13), as the perturbation yields

$$E_2=-P^2N^{-2}\sum_{\mathbf{q}}B^2(\mathbf{q})\sum_{\mathbf{q}'}B^2(\mathbf{q}')\cos^2\theta_{\mathbf{q},\mathbf{q}'}\left\{\frac{|n_{\mathbf{q}+\mathbf{q}'}|^2(N_{\mathbf{q}}+N_{\mathbf{q}'}+1)(1+\delta_{\mathbf{q},\mathbf{q}'})}{\hbar(\omega_{\mathbf{q}}+\omega_{\mathbf{q}'})}+\frac{|n_{\mathbf{q}-\mathbf{q}'}|^2(N_{\mathbf{q}'}-N_{\mathbf{q}})(1-\delta_{\mathbf{q},\mathbf{q}'})}{\hbar(\omega_{\mathbf{q}}-\omega_{\mathbf{q}'})}\right\} . \tag{17}$$

Kronecker deltas, $\delta_{\mathbf{q},\mathbf{q}'}$, enter into the two terms within the curly brackets of Eq. (17) for two distinct reasons. The Kronecker delta in the first term arises because the net value of the squares of the matrix elements is doubled when $\mathbf{q}=\mathbf{q}'$: $(N_{\mathbf{q}}+1)(N_{\mathbf{q}}+2)-N_{\mathbf{q}}(N_{\mathbf{q}}-1)=2(2N_{\mathbf{q}}+1)$ versus $(N_{\mathbf{q}}+1)(N_{\mathbf{q}'}+1)-N_{\mathbf{q}}N_{\mathbf{q}'}=(N_{\mathbf{q}}+N_{\mathbf{q}'}+1)$. The Kronecker delta enters in the second term in accordance with the prescription of second-order perturbation theory that explicitly excludes contributions to ΔE_2 from matrix elements that are diagonal in the set of phonon occupation numbers, $\{\cdots N_{\mathbf{q}}\cdots\}$. E_2 is proportional to Fourier transforms of the density-density correlation function of the large bipolarons. In particular, for particles labeled by their positions, **g**:

$$\int d\mathbf{s}\cos(\mathbf{k}\cdot\mathbf{s})\int d\mathbf{r}\,\rho(\mathbf{r})\rho(\mathbf{r}+\mathbf{s})$$

$$=\int d\mathbf{s}\cos(\mathbf{k}\cdot\mathbf{s})\int d\mathbf{r}\sum_{\mathbf{g}}\delta(\mathbf{r}-\mathbf{g})\sum_{\mathbf{g}'}\delta(\mathbf{r}+\mathbf{s}-\mathbf{g}')$$

$$=\sum_{\mathbf{g}}\sum_{\mathbf{g}'}\cos[\mathbf{k}\cdot(\mathbf{g}'-\mathbf{g})]=|n_{\mathbf{k}}|^2\ , \qquad (18)$$

where $n_{\mathbf{k}}^{*}=n_{-\mathbf{k}}$.

Expressing the density-density correlation function in real space, Eq. (16) may be rewritten as

$$E_2=-nE_{\mathrm{bi2}}-\tfrac{1}{2}\int d\mathbf{r}\,\rho(\mathbf{r})\int d\mathbf{s}[\rho(\mathbf{r}+\mathbf{s})-\delta(\mathbf{s})]\varepsilon_A(\mathbf{s})\ , \qquad (19)$$

where

$$E_{\mathrm{bi2}}\equiv P^2N^{-2}\sum_{\mathbf{q}}B^2(\mathbf{q})\sum_{\mathbf{q}'}B^2(\mathbf{q}')\cos^2\theta_{\mathbf{q},\mathbf{q}'}F(\mathbf{q},\mathbf{q}')\ , \qquad (20)$$

$$\varepsilon_A(\mathbf{s})\equiv 2P^2N^{-2}\sum_{\mathbf{q}}B^2(\mathbf{q})\sum_{\mathbf{q}'}B^2(\mathbf{q}')\cos^2\theta_{\mathbf{q},\mathbf{q}'}\times\cos[(\mathbf{q}-\mathbf{q}')\cdot\mathbf{s}]F(\mathbf{q},\mathbf{q}')\ , \qquad (21)$$

and

$$F(\mathbf{q},\mathbf{q}')\equiv\frac{(1+\delta_{\mathbf{q},-\mathbf{q}'})}{\hbar(\omega_{\mathbf{q}}+\omega_{\mathbf{q}'})}+2N_{\mathbf{q}}\left[\frac{(1+\delta_{\mathbf{q},-\mathbf{q}'})}{\hbar(\omega_{\mathbf{q}}+\omega_{\mathbf{q}'})}-\frac{(1-\delta_{\mathbf{q},\mathbf{q}'})}{\hbar(\omega_{\mathbf{q}}-\omega_{\mathbf{q}'})}\right]\ . \qquad (22)$$

In the algebraic manipulations that were performed to obtain Eqs. (19)–(22), use was made of the equivalence of the summations over **q** and **q**′ in Eq. (17). In addition, the argument of the **q**′ summation was first converted from **q**′ to −**q**′ and then it was noted that $B^2(-\mathbf{q}')=B^2(\mathbf{q}')$ and $\omega_{-\mathbf{q}'}=\omega_{\mathbf{q}'}$. The total bipolaronic energy is found by combining the zeroth-order, first-order, and second-order contributions to the bipolarons' energy, Eqs. (5), (16), and (19), respectively:

$$E_T=-n(E_{\mathrm{bi}}+E_{\mathrm{bi1}}+E_{\mathrm{bi2}})+\tfrac{1}{2}\int d\mathbf{r}\,\rho(\mathbf{r})\int d\mathbf{s}[\rho(\mathbf{r}+\mathbf{s})-\delta(\mathbf{s})][\varepsilon_R(\mathbf{s})-\varepsilon_A(\mathbf{s})]\ . \qquad (23)$$

The magnitude and range of the phonon-mediated attraction $\varepsilon_A(\mathbf{s})$ is now investigated. Consider the Fröhlich interaction between charge carriers and optic modes, since the interaction must dominate the energetics if a large bipolaron is to form.[5] Then, as modeled below Eq. (15), the explicit **q** dependence of $B(\mathbf{q})$ vanishes for $qR<1$ and $B(\mathbf{q})$ itself vanishes for $qR>1$. To consider the ground state, take $N_{\mathbf{q}}=0$ for all **q**. Then, ignoring the dispersion of the optic phonon modes, $\omega_{\mathbf{g}}=\omega_0$, Eq. (20) is approximated by

$$\varepsilon_A(\mathbf{s})/(P^2B^4/\hbar\omega_0)\approx\left[\frac{3}{(q_0s)^3}\int_0^{s/R}du\,u\sin u\right]^2+(2/N)\frac{3}{(2q_0s)^3}\int_0^{2s/R}du\,u\sin u$$

$$\approx\left\{\frac{3}{(q_0s)^3}[\sin(s/R)-(s/R)\cos(s/R)]\right\}^2\ , \qquad (24)$$

where $B\equiv B(0)$, the **q** and **q**′ summations have been converted into integrals that extend over a Debye radius q_0, and the factor $\cos^2\theta_{\mathbf{q},\mathbf{q}'}$ has been approximated by unity for simplicity. In the second line of Eq. (24) the second term, that comes from the $\delta_{\mathbf{q},-\mathbf{q}'}$ in $F(\mathbf{q},\mathbf{q}')$, is ignored since it is proportional to the infinitesimal factor $1/N$. In the regime of interest, $s/R\gg 1$, the right-hand side of Eq. (24) is of order $(a^3/Rs^2)^2$. As noted below Eq. (15), PB^2 is proportional to $\hbar\omega_0(R/a)^3$. Therefore, at large separations, $s/R\gg 1$, Eq. (24) gives $\varepsilon_A(\mathbf{s})\approx\hbar\omega_0(R/s)^4$. It should be noted that the detailed manner with which $\varepsilon_A(\mathbf{s})$ falls off with increasing s depends on the model of the electron-lattice interaction and of the cutoff of the q integration when $qR\approx 1$.

This phonon-mediated attraction between bipolarons occurs because the carrier-induced reduction of a vibrational mode's zero-point energy is enhanced when the separation between large bipolarons is less than that phonon's wavelength. In these circumstances the bipolarons' effect on these phonons is coherent. This coherence effect is analogous to that which occurs in multiple scattering when a wave is scattered by centers that are separated by less than the wave's wavelength. The resulting attraction (proportional to $\hbar\omega_0$) is quantum mechanical in origin and associated with atomic motion. Unlike the van der Waals attraction between neutral molecules, it survives in the limit that $\varepsilon_0\rightarrow\infty$.

V. CONDENSATION TO A LARGE-BIPOLARONIC LIQUID

Since the formation of large bipolarons in a multidimensional system requires a very large static dielectric constant, $\varepsilon_0\gg\varepsilon_\infty$, it is consistent to consider the limit in which the static dielectric constant is large enough to suppress Coulomb repulsions between bipolarons. Then the sum of the repulsive energies of Eq. (6) and the attractive interaction described above can have a minimum at $s>R$. Such a potential well is illustrated in Fig. 1, where the sum of an exponential repulsion and an $(R/s)^4$ attraction is plotted. The presence of this attraction provides a

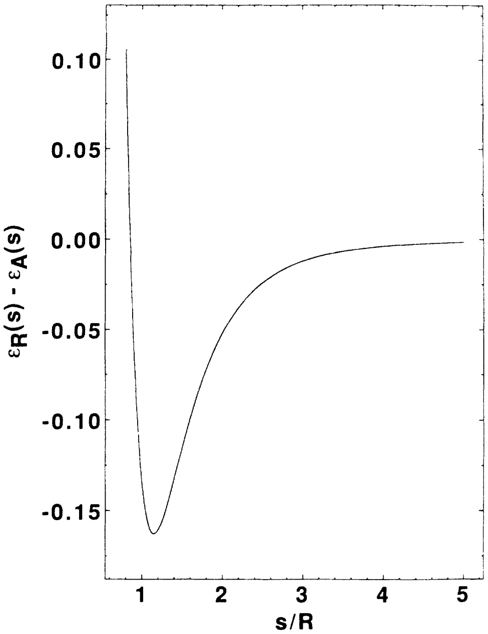

FIG. 1. Interaction energy (in dimensionless units) between two large bipolarons of radius R separated by the distance s. The short-range repulsion $\varepsilon_R(s)$ falls exponentially with s/R. The longer-range attraction $\varepsilon_A(s)$ diminishes as $(R/s)^4$ at large separations.

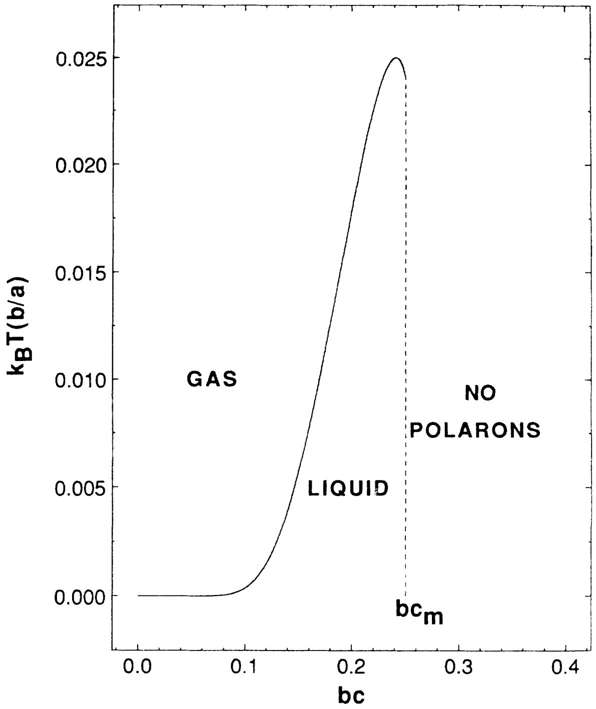

FIG. 2. Large bipolarons will be bound into a liquid only within a limited range of global carrier concentrations, c, and temperature, T. Here the constants b and a respectively characterize the short-range repulsion and the longer-range attraction of the van der Waals model of a liquid. Above the solid line, a plot of Eq. (B8), the liquid of large bipolarons has completely evaporated to a gas of large bipolarons. When $c > c_m$, the carrier density is too great to permit bipolaron formation.

mechanism for large bipolarons to condense into a liquid phase.

The interaction curve of Fig. 1 is analogous to that envisioned for the condensation of a gas of molecules to a van der Waals liquid. Therefore, the condensation of a gas of large bipolarons to a liquid is modeled as the condensation of a perfect gas to a van der Waals liquid. In making this association, the constant of the van der Waals model corresponding to a molecule's volume, b, is taken to be comparable to the volume of the large bipolaron. The constant of the van der Waals liquid associated with the intermolecular attraction, usually denoted as a, is roughly the product of the depth of the attractive potential, $\sim\hbar\omega_0$ for the case of large bipolarons, and a "volume" associated with the range over which the net interaction of Fig. 1 is attractive. This attractive "volume" is generally much greater than the particle's (large bipolaron's) volume. Thus, a/b is expected to be $\gg\hbar\omega_0$.

The conditions for phase equilibria for this model of the condensation of a bipolaronic gas to a bipolaronic liquid are considered in Appendix B. The resulting phase diagram is presented in Fig. 2, where the thermal energy, $k_B T$ in units of a/b, is plotted against the product of the global carrier concentration (the number of carriers per sample volume), c, and b, roughly the bipolaron's volume. In particular, the boundary between the liquid and gas phases of large bipolarons is plotted as a solid line in Fig. 2.

This evaporation curve is seen to remain near zero for $bc < 0.1$ and then rise sharply as bc increases when $bc > 0.1$. This feature indicates that the tendency of the liquid to evaporate increases as the global carrier density is decreased. In addition, a vertical line is drawn in Fig. 2 at the concentration beyond which large bipolarons are taken to no longer exist: $c = c_m$. In particular, in the "overdoped" regime, $c > c_m$, the atomic displacements responsible for the self-trapping of carriers are taken to interfere enough with one another to destabilize the large bipolarons so that large bipolarons do not form. Thus, a bipolaronic liquid only exists at sufficiently low temperatures within a temperature-dependent bounded range of overall carrier concentrations. Within this bounded region the fraction of the carriers that form a large bipolaronic liquid is determined by the lever rule. This fraction tends to increase with increasing c and decreasing temperature.

VI. DISCUSSION: POSSIBLE RELATIONSHIP TO SUPERCONDUCTIVITY

Superconductivity and superfluidity are recognized as cooperative phenomena of interacting carriers. In particular, bipolaronic superconductivity is usually conjectured to arise from interactions between bipolarons that behave as charged bosons. The approach to bipolaronic superconductivity is analogous to that adopted in understanding the superfluidity of liquid ^{4}He. That is, one considers real (infinitely lived) excitations of a liquid of interacting bipolarons having momentum $\mathbf{p}$ and energy $E(\mathbf{p})$. Since bipolarons are charged, the longest-wavelength excitations of a fluid of bipolarons of density n are plasmon-like[24] albeit with low energies: e.g.,

$$E(\mathbf{p})\to\hbar\sqrt{4\pi(2e)^2n/\varepsilon_0 m}\sim\hbar\omega_0\sqrt{(\varepsilon_\infty/\varepsilon_0)nR^3)}$$

as $|\mathbf{p}|\to 0$. In obtaining this estimate it is noted that the large mass of a large bipolaron is $\sim e^2\beta/(\omega_0)^2R^3$.[5,11] With suppression of the Coulomb interactions between bipolarons, as $\varepsilon_\infty/\varepsilon_0\to 0$, the long-wavelength excitations approach those of a liquid of neutral particles, sound waves: $E(\mathbf{p})\to c_s|\mathbf{p}|$, as $|\mathbf{p}|\to 0$, where c_s is the sound velocity of the liquid. With these spectra of real excitations, the Landau condition for the liquid's ground state to flow with velocity v without resistance can be fulfilled: $[E(\mathbf{p})/|\mathbf{p}|]_{\text{minimum}}>v$.[25] The Meissner effect has also been argued to be a property of the fluid ground state of a system of charged bosons.[26] Bipolaronic superconductivity is thus conjectured to occur when the liquid undergoes a Bose condensation so that its fluid ground state becomes occupied.

As in considerations of the superfluidity of ^{4}He, requiring that the excitations of the ground state be real (infinitely lived) necessitates having a liquid rather than a gas.[27] Then, one must ask how such a liquid might form. In particular, what attractive interaction between bipolarons can lead to liquid formation? This question takes on added meaning since analyses of experiments on the cuprates imply large-polaronic carriers that condense into a liquid as a prerequisite to becoming superconducting.[18,19] This paper addresses this question.

Bipolaronic superconductivity would not occur if the bipolaron's ground state were solidified rather than fluid. In the case of superfluid liquid ^{4}He, the atoms' zero-point energy is presumed to be sufficient to preclude their condensation to a solid phase. For bipolarons or polarons in a crystal full solidification entails ordering in a manner that is commensurate with the underlying lattice, i.e., forming a superlattice. Such a state is only possible at certain carrier densities. At other densities, the solid's potential will frustrate the bipolaron's simple solidification causing either liquid formation or multiphase and/or multidomain solidification. As noted in the introduction, the loss of superconductivity in doped La_2CuO_4 at some compositions may indicate superlattice formation.[14,15] Indeed, solidification and superlattice formation rather than superconductivity has been observed in $La_{2-x}Sr_xNiO_{4+y}$.[28] The observation that the carrier-induced absorption occurs at higher energies in the nickelates than in the cuprates implies a more compact polaronic state.[10] The absence of superconductivity in the nickelates may be related to bipolarons being too compact to avoid solidification.

VII. SUMMARY

The self-trapped carriers of large-polarons and bipolarons extend over several sites. As the atomic configurations change, the self-trapped electrons are redistributed among sites of their molecular orbitals. This polarizability reduces the stiffness of the atomic system. Therefore, large polarons and bipolarons lower a solid's vibrational frequencies. By contrast, small (single-site) polarons and bipolarons do not alter vibrational frequencies.[21]

To first order, these shifts of the vibrational frequencies are simply proportional to the number of large-polaronic carriers. However, to second order, the shifts of the vibrational frequencies depend on their spatial distribution. The vibrational frequencies fall as the separation between large-polaronic carriers is decreased. Since reducing the vibrational frequencies lowers the zero-point vibrational energy of the system, this effect constitutes a phonon-mediated attractive interaction between large bipolarons. This attractive interaction is proportional to the phonon energy $\hbar\omega_0$. That is, it is a dynamic quantum-mechanical effect.

This attractive interaction is opposed by the Coulomb repulsion between self-trapped carriers. However, for polaronic carriers this repulsion is reduced by the static dielectric constant. Therefore, in the high-static-dielectric materials in which large bipolarons are expected to form, the attractive interaction can prevail and bind the large bipolarons into a liquid whose density is limited by large bipolarons' "hard-core" repulsion.

Polaronic carriers can only form when their density is low enough that they are not destabilized by the interference of their atomic displacement patterns. The maximum carrier density for which superconductivity is found in doped La_2CuO_4 corresponds to only one bipolaron for every ten unit cells. As shown in Fig. 2, the temperature above which a large bipolaronic liquid evaporates rises with the global carrier density. Thus, at a finite temperature, a large-bipolaronic liquid at best only exists within a restricted range of carrier densities. When the carrier's ground state remains a bipolaronic liquid, superconductivity should result.

For definiteness, the carriers have herein been assumed to be large bipolarons. Were the carriers to be large polarons, the phonon-mediated attractive interaction would still result. Then, the hard-core repulsion between bipolarons that arises from the Pauli principle would be replaced by the repulsion that opposes the merger of large polarons into bipolarons.[5] Thus one can also envision the phonon-mediated attraction condensing large polarons into a liquid. In the liquid the individual carriers could remain large polarons or be driven to pair as large bipolarons. In particular, it is noted that the attractive forces associated with reducing the vibrational energies increase as the temperature is lowered toward absolute zero (where the vibrational free energy is just the zero-point energy).

Charge transport of a large-bipolaronic liquid is unlike that of free nonpolaronic carriers. For example, their large masses and the mechanism through which they are scattered by phonons differentiate large bipolarons from free carriers.[11,22] In addition, transport in the liquid will be collective as a result of the interactions between bipolarons. Unusual features of dc transport that are qualitatively similar to observations in the normal states of the oxide superconductors can result in these circumstances.[29]

ACKNOWLEDGMENTS

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APPENDIX A: POLARONS, BIPOLARONS, AND GRANDER POLARONS

In this appendix the conditions for the formation of self-trapped states containing multiple carriers are succinctly described. Here the method developed in Ref. (5) is extended to consider more than two carriers occupying a self-trapped state.

Consider the ground-state adiabatic energy of n carriers that cohabit a self-trapped state of radius R. The energy has four components: (1) the increase of the electronic energy associated with confining n carriers within a region of radius R, (2) the lowering of the carrier's potential energy resulting from residing within the self-trapping potential well, (3) the elastic energy required to produce this potential well, and (4) the Coulomb repulsion of the n carriers:

$$E_n = E_{\text{confine}} - E_{\text{trap}} + E_{\text{deform}} + E_{\text{Coul}} \; . \tag{A1}$$

Employing the commonly used linear electron-lattice interaction, one has $E_{\text{trap}} = 2E_{\text{deform}}$. The energies all depend upon the radius of the electronic state R (expressed here in dimensionless units):

$$E_{\text{confine}} = [nT + P(n)]/R^2 \; , \tag{A2}$$

$$E_{\text{trap}} = n^2[(1/\varepsilon_\infty - 1/\varepsilon_0)U/2R + E_b/R^d + E_{S-L}/R^2] \; , \tag{A3}$$

and

$$E_{\text{Coul}} = n(n-1)U/2\varepsilon_\infty R \; . \tag{A4}$$

In Eq. (A2), T is the electronic half-bandwidth and $P(n)/R^2$ is the energy associated with promoting carriers above their ground state. For example, in a four-carrier self-trapped state with two carriers in a singlet ground state and two carriers in a singlet excited state, $P(4)/R^2 = 2\Delta$, where Δ is the energy difference between the ground and excited electronic states. The self-trapping energy of Eq. (A3) results from considering both long-range and short-range components of the electron-lattice interaction. The first term results from the long-range (Fröhlich) electron-lattice interaction of carriers with the anions and cations of an ionic lattice. U is a Coulomb integral and ε_0 and ε_∞ are the static and optical dielectric constants of the ionic solid, respectively. The second term of Eq. (A3) results from the short-range electron-lattice interaction. It is characterized by the energy E_b (Holstein's small-polaron binding energy) and depends on the dimensionality of the *electronic* system, d. The final term is a cross term that results from having both long-range and short-range components of the electron-lattice interaction in a three-dimensional deformable medium. Here, E_{S-L} is proportional to $[(1/\varepsilon_\infty - 1/\varepsilon_0)UE_b]^{1/2}$. Equation (A4) represents the Coulomb interaction of the n carriers.

For simplicity, we consider a system that is electronically two dimensional, $d=2$. Then, the contributions to the net energy are combined to obtain

$$\begin{aligned} E_n = n\{[T + P(n)/n - n(E_b + E_{S-L})]/R^2 \\ -(1/\varepsilon_\infty - n/\varepsilon_0)U/2R\} \; . \end{aligned} \tag{A5}$$

This function has a finite-radius minimum corresponding to a large-polaronic state, provided that $\varepsilon_0 > n\varepsilon_\infty$ and $T + P(n)/n > n(E_b + E_{S-L})$. Minimizing E_n with respect to R yields the ground-state radius and the ground-state binding energy:

$$R_0 = 4[T + P(n)/n - n(E_b + E_{S-L})]/(1/\varepsilon_\infty - n/\varepsilon_0)U \; , \tag{A6}$$

and

$$E_{\text{GS}}(n) = n\frac{[(1/\varepsilon_\infty - n/\varepsilon_0)U]^2}{16[T + P(n)/n - n(E_b + E_{S-L})]} \; . \tag{A7}$$

It is energetically favorable for two polarons to pair if $E_{\text{GS}}(2) > 2E_{\text{GS}}(1)$. However, it is energetically unfavorable for two bipolarons to pair to form a quadrapolaron if $E_{\text{GS}}(4) < 2E_{\text{GS}}(2)$. These requirements may be summarized as $E_{\text{GS}}(2)/2 > E_{\text{GS}}(1), E_{\text{GS}}(4)/4$. That is, to have a system of bipolarons the binding energy per carrier must be maximized when carriers form bipolarons.

From Eq. (A7) we write the binding energy per carrier in units of the binding energy of a large polaron as

$$\begin{aligned} \frac{E_{\text{GS}}(n)}{nE_{\text{GS}}(1)} &= \frac{(1 - n\varepsilon_\infty/\varepsilon_0)^2[1 - (E_b + E_{S-L})/T]}{(1 - \varepsilon_\infty/\varepsilon_0)^2[1 + P(n)/nT - n(E_b + E_{S-L})/T]} \\ &\approx \frac{[1 - (n-1)\varepsilon_\infty/\varepsilon_0]^2}{[1 + P(n)/nT - (n-1)(E_b + E_{S-L})/T]} \\ &\approx \frac{1 + (n-1)\{(E_b + E_{S-L})/[T + P(n)/n] - 2\varepsilon_\infty/\varepsilon_0\}}{[1 + P(n)/nT]} \; , \end{aligned} \tag{A8}$$

where

$$E_{\mathrm{GS}}(1)=\frac{[(1/\varepsilon_\infty-1/\varepsilon_0)U]^2}{16(T-E_b-E_{S\text{-}L})} . \tag{A9}$$

The simplifications of Eq. (A8) are justified when the conditions for the existence of a large-radius polaronic state, below Eq. (A5), are satisfied. Thus, we regard Eq. (A8) as generally valid for a large-polaronic state.

The questions of bipolaron and multipolaron formation are readily addressed with the final expression of Eq. (A8). The formation of a singlet bipolaron with both carriers in the electronic ground state is energetically favorable when $(E_b+E_{S\text{-}L})/T>2\varepsilon_\infty/\varepsilon_0$, since then $P(2)=0$. In addition, the requirement that the bipolaron remain large, from below Eq. (A5), is that $\frac{1}{2}>(E_b+E_{S\text{-}L})/T$. Forming grander large multipolarons requires satisfying conditions that become increasingly stringent as the number of cohabiting carriers is increased:

$$[T+P(n)/n]/n>E_b+E_{S\text{-}L}>(2\varepsilon_\infty/\varepsilon_0)[T+P(n)/n]$$

with $P(n)>0$.

The promotion energy associated with an n-carrier multipolaron, $P(n)/R^2$, can be estimated for our model of large bipolarons. To begin, we note that our large polarons and bipolarons are self-trapped carriers bound in a nearly hydrogenic potential. That is, with only one or two carriers, the energy functional of Eq. (A5) is nearly hydrogenic: $E_n\approx n[T/R^2-U/2\epsilon_\infty R]$ when $P(1)=P(2)=0$. It is the remaining n-dependent terms of Eq. (A5) that stabilize a bipolaron when $(E_b+E_{S\text{-}L})/T>2\varepsilon_\infty/\varepsilon_0$. The binding energy of an electronic carrier in the 1s ground state of this hydrogenic well is $\approx 3U^2/16T(\varepsilon_\infty)^2\approx 3E_{\mathrm{GS}}(1)$. The first excited electronic state in this hydrogenic well is three-quarters of the binding energy, $9E_{\mathrm{GS}}(1)/4$. Thus, for the case of a quadrapolaron, $P(4)/R^2=2\Delta=9E_{\mathrm{GS}}(1)/2$. Noting that $E_{\mathrm{GS}}(1)\approx T/R^2$ in our hydrogenic model, we have $P(4)\approx 9T/2$.

With this result and Eq. (A8) we find the binding energy of a quadrapolaron to be about half that of two bipolarons:

$$E_{\mathrm{GS}}(4)/2E_{\mathrm{GS}}(2)\approx 1/[1+P(n)/nT]=1/(1+\tfrac{9}{8})\approx\tfrac{1}{2} . \tag{A10}$$

Thus, it is not energetically favorable for two bipolarons to merge into a quadrapolaron. Furthermore, since the net binding energy of two separate large bipolarons is $4E_{\mathrm{GS}}(1)$, the short-range repulsive energy of two bipolarons is $2E_{\mathrm{GS}}(1)$.

In summary, with an isolated large-polaron's binding energy being $E_{\mathrm{GS}}(1)$, two large polarons can increase their binding energy somewhat from $2E_{\mathrm{GS}}(1)$ by merging into a large bipolaron if $(E_b+E_{S\text{-}L})/T>2\varepsilon_\infty/\varepsilon_0$. However, mergers of bipolarons into quadrapolarons force half the self-trapped electrons from their 1s hydrogenic orbitals into higher-lying orbitals, 2s. This effect greatly reduces the binding energy of a quadrapolaron [by $\approx 2E_{\mathrm{GS}}(1)$], rendering the merger of large bipolarons energetically unfavorable.

APPENDIX B: VAN DER WAALS MODEL OF THE CONDENSATION TO A LARGE-BIPOLARON LIQUID

To treat the thermodynamics of the condensation of large bipolarons into a liquid, the large-bipolaronic liquid is modeled as a van der Waals liquid. The gas of large bipolarons is described as a perfect gas. Then the free energies of the large-bipolaronic liquid, F_l, and the large-bipolaronic gas, F_g, are written as:

$$F_l=-n_lk_BT\ln(N_l/n_l)-n_lk_BT\ln(1-bn_l/N_l)-(n_l)^2a/N_l , \tag{B1}$$

and

$$F_g=-n_gk_BT\ln(N_g/n_g) . \tag{B2}$$

Here, the lower-case n refers to the number of carriers and the upper-case N refers to the number of elementary structural units, sites or unit cells. For example, the liquid is composed of n_l large bipolarons among N_l structural units. The thermal energy is k_BT, where k_B is the Boltzman constant and T is the absolute temperature. Adopting the customary notation for the van der Waals liquid, the short-range repulsion is characterized by the constant b and the longer-range attraction is denoted by the constant a. For large bipolarons the constant b is comparable to the volume of the large bipolaron. The constant a is roughly the product of the depth of the attractive potential, $\sim\hbar\omega_0$, and the bipolaron's volume. Thus, the energy scale for the condensation of a bipolaron gas into a bipolaron liquid is a/b. This energy is of the order of $\hbar\omega_0$.

At equilibrium between the large-bipolaronic liquid and a gas of large bipolarons or free carriers, the pressures of the two systems must equal one another. The pressure of a system is the negative of the derivative of its free energy with respect to its volume, N. The requirement that the pressure of the large-bipolaronic liquid equal that of the large-bipolaronic gas is:

$$c_g=c_l\left[\frac{1}{1-bc_l}-\frac{bc_l}{u}\right] , \tag{B3}$$

where the carrier concentrations in the two phases have been defined: $c_g\equiv n_g/N_g$, $c_l\equiv n_l/N_l$, and $u\equiv bk_BT/a$. To form a van der Waals liquid the attraction between particles must be sufficiently strong, $u<1$. Equation (B3) gives the concentration of bipolarons in a gas required for its partial pressure to equal that of a concentration of c_l large bipolarons in the liquid.

Equilibrium between the large-bipolaronic liquid and the gas also requires equality of their respective chemical potentials. The chemical potential of each system is the derivative of its free energy with respect to its carrier number. Equating the chemical potential of the liquid with that of the gas yields

$$\frac{c_g}{c_l}=\frac{\exp\{(bc_l)[1/(1-bc_l)-2/u]\}}{(1-bc_l)} . \tag{B4}$$

Eliminating c_g between Eqs. (B3) and (B4) gives an equation that determines c_l when equilibrium exists between the bipolaronic liquid and the bipolaronic gas:

$$\frac{1}{1-bc_l}-\frac{bc_l}{u}=\frac{\exp\{(bc_l)[1/(1-bc_l)-2/u]\}}{(1-bc_l)} \;. \tag{B5}$$

The bipolaronic liquid will ultimately condense to a density determined by its repulsive energy as the temperature is reduced. For this reason, a new variable is defined: $f\equiv 1-bc_l$ with the anticipation that $f\rightarrow 0$ as $u\equiv bk_BT/a\rightarrow 0$. Introducing this notation into Eq. (B5) yields:

$$1-\frac{f(1-f)}{u}=\exp\left[\frac{(1-f)}{f}\left[1-\frac{2f}{u}\right]\right] \tag{B6}$$

for the bipolaronic liquid to bipolaronic gas equilibrium. As u and $f\rightarrow 0$ the magnitude of the exponentiated square-bracketed terms on the right-hand side of Eq. (B6) becomes infinite. However, the sign of the argument of the exponential factor is negative if $2f/u>1$ and is positive if $2f/u<1$.

The transition from a large-bipolaronic liquid to a large-bipolaronic gas occurs because the attraction between the large bipolarons competes with the thermal energy. To examine this transition, presume the attractive interaction, proportional to $2f/u>1$ in Eq. (B6), to dominate the repulsive term in the exponential of Eq. (B6). That is, consider $f\rightarrow 0$ and $u\rightarrow 0$ with $2f/u>1$. Then the right-hand side of Eq. (B6), represented by ε, becomes vanishingly small as $f\rightarrow 0$. Solving Eq. (B6) in this situation yields $f=[1-\sqrt{1-4u(1-\varepsilon)}]/2$ and

$$\begin{aligned} bc_l&=[1+\sqrt{1-4u(1-\varepsilon)}]/2\\ &=\{1+\sqrt{1-4u[1-\exp(-1/u)]}\}/2 \;, \end{aligned} \tag{B7}$$

where ε is replaced by $\exp(-1/u)$ in the second of these relations, since $\varepsilon\rightarrow\exp(-1/u)$ as $f\rightarrow u\rightarrow 0$.

The boundary between the domain of carrier concentrations, c, within which at least some large bipolarons condense into the liquid and the regime in which all large bipolarons exist in the gaseous state can now be found. At this boundary the concentration of large bipolarons in the gaseous state approaches the total concentration of carriers, c. Using Eq. (B3) with Eq. (B7) and setting $c_g=c$ yields, after some algebra, the desired relation between the carrier concentration and the temperature at the phase boundary:

$$bc=\exp(-1/u)\frac{\{1+\sqrt{1-4u[1-\exp(-1/u)]}\}}{\{1-\sqrt{1-4u[1-\exp(-1/u)]}\}} \;, \tag{B8}$$

where it is recalled that u is proportional to the temperature. This curve gives the boundary between the liquid and gas of large bipolarons that is plotted as a solid line in Fig. 2. This curve is seen to remain near zero for $bc<0.1$ and then rise sharply as bc increases when $bc>0.1$. In addition, a vertical line is drawn in Fig. 2 at the concentration beyond which large bipolarons are taken to no longer exist: $c=c_m$. Within the bounded region of Fig. 2 some fraction of the carriers form into a large-bipolaronic liquid. The fraction of the carriers in the liquid is determined by the lever rule. Outside of the bounded region the large-bipolaronic liquid does not exist.

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