Stability of multipolaron matter

M. A. Smondyrev
Laboratory of Theoretical Physics, Joint Institute for Nuclear Research, 141980 Dubna, Russia

G. Verbist,* F. M. Peeters, and J. T. Devreese†
Department of Physics, Universiteit Antwerpen (UIA), Universiteitsplein 1, B-2610 Antwerpen, Belgium
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The phase diagram for multipolaron formation in two and three dimensions is obtained in the strong-coupling limit. Results are presented for the multipolaron energy, mass, radius, and number of virtual phonons surrounding the multipolaron.

Recently there is renewed interest in strong electron-phonon coupling problems. This is mainly fueled by (i) the discovery of the high-T_c superconductors,[1] which are oxides and highly polar, and (ii) problems of excitation transfer by electrons[2] in, e.g., polymers, polar liquids, ionic conductors, etc. Previously we investigated[3,4] the formation of bipolarons, which is one of the candidates[5,6] which may be responsible for superconductivity in these materials. In the present paper we extend our previous analysis to the study of the formation of multipolarons. In view of the inherent complexity of this problem we limit ourselves for the moment to the strong-coupling case (see, e.g., Refs. 7–9). Related to the present problem we should mention the paper by Degani and Hipólito,[10] who investigated the formation of dimples consisting of multielectrons above the liquid helium film. The latter problem is analogous to a two-dimensional acoustical polaron problem[11] while in the present work we will study the two- and three-dimensional optical Fröhlich polaron.

In a recent paper[12] a system of n charged spinless distinguishable particles interacting with a quantized phonon field was studied. Such a system is described by the generalized Fröhlich Hamiltonian:

$$H=\sum_{j=1}^{n}\frac{\mathbf{p}_j^2}{2m}+\sum_{j=1}^{n}\sum_{l=1}^{j-1}V(|\mathbf{r}_j-\mathbf{r}_l|)+\sum_{\mathbf{k}}\hbar\omega_{\mathbf{k}}a_{\mathbf{k}}^{\dagger}a_{\mathbf{k}} +\sum_{j=1}^{n}\sum_{\mathbf{k}}\left(V_{\mathbf{k}}a_{\mathbf{k}}e^{i\mathbf{k}\cdot\mathbf{r}_j}+V_{\mathbf{k}}^{*}a_{\mathbf{k}}^{\dagger}e^{-i\mathbf{k}\cdot\mathbf{r}_j}\right) , \quad (1)$$

where $\mathbf{r}_j$ and $\mathbf{p}_j$ are, respectively, the coordinate and the momentum of the jth particle, $a_{\mathbf{k}}$ is the amplitude of the phonon mode with momentum $\mathbf{k}$ and energy $\hbar\omega_{\mathbf{k}}$, and $V(r)=U/r$ is the Coulomb repulsion potential. A similar Hamiltonian was studied in Refs. 13 and 14. For a Fröhlich optical polaron we have

$$\omega_{\mathbf{k}}=\omega_{\text{LO}} ,\qquad V_{\mathbf{k}}=-i\hbar\omega_{\text{LO}}\sqrt{\frac{4\pi\alpha}{k^2V}\sqrt{\frac{\hbar}{2m\omega_{\text{LO}}}}} , \quad (2)$$

where V is the volume of the system and α is the dimensionless coupling constant

$$\alpha=\frac{1}{\hbar\omega_{\text{LO}}}\frac{e^2}{2}\left(\frac{1}{\epsilon_\infty}-\frac{1}{\epsilon_0}\right)\sqrt{\frac{2m\omega_{\text{LO}}}{\hbar}} . \quad (3)$$

Here e is the electron charge, ϵ_∞ and ϵ_0 are the high-frequency and static dielectrical constants, respectively. In the framework of a Feynman-type path-integral method (but with a more simple trial-action) the effective mass M_n and an upper bound to the ground-state energy E_n of a system of n polarons bound to each other, were obtained in Ref. 12:

$$E_n=\frac{3}{4}[(n-1)\Omega+\Omega_n]+\frac{n(n-1)}{2}U\sqrt{\frac{2m\Omega}{\pi\omega_{LO}}} -\frac{n\alpha}{\sqrt{\pi}}\int_0^\infty ds\, e^{-s}[\Phi^{-1/2}(s)+(n-1)\Psi^{-1/2}(s)], \quad (4)$$

$$M_n/m=n\left\{1+\frac{\alpha}{3\sqrt{\pi}}\int_0^\infty ds\, s^2e^{-s}[\,\Phi^{-3/2}(s) +(n-1)\Psi^{-3/2}(s)]\right\}, \quad (5)$$

where

$$\Phi_n(s)=\frac{n-1}{n\Omega}(1-e^{-\Omega s})+\frac{1}{n\Omega_n}(1-e^{-\Omega_n s}),$$
$$\Psi_n(s)=\frac{1}{n\Omega}(n-1+e^{-\Omega s})+\frac{1}{n\Omega_n}(1-e^{-\Omega_n s}), \quad (6)$$

and Ω,Ω_n are the variational parameters. The variational calculations give us in the strong-coupling limit

$$\mathcal{E}_n=\frac{E_n}{nE_1}=-n^4F_n^{3/2}\frac{1+(n-1)\sqrt{F_n}}{(n-1+\sqrt{F_n})^3} ,$$
$$E_1=\frac{\alpha^2}{3\pi}\hbar\omega_{\text{LO}} ,$$
$$\mathcal{M}_n=\frac{M_n}{nM_1}=n^{10}\frac{F_n^3}{(n-1+\sqrt{F_n})^6} , \quad (7)$$
$$M_1=\frac{16\alpha^4}{81\pi^2}m .$$

Here the n-polaron energy E_n and mass M_n are scaled by n times the single polaron energy E_1 and mass M_1 in the strong-coupling limit. The quantity F_n in Eqs. (7), which depends on the number of particles in the system, serves as a variational parameter and follows from

$$\zeta = n^3 \frac{(1-F_n)^2}{(n-1+\sqrt{F_n})^3} , \quad 0 < F_n < 1 , \tag{8}$$

where ζ is the ratio of the characteristic Coulomb and polaron energies:

$$\zeta = \frac{mU^2}{2\hbar^3 \omega_{\rm LO} \alpha^2} . \tag{9}$$

Note that a solution of Eq. (8) exists when $\zeta < (\frac{n}{n-1})^3$ and under this condition the energy of a n-polaron state becomes negative.

Following Ref. 15 the average number of virtual phonons can be obtained from the ground-state energy E as

$$N = \left(\frac{1}{\hbar} \frac{\partial}{\partial \omega_{\rm LO}} - \frac{3}{2} \frac{\alpha}{\hbar \omega_{\rm LO}} \frac{\partial}{\partial \alpha} \right) E , \tag{10}$$

which is still valid for the present n-polaron problem. With this formula we obtain from Eqs. (7) and (8)

$$\mathcal{N}_n = \frac{N_n}{n N_1} = n^4 \frac{F_n}{(n-1+\sqrt{F_n})^2} , \qquad N_1 = \frac{2\alpha^2}{3\pi} , \tag{11}$$

where the average number of phonons N_n is scaled by n times the single-polaron expression N_1 in the strong-coupling limit.

Applying the Feynman-Hellmann theorem an approximate expression for the multipolaron radius R_n can be derived. Differentiation of Eqs. (7)–(9) with respect to U leads to

$$\mathcal{R}_n^{-1} = \frac{R_1}{R_n} = n^{5/2} \frac{F_n}{(n-1+\sqrt{F_n})^{3/2}} , \tag{12}$$

where R_1 is the single-polaron radius

$$R_1 = R_H^{(3)} = \frac{3\pi}{2\sqrt{2}\alpha} \sqrt{\frac{\hbar}{m\omega_{\rm LO}}} . \tag{13}$$

Note that this definition is equivalent to

$$R_n^{-1} = \frac{2}{n(n-1)} \left\langle \sum_{i<j} \frac{1}{|\mathbf{r}_i - \mathbf{r}_j|} \right\rangle . \tag{14}$$

Another possible definition of the multipolaron radius

$$R_n = \left(\frac{2}{n(n-1)} \left\langle \sum_{i<j} (\mathbf{r}_i - \mathbf{r}_j)^2 \right\rangle \right)^{1/2} , \tag{15}$$

results in the same Eq. (12) but with a slightly different expression for the single-polaron radius

$$R_1 = R_F^{(3)} = \frac{3\sqrt{3\pi}}{2\alpha} \sqrt{\frac{\hbar}{m\omega_{\rm LO}}} , \tag{16}$$

which is the strong-coupling limit within the Feynman approximation. The distinction between the above two definitions of polaron radii was discussed in Ref. 16.

Neglecting the Coulomb repulsion ($\zeta = 0$, $F_n = 1$), we readily obtain

$$\mathcal{E}_n = -n^2 , \ \mathcal{M}_n = n^4 , \ \mathcal{N}_n = n^2 , \ \mathcal{R}_n = \frac{1}{n} . \tag{17}$$

In Ref. 12 it was shown that such a n^3 dependence of the energy E_n appears not only in a variational upper estimate, but also in a lower bound to the ground-state energy as well. It implies that a multipolaron system, in the absence of Coulomb repulsion, is unstable: polarons collapse into macroscopic clusters as was already noted in Ref. 3. Evidently, this is true for distinguishable particles but the situation will be completely different when Fermi statistics are taken into account. When the Coulomb repulsion is included the multipolaron system can be stabilized even in the boson case, as we shall demonstrate in the following. In real systems the electrons repel each other through the Coulomb potential $V(r) = U/r$ with

$$U = \frac{e^2}{\epsilon_\infty} , \tag{18}$$

and Eq. (9) requires the form

$$\zeta = \frac{1}{(1-\eta)^2} , \tag{19}$$

where $\eta = \epsilon_\infty/\epsilon_0$ is the conventional notation for the ratio of the high- to zero-frequency dielectrical constants. Equation (19) implies that the physical region is restricted to $\zeta > 1$, or equivalently $U < \alpha(2\hbar^3\omega_{\rm LO}/m)^{1/2}$.

In Fig. 1 we show (a) the multipolaron ground-state energy per electron in units of $\hbar\omega_{\rm LO}$, (b) the multipolaron effective mass per electron in units of M_1, (c) the multipolaron radius in units of R_1, and (d) the number of virtual phonons per electron in units of N_1, as a function of the repulsion for $\alpha = 10$ and different numbers of electrons in the multipolaron state: $n = 1$ (polaron), 2 (bipolaron), 3, 4, ..., 10. A multipolaron with n electrons will be stable if its energy is less than the sum of the energies of any possible combination of multipolarons consisting of a smaller number of particles

$$\mathcal{E}_n < \sum_{i=1}^{m} \frac{n_i}{n} \mathcal{E}_{n_i} , \tag{20}$$

where

$$n \geq 2 , \ m \in [2,n] , \ n_i \in [1,n] , \text{ and } \sum_{i=1}^{m} n_i = n . \tag{21}$$

Otherwise the n-polaron state will decompose into two or more separate smaller multipolarons. These numerical results were obtained directly from Eqs. (4)–(6) without using the asymptotic strong-coupling limit. The corresponding phase diagram is shown in Fig. 2.

When the system consists of two polarons (i.e., $n = 2$) we found that in the present approximation a bipolaron could exist if $\zeta < 8$, namely its energy is negative and its radius is finite. But this state is a metastable one; only

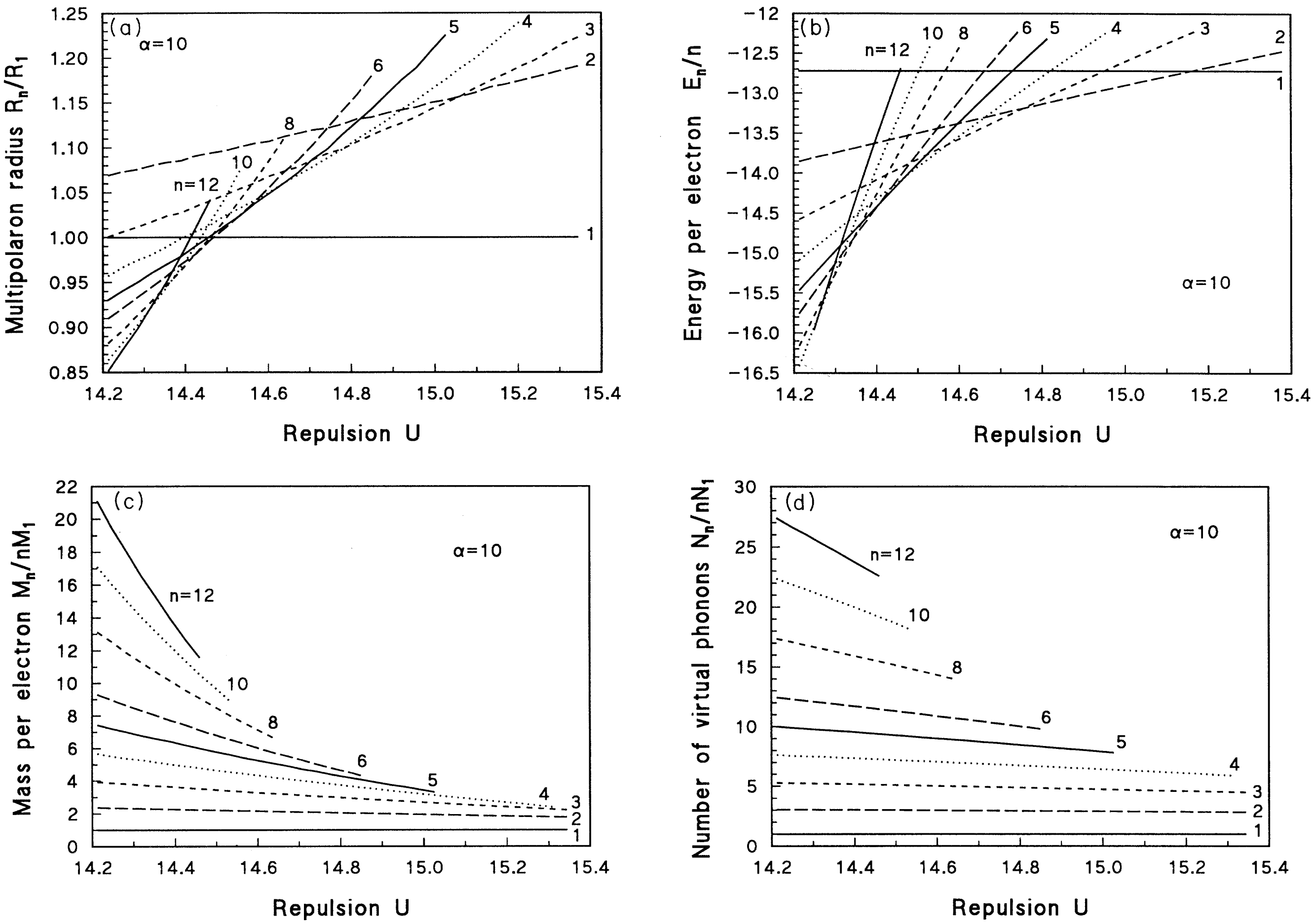

FIG. 1. Multipolaron ground-state energy per electron (a) in units of $\hbar\omega_{\mathrm{LO}}$ as a function of the repulsion for $\alpha = 10$. The effective mass per electron relative to the one-polaron mass (b), radius relative to one polaron radius (c), and the number of virtual phonons per electron relative to that of one polaron (d).

at $\zeta < \zeta_2 = 1.1778$ the bipolaron energy becomes lower than the total energy of two separate polarons: for $\zeta = \zeta_2$ $\mathcal{E}_2 = -1$ and this value decreases to $\mathcal{E}_2 = -1.148$ at the limiting point $\zeta = 1$. At the critical point $\zeta = \zeta_2$ the bipolaron mass and the average number of phonons per particle jump from $\mathcal{M}_2 = 1$ and $\mathcal{N}_2 = 1$, for two separate polarons, to $\mathcal{M}_2 = 1.72$ and $\mathcal{N}_2 = 1.90$, respectively. At the limiting point $\zeta = 1$ these quantities reach the values $\mathcal{M}_2 = 2.17$ and $\mathcal{N}_2 = 2.06$. The average separation of two independent polarons is infinity, but in the bipolaron state $\mathcal{R}_2 = 1.20$ at $\zeta = \zeta_2$ and $\mathcal{R}_2 = 1.10$ at $\zeta = 1$.

For $n = 4$ we note the following peculiarity: for any value of ζ the state of 3-polarons together with a separate single polaron is energetically less favorable than a state with two bipolarons or a bound state of 4-polarons.

Now we consider the important case of very many polarons in a crystal (i.e., $n \gg 1$). In order to find the critical points ζ_k between the phases of $(k-1)$-polarons and k-polarons one has to compare their energies per particle, that is to solve Eqs. (8) for $n = k - 1$ and $n = k$ at the same value $\zeta = \zeta_k$ and the equation $\mathcal{E}_{k-1} = \mathcal{E}_k$. The numerical data for the first five critical points are presented in Table I.

In the limit of large k values one obtains

$$\zeta = 1 + \sqrt{\frac{3}{2}}\frac{1}{k^{3/2}} + \mathcal{O}\left(\frac{1}{k^2}\right) , \tag{22}$$

and the formation of k-polarons is only possible in a narrow interval near the limiting point $\zeta = 1$. The polaron

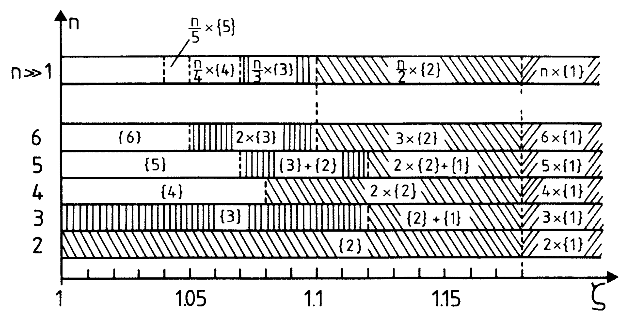

FIG. 2. Phase diagram for a finite number of electrons inside the multipolaron as a function of $\zeta = U^2/2\alpha^2$ for $\alpha = 10$. $n' * \{N\}$ indicates that n' multipolarons consisting each of N electrons are stable.

TABLE I. Polaron characteristics at the critical points ζ_k.

k	ζ_k	$\mathcal{E}_k$	$\mathcal{M}_{k-1}$	$\mathcal{M}_k$	$\mathcal{N}_{k-1}$	$\mathcal{N}_k$	$\mathcal{R}_{k-1}$	$\mathcal{R}_k$
2	1.178	-1.00	1.00	1.72	1.00	1.90	1.00	1.20
3	1.100	-1.06	1.90	2.71	1.97	2.90	1.16	1.14
4	1.068	-1.12	2.95	3.85	2.98	3.95	1.11	1.10
5	1.051	-1.16	4.11	5.09	4.04	5.03	1.08	1.06
6	1.040	-1.20	5.37	6.41	5.12	6.14	1.04	1.03

characteristics at the limiting point $\zeta = 1$ are given in Table II for different numbers of electrons in the multipolaron cluster.

In the large n limit we obtain the following expressions:

$$\begin{aligned}
\mathcal{E}_n &= -\frac{9}{4} + 3\sqrt{\frac{3}{2n}} - \frac{27}{4n} + \mathcal{O}\left(\frac{1}{n^{3/2}}\right) , \\
\mathcal{M}_n &= \frac{27n}{8} - \frac{81}{8}\sqrt{\frac{3n}{2}} + \frac{81}{2} + \mathcal{O}\left(\frac{1}{\sqrt{n}}\right) , \\
\mathcal{N}_n &= \frac{3n}{2} - \frac{3}{2}\sqrt{\frac{3n}{2}} + \frac{15}{4} + \mathcal{O}\left(\frac{1}{\sqrt{n}}\right) , \\
\mathcal{R}_n &= \frac{3}{2} - \frac{3}{2}\sqrt{\frac{3}{2n}} + \frac{3}{n} + \mathcal{O}\left(\frac{1}{n^{3/2}}\right) .
\end{aligned} \tag{23}$$

It is interesting to note that the binding energy per particle remains finite in the $n \to \infty$ limit even at the limiting point $\zeta = 1$. Also the radius of such a multipolaron is finite in this limit. Both are a consequence of the fact that the Coulomb repulsion prevents the collapse of the multipolaron. But the mass and the average numbers of phonons per particle increase linearly with n. This implies that the multipolaron tends to be more localized with increasing n. It is interesting to note that the value of the multipolaron mass *per virtual phonon* is finite at large n

$$\frac{M_n}{N_n} = \frac{\mathcal{M}_n}{\mathcal{N}_n}\frac{M_1}{N_1} = \frac{2\alpha^2}{3\pi}m\left[1 - \sqrt{\frac{6}{n}} + \frac{13}{2n} + \mathcal{O}\left(\frac{1}{n^{3/2}}\right)\right]. \tag{24}$$

All the above expressions were derived for bulk [three-dimensional (3D)] polarons. In Refs. 4 and 17 it was shown that within the Feynman-type approximation there exists a simple relation between polaron characteristics in two and three dimensions: the scaling

$$\omega_{\rm LO} \to \frac{2}{3}\omega_{\rm LO} , \; \alpha \to \frac{3\pi}{4}\alpha , \; U \to \frac{\pi\sqrt{6}}{4}U , \tag{25}$$

converts the 3D-polaron energy and mass into that of a 2D polaron. Such a scaling influences only the properties of a single polaron

$$\begin{aligned}
E_1^{(2D)} &= -\hbar\omega_{\rm LO}\frac{\pi\alpha^2}{8} , \\
M_1^{(2D)} &= m\frac{\pi^2\alpha^4}{16} , \\
N_1^{(2D)} &= \frac{\pi\alpha^2}{4} , \\
R_H^{(2D)} &= \frac{2\sqrt{2}}{\pi\alpha}\sqrt{\frac{\hbar}{m\omega_{\rm LO}}} , \\
R_F^{(2D)} &= \frac{2\sqrt{2}}{\sqrt{\pi}\alpha}\sqrt{\frac{\hbar}{m\omega_{\rm LO}}} ,
\end{aligned} \tag{26}$$

and all the formulas for the relative multipolaron characteristics ($\mathcal{E}_n, \mathcal{M}_n, \mathcal{N}_n, \mathcal{R}_n$) which were referred to the single-polaron results will remain the same. As a consequence, the 3D stability analysis also applies in 2D and the ranges of ζ values, where the different multipolaron phases exist, are the same. This is a result of the strong-coupling limit considered in the present approximation. Please note that in the figures we took the repulsion U dimensionless while above it has dimensions of energy/length. As a consequence the numerical results in the figures for U/α are the identical in 2D and 3D.

To study the intermediate coupling region we use Eqs. (4)–(6). Our results are summarized in Figs. 3(a) and 3(b), which represent the most stable multipolaron, i.e., the one with the lowest energy per electron (E_n/n), for a given value of the coupling constant α versus the scaled repulsion ζ. It is only in the limit of an infinite number of electrons that all types of multipolarons ($n = 1, 2, \ldots$) appear. If the total number of electrons is finite [e.g., $n = 24$ in Fig. 3(a)] not all combinations are possible which are compatible with our example of $n = 4$ in the strong-coupling regime. From Fig. 3(b) it is seen that the system has a tendency to allow for multipolarons which are the most stable in the infinite-number limit with the supplementary condition that the quotient

TABLE II. Polaron characteristics at the limiting point $\zeta = 1$.

n	$\mathcal{E}_n$	$\mathcal{M}_n$	$\mathcal{N}_n$	$\mathcal{R}_n$
2	-1.148	2.170	2.055	1.103
3	-1.241	3.518	3.163	1.041
4	-1.308	4.997	4.308	1.000
5	-1.361	6.581	5.479	0.972
6	-1.404	8.252	6.673	0.949
⋮	⋮	⋮	⋮	⋮
100	-1.940	245.053	134.819	0.745

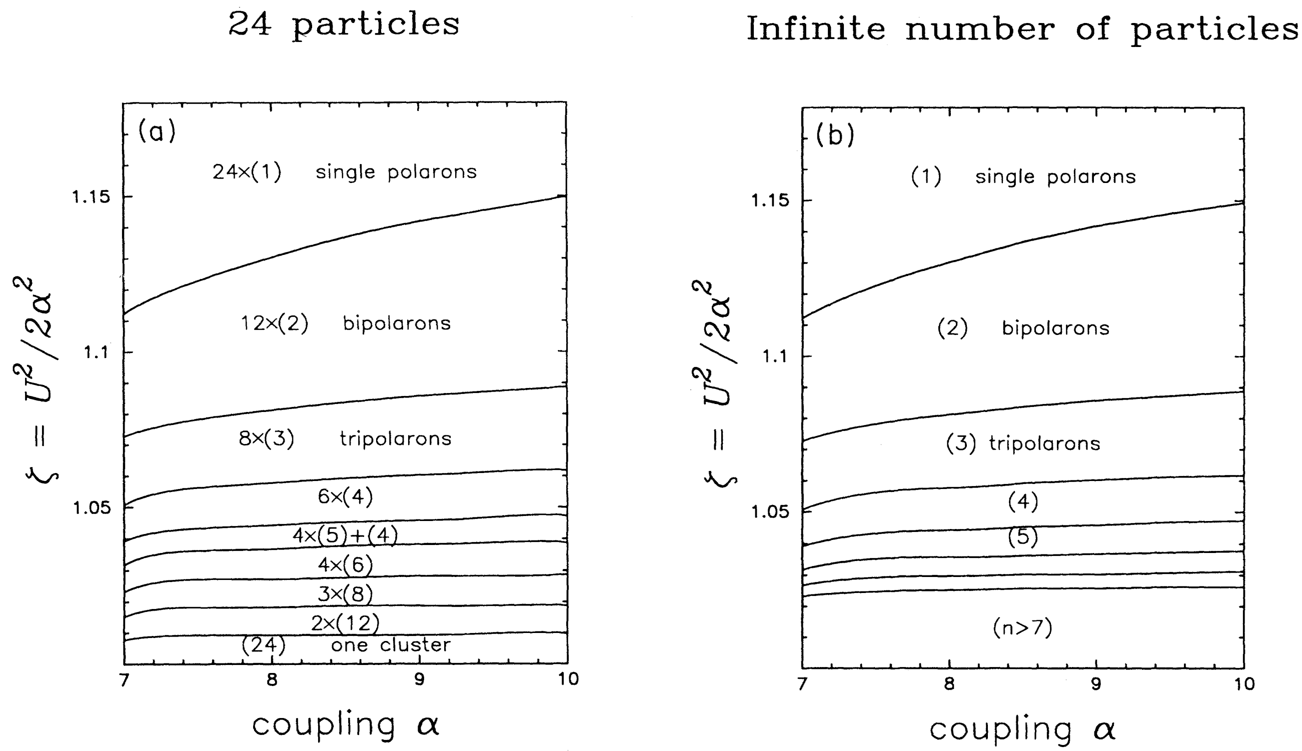

FIG. 3. Phase diagram in the (ζ, α) plane for multipolaron formation for (a) a system consisting of 24 electrons and (b) a system with an infinite number of electrons.

of the total number by the order of this multipolaron is (approximately) a natural number. The cluster of polarons has a natural tendency to form n multipolarons, where n has the lowest $\mathcal{E}_n$ for specified α and $U(\alpha)$. For a finite number, e.g., total number $N = 24$, it might not always be possible to realize this: suppose $n = 10$ has the lowest $\mathcal{E}_n$; then we can make two 10-polarons and one 4-polaron. However, the energy associated with this configuration "2*(10)+(4)" is always higher than either "3*(8)" or "2*(12)." Consequently it is not realized. Therefore, configurations of the type "p*(q)" are the most stable, meaning that the divisors (q) of N will appear. Possible exceptions are q values which are not too different from a divisor. For $N = 24$, the latter case is realized in the configuration "4*(5)+4." In both Figs. 3(a) and 3(b) we note that the dependences on α are weaker for higher-order multipolarons.

To conclude, we have studied the problem of electron clustering due to interaction with optical phonons. This leads to a quasiparticle which is called the multipolaron. We calculated the phase diagram for multipolaron formation for a system of a finite and an infinite number of electrons.

Although we did not take into account the Fermi-Dirac statistics for the electrons, we found that the Coulomb repulsion alone can already stabilize the cluster and prevent it from collapsing. This is what one also expects for Fermi particles even in the absence of the repulsion.

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*Present address: Koninklijke/Shell Laboratorium, Postbus 3003, 1003 AA, Amsterdam, The Netherlands.
†Also at University of Antwerp (RUCA), B-2020 Antwerpen, Belgium; and Eindhoven University of Technology, NL-5600 MB Eindhoven, The Netherlands.
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