Bipolarons in disordered media

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We examine the formation of small bipolarons in disordered systems by combining the scaling arguments of Emin and Holstein for polarons with the scaling theory of localization. For extended states away from the mobility edge, we find that for a sufficiently small Coulomb interaction the bipolaron forms at a lower electron-phonon coupling constant λ than the polaron and is of lower energy than two polarons when these become stable. For larger Coulomb interactions, there can be a range of λ for which only the polaron is stable and above that a range for which the bipolaron is the lower-energy form. As we approach the mobility edge, the extended states tend to collapse into localized polarons or bipolarons, and the region of the stability diagram corresponding to extended states shrinks and eventually disappears as the mobility edge is reached.

I. INTRODUCTION

Emin and Holstein[1] (EH) have introduced an elegantly simple method of studying polaron formation in the adiabatic limit. They have examined the coupling of the electron both to optical and acoustic modes and have considered the effect of a Coulombic impurity potential. The simplicity of their method derives from the simplicity of the scaling properties of the individual terms in the total energy of the electron-phonon system. We have extended their theory to the case of an impurity potential of finite range, showing that the existence of a characteristic length in the problem, the range, does not destroy the possibility of the scaling argument,[2] although it makes it more complicated. We have also found the EH method to provide a very powerful way of attacking successfully the far more difficult problem of the influence of the electron-phonon interaction on electron states near the mobility edge in disordered systems.[3] We have also applied the EH method to the question of the bipolaron in a periodic system.[4] Specifically, we have studied whether two electrons will be bound together into a small bipolaron by coupling to acoustic phonons at some value of the electron-phonon coupling constant different in general from that required for small-polaron formation. In this paper we attack the problem of the bipolaron in a disordered system by combining the EH method with the scaling theory of localization.

II. FORMALISM

The formalism follows closely that of our previous work on the question of the bipolaron in a periodic system,[4] but for completeness and clarity we repeat it here, in part. The total energy of the two-electron-plus-phonon system can be written as

$$E^{(2)}=\langle H_{\rm el}\rangle+E_s\int d^3r_1 d^3r_2\,|\psi(\vec{r}_1,\vec{r}_2)|^2 \times[\Delta(\vec{r}_1)+\Delta(r_2)] +\tfrac{1}{2}K\int d^3r\Delta^2(r)\,, \tag{1}$$

where $\psi(\vec{r}_1,\vec{r}_2)$ is the orbital part of the two-particle wave function and is symmetric with respect to the interchange $\vec{r}_1\leftrightarrow\vec{r}_2$. $H_{\rm el}$ is the sum of the one-electron energies and the Coulomb repulsion between the electrons. $\Delta(\vec{r})$ is the dilation of the lattice at $\vec{r}$. The electron-phonon interaction has been assumed to be of the deformation-potential type: $H_{e\text{-ph}}(\vec{r})=E_s\Delta(\vec{r})$. K is a proper combination of elastic constants. Minimizing the total energy with respect to the dilation $\Delta(\vec{r})$, we find that $\Delta(\vec{r})=-2E_s\rho(\vec{r})/K$, where

$$\rho(\vec{r})=\int d^3r_1\,|\psi(\vec{r},\vec{r}_1)|^2\,. \tag{2}$$

Substituting back into Eq. (1) we obtain

$$E^{(2)}=\langle H_{\rm el}\rangle-4A\int d^3r\,\rho^2(\vec{r})\,, \tag{3}$$

where $A=E_s^2/2K$.

We now force the two electrons to stay within a domain of linear dimension L. For a disordered system, we have the following L dependence of the various terms contributing to $E^{(2)}$. The band energy term, which was examined in detail in Ref. 3, behaves as

$$E_b=\frac{2Bg(L)}{\rho L^3}\,, \tag{4}$$

where B is a constant of the order of 100, ρ is the density of states (DOS) per unit volume, and $g(L)$, the dimensionless conductance,[5] is given by[3]

$$g(L)=\frac{1}{\pi^3}\left[\frac{1}{1+\eta'/L}+\frac{\pi}{2}\frac{L}{\xi}\right]. \tag{5}$$

The length ξ characterizes the largest extent of the amplitude fluctuation of the eigenfunction in a disordered system; beyond ξ the eigenfunction looks uniform. The inner length η' is of interatomic size, and it has been introduced in order to make the formula for E_b proportional to $1/L^2$ when L is equal or less to interatomic distances; in what follows we have chosen $\eta'=5a_{\rm B}\approx 2.65$ Å ($a_B=\hbar^2/me^2=0.529$ Å is the Bohr radius).

The lattice-mediated interaction [second term in Eq.

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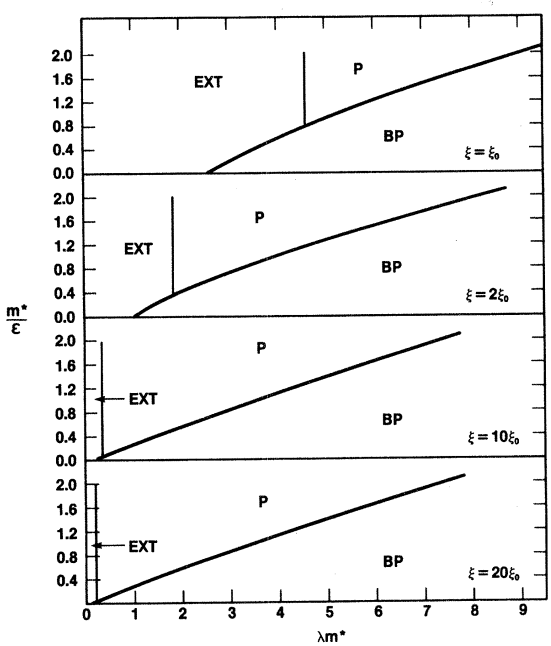

FIG. 1. Phase diagram in the plane $m^*/\epsilon, \lambda m^*$ indicating the regions of extended eigenstates ($l=\infty$), small polarons (positive U), and small bipolarons (negative U) for different values of ξ.

(3)] is proportional to

$$\int_0^L \rho^2(r) 4\pi r^2 dr \ .$$

If the two electrons are uncorrelated, i.e., $\psi(\vec{r}_1,\vec{r}_2)=\phi(\vec{r}_1)\phi(\vec{r}_2)$, we have immediately that $\rho^2(\vec{r})=|\phi(\vec{r})|^4$. In Ref. 3 we have developed some arguments based on the assumed fractal character of the eigenfunction ϕ and on numerical data for the participation ratio to estimate the integral of $|\phi|^4$. A more direct and physically transparent alternative way of obtaining the integral of $|\phi|^4$ is based upon the assumption[6] that the strongly fluctuating eigenfunctions above the mobility edge are the analogs of resonance states[7] in potential wells. This analogy (which works well for localized states[8]) allows one to prove[6] that

$$\int_0^L |\phi|^4 4\pi r^2 dr \sim \xi/\eta L^3$$

when $L \gg \xi$ and $\sim 1/\eta L^2$ when $L \ll \xi$. We have interpolated between these forms and we have fixed the overall proportionality constant from the requirement that the present results must reduce to those of the periodic case when the disorder disappears, i.e., when $\xi=\xi_0$, where ξ_0 is of interatomic size. In our explicit results below we have chosen $\xi_0=\eta'/2$. Therefore, the sum of the electron-phonon interaction and the polarization energy of the phonon is given by

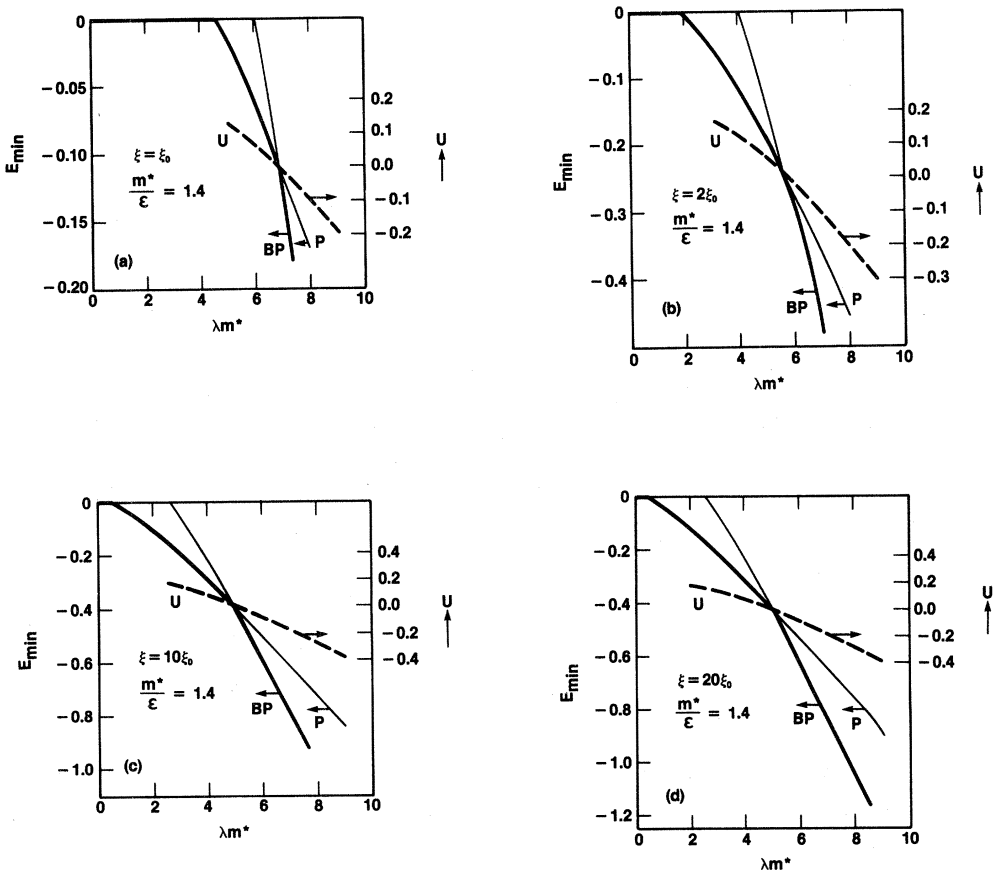

FIG. 2. Plot of $\epsilon_{\min}^{(2)}$ (BP solid line), $2\epsilon_{\min}^{(1)}$ (P solid line), and $U=\epsilon_{\min}^{(2)}-2\epsilon_{\min}^{(1)}$ (dashed line) vs λm^* for (a) $\xi=\xi_0$, (b) $\xi=2\xi_0$, (c) $\xi=10\xi_0$, and (d) $\xi=20\xi_0$ for $m^*/\epsilon=1.4$. $\xi_0=\eta'/2$ and $\eta'=5a_B$. The ground-state energy is denoted by a heavy solid line.

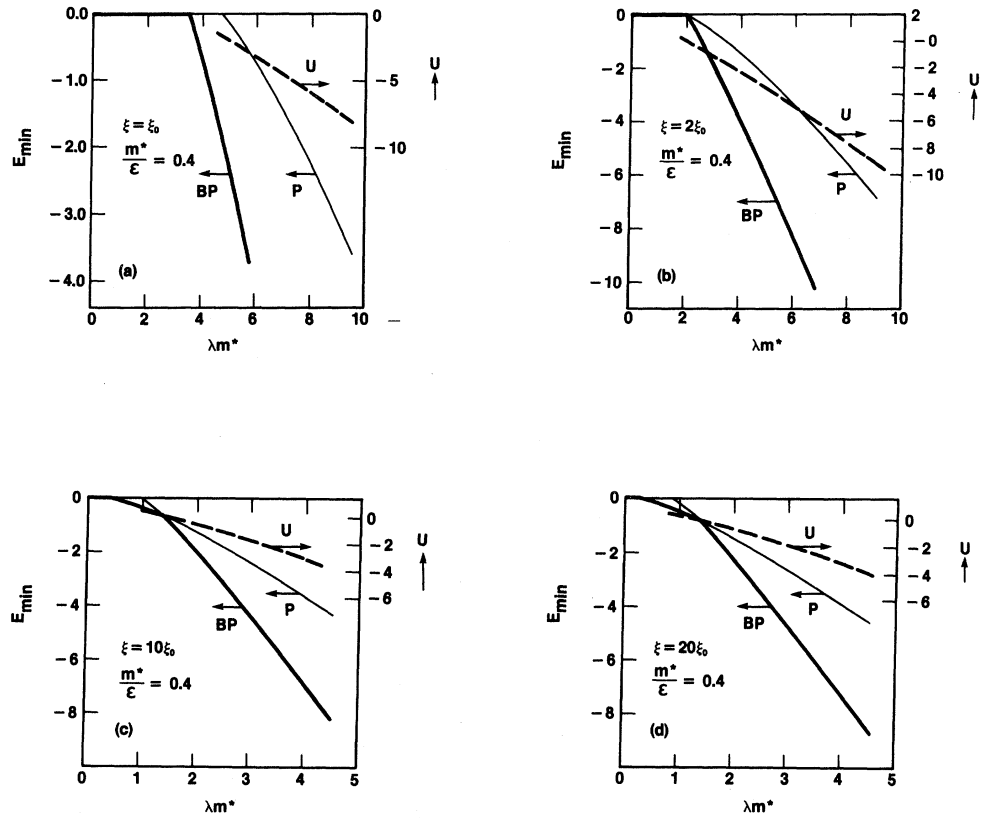

FIG. 3. Plot of $\epsilon^{(2)}_{\min}$ (BP solid line), $2\epsilon^{(1)}_{\min}$ (P solid line), and $U=\epsilon^{(2)}_{\min}-2\epsilon^{(1)}_{\min}$ (dashed line) vs λm^* for (a) $\xi=\xi_0$, (b) $\xi=2\xi_0$, (c) $\xi=10\xi_0$, and (d) $\xi=20\xi_0$ for $m^*/\epsilon=0.4$. $\xi_0=\eta'/2$ and $\eta'=5a_B$. The ground-state energy is denoted by a heavy solid line.

$$E_{\rm ph}=\frac{7.05A}{\eta' L^2(1+L/\xi)+\eta'^3}\ . \tag{6}$$

We have introduced $(\eta')^3$ in the denominator as a cutoff at atomic sizes. The presence of η' satisfies the obvious physical requirement that compressing the wave function below the interatomic distance does not increase further the lattice-mediated self-interaction, while it still increases the kinetic and Coulomb energies. The form of the lattice-mediated interaction in Eq. (6) for $L \gg \xi$ is essentially identical to that used in Ref. 3. However, for $\eta' \ll L \ll \xi$ the two forms are different. This difference is of no qualitative consequence since both forms produce the same enhancement, ξ/η', for large values of L. This enhancement combined with the reduction of the band energy by a factor of η'/ξ [see Eqs. (4) and (5)] is the mechanism by which the eigenstates with fluctuating amplitude tend to collapse to polarons or bipolarons even for weak electron-phonon coupling.

For the Coulomb interaction, we have used the expression $\gamma(L)/L$ valid for $L \gg \xi$ where no correlation is present. We have already shown[4] that the correlation (which appears for large L) does not change γ by a factor of more than 2. For $\xi < L$ the single potential-well analogy[6] produces an expression of the form $\gamma \ln(L/\eta')/L$. We have interpolated between these limits as follows:

$$E_{\rm Coulomb}=\frac{\gamma}{L}\left[\frac{1}{1+(\xi/L)^2}+\frac{(\xi/L)^2}{1+(\xi/L)^2}\ln\frac{L+\eta'}{\eta'}\right]\ . \tag{7}$$

We have found that Eq. (7) for the Coulomb interaction produces essentially the same results as the simple term $1/L$. Therefore, we adopt the γ/L on the Coulomb-interaction term, with γ fixed so that for $\xi=\xi_0$ we obtain the same results as in the periodic case.

Defining

$$\epsilon^{(2)}=\frac{E^{(2)}}{E_H}\frac{\epsilon^2}{m^*}\ , \tag{8}$$

$$l=\frac{L}{a_B}\frac{m^*}{\epsilon}\ , \tag{9}$$

$$\lambda^*=\frac{E_s^2}{2KE_Ha_B^3}\frac{m^{*2}}{\epsilon}\ , \tag{10}$$

$$\eta=\frac{\eta'}{a_B}\frac{m^*}{\epsilon}\ , \tag{11}$$

we can write the total energy for a disordered system as follows:

$$\epsilon^{(2)}=\frac{a(l)}{l^2}+\frac{2.2}{l}-\frac{7.05\lambda^*}{\eta l^2(1+l/\xi)+\eta^3}\ . \tag{12}$$

In the above formulas, $E_H=e^4m/\hbar^2\approx 27.2$ eV is the Hartree unit of energy, m^* is the ratio of the effective mass to the electronic mass, and ϵ is the dielectric constant. The quantity $a(l)$ is given by

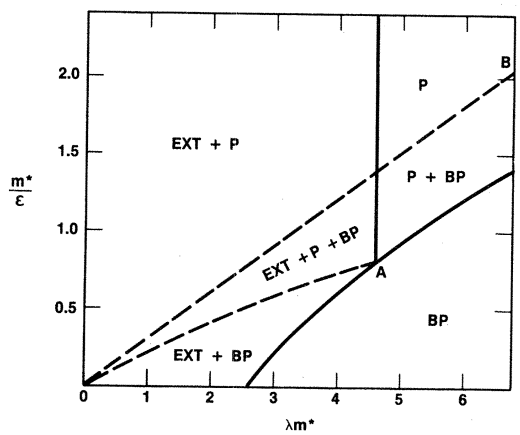

FIG. 4. Projection of the three-dimensional phase diagram on the $m^*/\epsilon,\lambda m^*$ plane. The lines of projection are plotted as dashed lines. OA is the locus of triple points and OB is the limit of the line separating the P and BP regions as $\xi\rightarrow\infty$ (see Fig. 1).

$$a(l)=\frac{2Bm^*}{\rho E_H a_B^3}\frac{a_B}{\eta'}\frac{\eta g(l)}{l} . \tag{13}$$

Substituting for m^* and ρ typical values corresponding to Si we find that $m^*/\bar{\rho}E_H a_B^3\approx 3$. Since both $\bar{\rho}$, the DOS per volume averaged over the band, and m^* are inversely proportional to the bandwidth, we expect that the approximate equality $m^*/\bar{\rho}E_H a_B^3\approx 3$ to be valid for most materials. In our explicit calculations we have chosen $2Bm^*a_B/\rho E_H a_B^3\eta'=7\pi^2$ (corresponding to a value of $B=57.6$) again by the criterion that our results coincide with those of the periodic case when $\xi=\xi_0$. It is worthwhile to point out that the above choices do not produce exactly the periodic expression for $\epsilon^{(2)}$ for all l. For example, for $\xi=\xi_0$ and $l\gg\xi_0$, Eqs. (12) and (13) yield $\epsilon^{(2)}=(7/l^2)+(2.2/l)-(3.53\lambda^*/l^3)$ as opposed to $\epsilon^{(2)}=(10/l^2)+(2/l)-(4\lambda^*/l^3)$ for the periodic case.[4] Given the uncertainties in the various parameters and the generic nature of our calculations, we consider those differences as unimportant for our purposes.

In our study of polaron formation in disordered media[3] as well as in the study of the bipolaron in periodic systems,[4] we found it useful to introduce a phonon coupling λ defined by the relation

$$\lambda=\frac{E_s^2}{2K}\bar{\rho} \tag{14}$$

similar to the quantity denoted by the same symbol in the theory of superconductivity. The relation between λ^* and λ is

$$\lambda^*=\frac{1}{a_B^3 E_H\bar{\rho}}\lambda\frac{m^{*2}}{\epsilon} . \tag{15}$$

In our subsequent calculations we have chosen $a_B^3E_H\bar{\rho}=0.1$, the value appropriate to Si, so that $\lambda^*=10\lambda m^{*2}/\epsilon$.

The energy of two well-separated electrons interacting with the lattice is

$$2\epsilon^{(1)}=\frac{a(l)}{l^2}-\left[\frac{7.05\lambda^*}{2}\right]\frac{1}{\eta l^2(1+l/\xi)+\eta^3} . \tag{16}$$

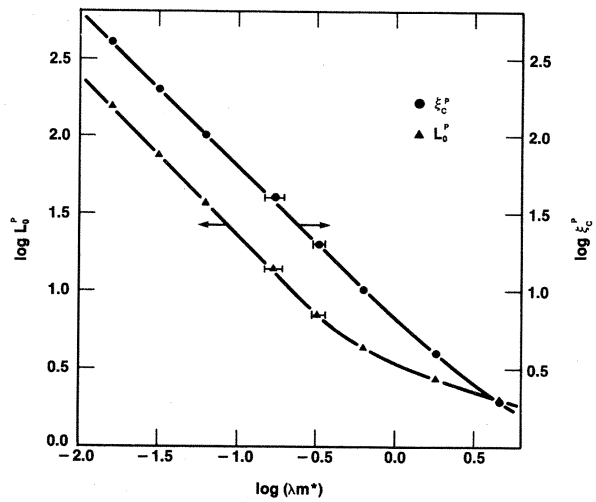

FIG. 5. Critical value $\xi_c^{\rm P}$ below which no polaron is formed as a function of λm^*. The initial value of the polaron size $L_0^{\rm P}$ is also plotted vs $\log(\lambda m^*)$. $m^*/\epsilon=1.0$. Here $\xi_c^{\rm P}$ and $L_0^{\rm P}$ are in units of $\xi_0=\eta'/2$ and $\eta'=5a_B$.

III. RESULTS AND DISCUSSION

The important parameters in our expressions for $\epsilon^{(2)}$ and $2\epsilon^{(1)}$ are the dimensionless ratio m^*/ϵ, which determines the length scale, and the product λm^*, which together with m^*/ϵ determine the relative strength of the lattice-mediated self- and mutual interaction and the correlation length ξ which is a measure of disorder above the mobility edge.

By minimizing the total energies $\epsilon^{(2)}$ and $2\epsilon^{(1)}$ with respect to l, we can find for a given set of parameters $(m^*/\epsilon,\lambda m^*,\xi)$ which configuration (two polarons, bipolaron, or two electrons in extended states) has the lowest energy. In Fig. 1 the $m^*/\epsilon,\lambda m^*$ phase diagram is shown for different values of ξ. For $\xi=\xi_0$, we reproduce by construction the phase diagram for the periodic case.[4] The main characteristic of this phase diagram is that for small λ and/or small m^* (i.e., wide band materials) no polarons or bipolarons are formed. For narrow band materials (large m^*) with small ϵ polaron formation is favored. On the other hand, for large ϵ and/or large λ, the ground state switches to bipolaron. As we approach the mobility edge and ξ increases the extended states are progressively occupying less and less space in the stability diagrams. Also, the tricritical point approaches the origin in the $m^*/\epsilon,\lambda m^*$ phase diagram. For disordered semiconductors m^* does not have a clear meaning, but its most likely value would be of the order of 1. ϵ is of the order of 10, and λ is of the order of 0.1 to 1. Therefore, we are near the λm^* axis since m^*/ϵ is less than 0.1. Our work suggests that there is only a very small region in which the polaron is stabler than the bipolaron.

In Figs. 2(a)–2(d) we plot the bipolaron and polaron minima as well as their difference U for $m^*/\epsilon=1.4$ and different ξ. The difference between the two minima can be interpreted as a renormalized U in the Hubbard sense: $U=E_{\min}^{(2)}-2E_{\min}^{(1)}$. U is positive (repulsive) when bipolarons are stabler and U is negative (attractive) when bipolarons are stabler. From Fig. 2(a) we see that as λm^* in-

creases the ground state starts from extended states ($l=\infty$) and then switches to polarons with a positive (repulsive) U. Finally, at a still higher value of λm^*, U becomes negative (attractive) and, consequently, the ground state is a small bipolaron. This sequence of events is expected on physical grounds, since increasing λm^* implies an increasing self-attraction which first overcomes the kinetic energy [when m^* is large (i.e., small kinetic energy) and ϵ small (i.e., large Coulomb repulsion)] to form polarons and then the Coulomb repulsion as well to form bipolarons. As we increase ξ [Figs. 2(b)—2(d)], there is no qualitative difference except that the value of λm^* at which extended states switch to polarons gets smaller and smaller. At the same time for a given value of λm^*, $|U|$ increases as ξ increases. On the other hand, for small values of m^*/ϵ, i.e., large kinetic energy and/or small Coulomb repulsion, as is seen in Fig. 3(a) for $m^*/\epsilon=0.4$ and $\xi=\xi_0$. The ground state switches directly from extended states to small bipolarons. U is negative for all values of λm^*. As we approach the mobility edge and ξ increases, as can be seen from Fig. 1 and Figs. 3(b)—3(d) the extended states for the small λm^* values transform to polarons and the tricritical point moves towards the origin in the $m^*/\epsilon,\lambda m^*$ phase diagram.

In Fig. 1 we have summarized our findings in a phase diagram of m^*/ϵ vs λm^* for different values of ξ. Actually it would be better if we could draw a three-dimensional phase diagram in the space $m^*/\epsilon,\lambda m^*$ and ξ. A projection of this three-dimensional phase diagram on the $m^*/\epsilon,\lambda m^*$ plane is shown in Fig. 4. To avoid confusion the lines which are projections are plotted as dashed lines. The line OA is the projection of the lines of the triple points. The line OB is the limit of the line separating the polaron region from the bipolaron region as $\xi\rightarrow\infty$ (see Fig. 1). The symbols in each region must be interpreted as follows: e.g., the EXT + P + BP region means that the states at any point in this region are extended for $\xi=\xi_0$ (periodic system). As disorder increases, i.e., as ξ increases a critical value ξ_c^{P} is passed beyond which polarons are the lowest-energy states. As ξ is increased further a second critical value ξ_c^{BP} is reached beyond which the ground state is bipolaron.

In Fig. 5 we plot the critical value ξ_c^{P} vs $\log(\lambda m^*)$ for $m^*/\epsilon=1$. In the same figure the size of the just-formed polaron L_0^{P} (corresponding to $m^*/\epsilon=1,\xi=\xi_c^{\mathrm{P}}$) is plotted against $\log(\lambda m^*)$. These results are qualitatively similar to our previous results shown in Fig. 2 of Ref. 3. For example, in the present case, as in Ref. 3, both ξ_c^{P} and L_0^{P} exhibit a power-law dependence on λ. However, in the present case both exponents are very close to -1:

$$\xi_c^{\mathrm{P}}=3.5\eta'(\lambda m^*)^{-1}\,, \tag{17}$$

$$L_0^{\mathrm{P}}=\eta'(\lambda m^*)^{-1} \tag{18}$$

while in the previous case the exponents for ξ_c^{P} and L_0^{P} were found to be equal to $-\frac{2}{3}$ and $-\frac{1}{2}$, respectively. Furthermore, in the present case the rather precipitous drop of ξ_c^{P} and L_0^{P} exhibited before is absent. As a matter of fact, L_0^{P} shows a tendency to saturate for large values of λm^*. These minor quantitative differences are due to the different form of the e-ph and phonon term used in the present work [compare Eq. (6) vs Eqs. (3)—(5) of Ref. 3], and we think that Eq. (6) for E_{ph} is a better choice than that of Ref. 3. The differences especially for large λm^* are insignificant, since both expressions give L_0^{P} of the order of interatomic distance for $\lambda m^*\gtrsim 1$ as expected. The saturation feature exhibited by L_0^{P} in Fig. 5 at large values of λm^* is a desirable one. However, one must not expect from the present theory to describe in detail accurately what is happening as the polaron or bipolaron reaches atomic sizes, since such a description requires detailed input regarding the atomic structure of each material. In conclusion, we would like to point out that the main results of this work are summarized in Fig. 1.

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