Phonon-Mediated Attraction between Large Bipolarons: Condensation to a Liquid

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Self-trapped carriers of large bipolarons are redistributed among sites of their molecular orbitals in response to atomic motions. This effect lowers the phonon frequencies. The dependence of the zero-point energy on the spatial distribution of large bipolarons produces a phonon-mediated attraction between them. This dynamic quantum-mechanical effect fosters the condensation of large bipolarons into a liquid at sufficiently low temperatures.

Self-trapping occurs when an electronic charge carrier is bound in a potential well produced by displacements of atoms from the equilibrium positions they assume in the carrier's absence. The binding energy of the self-trapped carrier, denoted as E_{st}, may be measured by photoionizing it.

Upon self-trapping, an electronic carrier can only move when the surrounding atoms change their locations. Self-trapping is therefore treated within the adiabatic approach which constrains the electronic carriers to follow the atomic motions. The adiabatic treatment applies when the motion of the electronic carrier within its self-trapping potential well is faster than the vibrational frequency, ω: $E_{st} > \hbar\omega$. Aside from one-dimensional models, adiabatic treatments yield two distinct types of self-trapped states distinguished by the range of the predominant electron-lattice interactions [1–5].

A "large" polaron can form when the long-range electron-lattice interaction produced by the dependence of a carrier's energy on the positions of ions of an ionic solid (through their Coulomb interactions) dominates [1–3,5]. The strength of this interaction is proportional to $\beta \equiv (\varepsilon_\infty)^{-1} - (\varepsilon_0)^{-1}$, where ε_0 and ε_∞ are the static and optical dielectric constants, respectively. Formation of a large polaron requires $W > E_{st} > \hbar\omega$, where W is the free-carrier electronic bandwidth. The radius of the large polaron's self-trapped state is then $R \approx a\sqrt{W/E_{st}}$, where a is the lattice constant. Since the large polaron extends over multiple atomic sites, it moves in a continuous manner through a medium that may be approximated as being continuous.

A "small" polaron forms when a short-range electron-lattice interaction (e.g., the deformation potential in covalent materials) is paramount. A self-trapped carrier then collapses to a single site [1,2,4,5]. The energetic stability of a small polaron requires $E_{st} > W$. As a result of its severe confinement, a small polaron typically moves incoherently by phonon-assisted hops between adjacent sites.

A bipolaron forms when two carriers are self-trapped within a common potential well. With *only* the long-range interaction two carriers can be bound within the same potential well if $\varepsilon_0 > 2\varepsilon_\infty$ [5]. This large bipolaron is energetically unstable with respect to forming two

separate large polarons by at most $e^2/\varepsilon_0 R$ [5]. However, the omnipresent short-range electron-lattice interaction provides an additional driving force to stabilize the paired state relative to that of separated polarons. Thus, large bipolaron formation is expected when $\varepsilon_0 \gg 1$ and ε_∞. This situation prevails in the insulating parents of superconducting oxides [6].

First consider a large polaron. Within the adiabatic approach the Hamiltonian is $H = T_c + V_c + E_{el}$, where T_c is the kinetic energy associated with atomic motions, V_c is the potential energy due to direct interaction between atoms, and E_{el} is the electronic energy of the self-trapped carrier. In a continuum the electronic energy is

$$E_{el} = \int d\mathbf{r} \left[\frac{\hbar^2 |\nabla\Psi(\mathbf{r})|^2}{2m} + |\Psi(\mathbf{r})|^2 \int d\mathbf{u}\, Z(\mathbf{r}-\mathbf{u})\Delta(\mathbf{u}) \right],$$

(1)

where $Z(\mathbf{r}-\mathbf{u})$ describes the electron-lattice interaction between an electronic carrier at position $\mathbf{r}$ and atomic displacements, modeled by scalar parameters, $\Delta(\mathbf{u})$, centered at positions denoted by $\mathbf{u}$. Within the harmonic approximation, the strain energy resulting from direct interatomic interactions is $V_c \equiv S\int d\mathbf{u}\, \Delta^2(\mathbf{u})/2$, where $S \equiv k/a^3$, the stiffness constant k per unit volume.

In the customary manner $\varepsilon(\mathbf{u}) \equiv V_c + E_{el}$ is expanded about its minimum value. The first and second derivatives of $\varepsilon(\mathbf{u})$ with respect to variations of $\Delta(\mathbf{u})$ are

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

(2)

and

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

$$\equiv S\delta(\mathbf{u}-\mathbf{u}') + \Delta S(\mathbf{u},\mathbf{u}').$$

(3)

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. (2). 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. (2) to zero. When atoms are constrained to these equilibrium positions, the energy of the system is $E_p = -S\int d\mathbf{u}[\Delta_0(\mathbf{u})]^2/2$.

Following Ref. [5] the adiabatic procedure can be readily generalized to obtain the adiabatic energy minimum for a system of n large bipolarons that each has a binding energy of E_{bp}:

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

(4)

Here $\rho(\mathbf{r})$ is the density of bipolarons centered at the position $\mathbf{r}$ and the direct interactions are described by

$$\varepsilon_R(\mathbf{s}) \equiv (2e)^2/\varepsilon_0[|\mathbf{s}| + R] + C_1 E_p \exp(-C_2|\mathbf{s}|/R),$$

(5)

where C_1 and C_2 are numerical constants. The first of the terms in Eq. (5) 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. At sufficiently large separations, $|\mathbf{s}| \gg R$, this Coulomb repulsion approaches that of static charge point charges separated by $\mathbf{s}$.

The second term in the square brackets describes the repulsion between large bipolarons that occurs when the wave functions of the self-trapped carriers of different large bipolarons overlap with 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 [7]. 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 should not coalesce into grander polarons such as quadpolarons. Equation (5) shows that the direct interactions between large bipolarons are repulsive.

Bipolarons' effects on atomic vibrations are now considered. Treating the change of the carriers' wave function with atomic displacements perturbatively, the car-

rier-induced change of the stiffness tensor of Eq. (3) is expressed in terms of matrix elements of the electron-lattice coupling function between the ground and excited states of the self-trapped carriers. For the two carriers of a large bipolaron,

$$\Delta S(\mathbf{u},\mathbf{u}') = -4\sum_{\mathbf{g}} \sum_{n\neq 0} \langle \mathbf{g},0|Z(\mathbf{r}-\mathbf{u})|\mathbf{g},n\rangle$$
$$\times \langle \mathbf{g},n|Z(\mathbf{r}-\mathbf{u}')|\mathbf{g},0\rangle/(E_n - E_0).$$

(6)

Here the nth electronic energy level and the state of the polaron centered at $\mathbf{g}$ are denoted by E_n and $|\mathbf{g},n\rangle$, respectively. Electronic overlap between self-trapped carriers of different bipolarons is ignored. Expanding the electron-lattice interaction function about its value at the bipolaron's centroid: $Z(\mathbf{r}-\mathbf{u}) \approx \partial Z(\mathbf{g}-\mathbf{u})/\partial \mathbf{g} \cdot (\mathbf{r}-\mathbf{g})$, the tensor of Eq. (6) becomes

$$\Delta S(\mathbf{u},\mathbf{u}') = -4\sum_{\mathbf{g}} P_{\mathbf{g}}[\partial Z(\mathbf{g}-\mathbf{u})/\partial \mathbf{g}][\partial Z(\mathbf{g}-\mathbf{u}')/\partial \mathbf{g}],$$

(7)

where the polarizability of a self-trapped carrier is defined by

$$P_{\mathbf{g}} \equiv \sum_{n\neq 0} \langle \mathbf{g},0|(\mathbf{r}-\mathbf{g})|\mathbf{g},n\rangle\langle \mathbf{g},n|(\mathbf{r}-\mathbf{g})|\mathbf{g},0\rangle/(E_n - E_0).$$

(8)

For equivalent sites, $P_{\mathbf{g}} = P$. This polarizability arises from the redistribution of the self-trapped charge among different atomic sites enveloped by the bipolaron. A large bipolaron's polarizability is essentially the square of the radius of the self-trapped carrier divided by its binding energy, $E_{st} \approx 3E_p$ for a large bipolaron.

The potential energy arising from displacing atoms from the equilibrium values they assume when bipolarons form, $d(\mathbf{u}) \equiv \Delta(\mathbf{u}) - \Delta_0(\mathbf{u})$, is $V_L \equiv S\int d\mathbf{u}\, d^2(\mathbf{u})/2 + V_{pol}$, where

$$V_{pol} \equiv -2P\sum_{\mathbf{g}} \int d\mathbf{u} \int d\mathbf{u}'[\partial Z(\mathbf{g}-\mathbf{u})/\partial \mathbf{g}][\partial Z(\mathbf{g}-\mathbf{u}')/\partial \mathbf{g}]d(\mathbf{u})d(\mathbf{u}')$$

$$= -2P\sum_{\mathbf{g}} \int d\mathbf{u} \int d\mathbf{u}'[\partial Z(\mathbf{g}-\mathbf{u})/\partial \mathbf{u}][\partial Z(\mathbf{g}-\mathbf{u}')/\partial \mathbf{u}]d(\mathbf{u})d(\mathbf{u}')$$

$$= -2P\sum_{\mathbf{g}} \int d\mathbf{u} \int d\mathbf{u}'Z(\mathbf{g}-\mathbf{u})Z(\mathbf{g}-\mathbf{u}')[\partial d(\mathbf{u})/\partial \mathbf{u}] \cdot [\partial d(\mathbf{u}')/\partial \mathbf{u}'],$$

(9)

where the third equality follows an integration by parts. The polarizability of large-polaronic carriers reduces the stiffnesses of atomic vibrations through V_{pol}.

Expressing the atomic displacement parameters, $d(\mathbf{u})$, in terms of operators that respectively create and destroy phonons of wave vector $\mathbf{q}$ and frequency $\omega_{\mathbf{q}}$ of the lattice prior to consideration of carrier-induced stiffness changes, $(b_{\mathbf{q}})^*$ and $b_{\mathbf{q}}$:

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

(10)

where $\cos\theta_{\mathbf{q},\mathbf{q}'}$ is the cosine of the angle between $\mathbf{q}$ and $\mathbf{q}'$, and

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

(11)

is the Fourier transform of the carrier density, $\rho(\mathbf{r})$. For the long-range electron-lattice interaction with optic phonons whose dominance is required for large-bipolaron formation, $B(\mathbf{q}) \equiv 2(\beta e^2 \hbar \omega_\mathbf{q} \pi / a^3)^{1/2}$ [5]. Since $P \approx R^2/(\beta e^2/R)$ for a large bipolaron's self-trapped carriers, $PB^2(\mathbf{q}) \approx 4\pi\hbar\omega_\mathbf{q}(R/a)^3$. Consistent with the approximation employed in Eq. (7), the summations over $\mathbf{q}$ and $\mathbf{q}'$ are only to be carried out up to a maximum value $\approx 1/R$.

Treating V_{pol} as a perturbation on the carrier-free vibrational system, the carrier-related energy through second order is found to be

$$E_T = -n(E_{bp}+E_{bp1}+E_{bp2}) + \tfrac{1}{2}\int d\mathbf{r}\rho(\mathbf{r})\int ds [\rho(\mathbf{r}+\mathbf{s}) - \delta(\mathbf{s})][\varepsilon_R(\mathbf{s}) - \varepsilon_A(\mathbf{s})] , \qquad (12)$$

where E_{bp1} and E_{bp2} are the first and second order corrections to the bipolaron's single-particle energy. Phonon-mediated interactions between the large bipolarons that enter in second order are contained in the attractive energy, $\varepsilon_A(\mathbf{s})$. Explicitly,

$$E_{bp1} = 2PN^{-1}\sum_\mathbf{q} B^2(\mathbf{q})[N_\mathbf{q} + \tfrac{1}{2}] , \qquad (13)$$

$$E_{bp2} \equiv P^2 N^{-2}\sum_\mathbf{q} B^2(\mathbf{q})\sum_{\mathbf{q}'} B^2(\mathbf{q}')\cos^2\theta_{\mathbf{q},\mathbf{q}'} F(\mathbf{q},\mathbf{q}') , \qquad (14)$$

$$\varepsilon_A(\mathbf{s}) \equiv 2P^2 N^{-2}\sum_\mathbf{q} B^2(\mathbf{q})\sum_{\mathbf{q}'} B^2(\mathbf{q})\cos^2\theta_{\mathbf{q},\mathbf{q}'}$$

$$\times \cos[(\mathbf{q}-\mathbf{q}')\cdot\mathbf{s}]F(\mathbf{q},\mathbf{q}') , \qquad (15)$$

and

$$F(\mathbf{q},\mathbf{q}') \equiv \frac{1+\delta'_{\mathbf{q},-\mathbf{q}}}{\hbar(\omega_\mathbf{q}+\omega_{\mathbf{q}'})}$$

$$+2N_\mathbf{q}\left[\frac{1+\delta'_{\mathbf{q},-\mathbf{q}}}{\hbar(\omega_\mathbf{q}+\omega_{\mathbf{q}'})} - \frac{1-\delta'_{\mathbf{q},\mathbf{q}}}{\hbar(\omega_\mathbf{q}-\omega_{\mathbf{q}'})}\right] , \qquad (16)$$

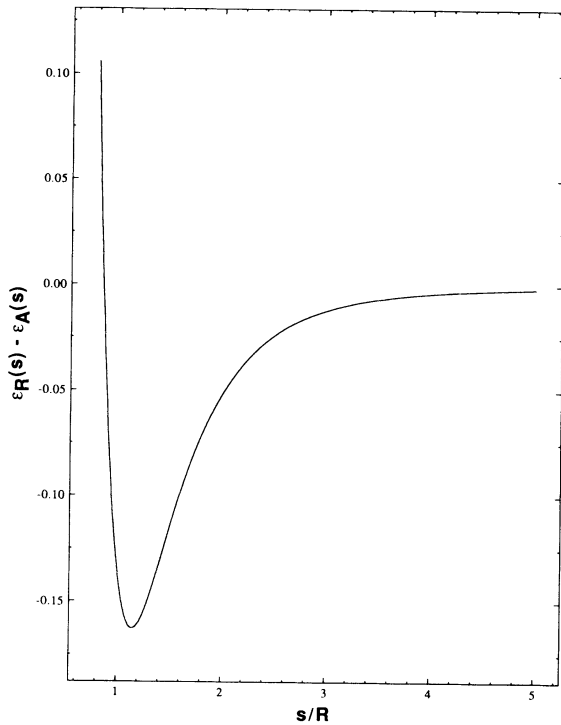where $N_\mathbf{q}$ is the phonon population of the qth vibrational mode of the carrier-free system.

The ground state of the system can be a bipolaronic liquid if the attractive interbipolaron interactions dominate the repulsive interactions over some range of separations. The phonon-mediated attraction, $\varepsilon_A(\mathbf{s})$, is now investigated. To consider the ground state, take $N_\mathbf{q}=0$ for all $\mathbf{q}$. Then, ignoring the dispersion of the optic phonon modes, $\omega_\mathbf{q}=\omega$, evaluation of Eq. (15) yields $\varepsilon_A(\mathbf{s}) \approx \hbar\omega(R/s)^4$ for $s/R \gg 1$, where a numerical factor comparable to unity is ignored.

Since the attractive interaction falls off with separation as a power law, it will dominate the short-range repulsive energy at sufficiently large separations. Such a potential well is illustrated in Fig. 1, where the sum of an exponential repulsion and a $(R/s)^4$ attraction is plotted. Thus, if the static dielectric constant is large enough to suppress the Coulomb repulsion sufficiently, large bipolarons can condense into a liquid.

Further condensation of the large bipolarons into a solid is also possible. However, complete crystallization would entail forming a supercrystalline configuration that is commensurate with the underlying lattice. This may occur when carriers induce a structural transformation to
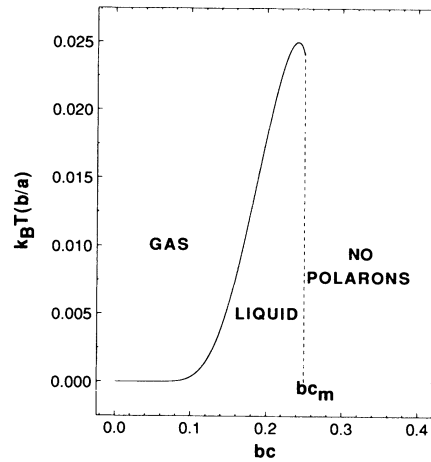
FIG. 1. The interaction energy between two large bipolarons of radius R separated by the distance s.

FIG. 2. Large bipolarons will be bound into a liquid only within a limited range of global carrier concentrations, c, and temperature, T. The constants b and a characterize the van der Waals' liquid. Above the solid line 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.

a tetragonal insulating state (with a square geometry in the CuO_2 layers) when there is $\frac{1}{8}$ hole per unit cell in doped La_2CuO_4 [8,9]. This result is consistent with forming a state that is commensurate with the lattice geometry in which there is one bipolaron for each four-by-four superlattice unit, $1/8 = 2/4^2$.

To address the condensation of large bipolarons into a liquid, the large-bipolaronic liquid is modeled as a van der Waals liquid. The short-range repulsion constant, b, is comparable to the volume of the large bipolaron. The longer-range attraction constant, usually denoted as a, is roughly the product of the depth of the attractive potential $\sim \hbar\omega$ and the volume over which the interaction is attractive. The gas of large bipolarons is described as a perfect gas. The resulting phase diagram is presented in Fig. 2, where a/b is $\gg \hbar\omega$.

At low enough temperatures, large bipolarons condense into a liquid. As the global carrier density (the number of carriers per sample volume), c, is increased, the volume of large-bipolaron liquid increases. However, if "over-doping" produces too many carriers, $c > c_m$, the atomic displacements responsible for the self-trapping of carriers interfere enough with one another to destabilize the large bipolarons so that large bipolarons do not form. With rising temperature the liquid will evaporate. The condensation temperature falls as the global carrier density is reduced.

In oxide superconductors and their insulating parents carrier-induced photoabsorptions consistent with the photoionization of self-trapped carriers are observed. Carrier-induced alterations of atomic motions also occur. Recently, it has been argued from such empirical evidence that superconductivity in oxides is associated with a "distinguishable thermodynamic state" in which multisite polaronic carriers form a liquid [10]. Having superconductivity being a property of such a liquid phase would also explain the tendency of T_c in cuprates to be nearly independent of the doping level within the restricted doping region in which superconductivity occurs [11]. In this work, I describe a mechanism for the condensation of large (multisite) bipolarons to a liquid state. This mechanism is inapplicable for small (single-site) bipolarons since the carriers' restriction to a single site constrains its intersite polarizability, P, to vanish.

In summary, the self-trapped carriers of a large (multisite) bipolaron redistribute themselves among sites of their molecular orbitals as the self-trapping potential well is altered by changing atomic positions. Through their polarizability, large bipolarons interact with atomic vibrations, thereby reducing the phonon frequencies. This lowering of the zero-point energy depends on the spatial distribution of large bipolarons. This effect produces a phonon-mediated attraction between large bipolarons. The attraction is a dynamic quantum-mechanical effect, proportional to (and comparable to) $\hbar\omega$.

The bipolaron polarizability, which is responsible for these effects, decreases as a bipolarons' radius is reduced. Since the radius of a large bipolaron varies inversely with the bipolaron's binding energy, the attractive forces *decrease* as the electron-lattice interaction strength is increased. Thus, for liquid formation to occur, the electron-lattice interaction must be large enough so that (adiabatic) large bipolarons form, but not so large as to suppress the attractive interaction.

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