Formation of polaron clusters

C.A. Perroni$^{1,2}$, G. Iadonisi$^{1,2}$, and V.K. Mukhomorov$^3$

$^1$Coherentia-INFM, UdR di Napoli, via Cinthia 80126 Naples, Italy
$^2$Dipartimento di Scienze Fisiche, Università "Federico II" di Napoli, via Cinthia 80126 Naples, Italy
$^3$Agrophysical Institute, St. Petersburg 195220, Russia

The formation of spherical polaron clusters is studied within the Fröhlich polaron theory. In a dilute polaron gas, using the non-local statistical approach and the polaron pair interaction obtained within the Pekar strong coupling theory, the homogeneous phase results to be unstable toward the appearance of polaron clusters. The physical conditions of formation for the clusters are determined calculating the critical values of electron-phonon interaction for which bound states in the collective polaron potential develop. Finally the sequence in the filling of the states is found and the stability of the clusters is assessed.
I. INTRODUCTION

In the last years the presence of strong electron-phonon coupling and polaronic effects has been pointed out by many experimental results in several compounds, such as high-temperature cuprate superconductors,\(^1\) colossal magneto-resistance manganites,\(^4\) nickelates and quasi-1D materials organic conjugated polymers.\(^3\) Furthermore it has been debated if the electron-phonon interaction can give rise in perovskite oxides to charge-ordered states or to more complex electronic phases such as stripes, strings or clustered states.\(^4\)

The large amount of experimental data has renewed the interest in studying simplified electron-phonon coupled systems of the Holstein\(^5\) or Fröhlich\(^6\) type. The formation of the polaron have been long studied in the frame of the Fröhlich model, where the polar long-range interaction between electronic and ionic charges is taken into account and the medium is considered continuous. For its relation to theories regarding cuprate superconductors, large attention has been devoted to the formation of the bipolaron (bound state of two polarons), establishing the range of the values of the electron-phonon coupling constant and of the dielectric parameters of medium which allow its existence.\(^7\) Also the binding energy, the effective mass, its internal structure and optical features have been studied.\(^8\)–\(^12\) Actually many methods have been used to study the bipolaron formation in the Fröhlich scheme: Lee-Low-Pines approach for intermediate values of the electron-phonon coupling constant,\(^9\) Pekar polaron strong coupling theory,\(^8\)\(^,\)\(^11\)\(^,\)\(^12\) and path-integral technique.\(^10\) They give the possibility to define an effective polaron-polaron potential, which is repulsive both at large and small distance between the particles, while it is attractive at intermediate distance. This polaron-polaron interaction has been used as starting point for many-body calculations finding that, for densities smaller than those typical of metals, the many-polaron system exhibits a charge density instability in the intermediate coupling regime.\(^13\)

A related research activity concerns the study of the conditions under which electronic or polaronic Wigner crystals,\(^14\)\(^,\)\(^15\) polaron molecules or clusters\(^16\) and strings\(^17\) can form. Indeed in the regime of very low densities the Wigner crystal of electrons can transform into a polaronic crystal by increasing the electron-phonon coupling.\(^14\) However increasing the density at strong electron-phonon coupling the Wigner crystal of polarons becomes unstable.\(^15\)

Such an instability suggests that novel types of electronic or polaronic structures such as clusters, molecules or strings can be stabilized by a strong electron-phonon interaction. Actually the molecules can arise at conditions determined by the structure of an effective interaction at short and long distances.\(^16\) Their behavior is very quantum, and they can assume a stringed form. It has been suggested that in perovskite oxides, such as manganites and cuprates, these molecules could represent the intermediate step of more complex structures such as stripes.\(^17\) Finally the electronic and ionic structure of Metal-Ammonia solutions\(^18\)\(^,\)\(^19\) represents a system where polaronic clusters can be actually observed.

In this work we start from the knowledge of the effective polaron-polaron interaction within the Pekar strong coupling theory.\(^8\)\(^,\)\(^9\)\(^,\)\(^11\)\(^,\)\(^22\) Using the non-local statistical approach,\(^12\)\(^,\)\(^23\) we show that in the homogeneous phase the mode due to the collective polaron potential is unstable suggesting that polaron clusters can form in the system. Next we show that there is a range of values of the electron-phonon interaction and of the static and high frequency dielectric constants which allow the formation of clusters with a number of polarons larger than two. Finally we discuss some features of the cluster such as its radius and its stability.

In sect. II we discuss the basic equations; in sect. III we analyze the collective excitations of the homogeneous polaron phase and its instability due to the attractive interaction between polarons; in sect. IV we indicate the conditions for which the polaron cluster forms, we discuss the shell structure in the cluster and finally we study the stability of the polaron clusters.

II. BASIC EQUATIONS

In the system we have two types of particles, the polarons and the ions, with distribution functions \(f_p(\vec{r}, \vec{v}, t)\) and \(f_i(\vec{r}, \vec{v}, t)\), respectively, in the single-particle phase space. In the non-local and non-linear Vlasov kinetic equations\(^22\) the distribution functions \(f_p(\vec{r}, \vec{v}, t)\) and \(f_i(\vec{r}, \vec{v}, t)\) are solutions of the equations

\[
\frac{\partial f_p(\vec{r}, \vec{v}, t)}{\partial t} + \vec{v} \cdot \nabla_r f_p(\vec{r}, \vec{v}, t) - \frac{1}{m_p} \nabla_r \left[U(\vec{r}, t) - e \Phi(\vec{r}, t)\right] \cdot \nabla_v f_p(\vec{r}, \vec{v}, t) = 0
\]  

\[
\frac{\partial f_i(\vec{r}, \vec{v}, t)}{\partial t} + \vec{v} \cdot \nabla_r f_i(\vec{r}, \vec{v}, t) - \frac{e}{m_i} \nabla_r \Phi(\vec{r}, t) \cdot \nabla_v f_i(\vec{r}, \vec{v}, t) = 0,
\]

where \(m_p\) and \(m_i\) are the effective masses of polaron and ion, respectively, \(e\) is the electron charge, and \(U(\vec{r}, t)\) is the collective self-consistent potential.
with the kernel $K$ indicating the polaron-polaron potential depending only on the relative distance between particles. The distribution function $f_p$ is determined not only by the polaron collective potential $U$ but also by the electrostatic potential $\Phi$ arising from the non-punctual compensation between the polaron and ionic charges. Indeed the potential $\Phi$ satisfies the Poisson equation

$$\Delta \Phi(\vec{r}, t) = -\frac{4\pi e}{\epsilon_s} \rho(\vec{r}, t),$$

where the density $\rho(\vec{r}, t)$ is defined as

$$\rho(\vec{r}, t) = \rho_i(\vec{r}, t) - \rho_p(\vec{r}, t) = \int d\vec{v} f_i(\vec{r}, \vec{v}, t) - \int d\vec{v} f_p(\vec{r}, \vec{v}, t).$$

We note that the force acting on the ions is related only to the electrostatic potential $\Phi$ screened by the static dielectric constant $\epsilon_s$.

In order to solve the Vlasov equations, the polaron-polaron potential $K$ has to be specified. We use the potential $K$ obtained within the Pekar strong coupling bipolaron theory\textsuperscript{8,11,12,24} which has been adapted in order to find reliable results in the intermediate to strong coupling regime. This polaron-polaron potential is attractive at intermediate distances, this behaviour resulting by the Fröhlich interaction and effects of quantum mechanical exchange and inter-electron correlations. Moreover the potential depends on the ratio $\epsilon^*/\epsilon_{\infty}$, where $\epsilon^*$ is defined through the equation $1/\epsilon^* = 1/\epsilon_{\infty} - 1/\epsilon_s$, with $\epsilon_{\infty}$ high frequency dielectric constant. In Fig. 1 we show the potential $K$ for different values of the ratio $\epsilon^*/\epsilon_{\infty}$ when the bipolaron is in its singlet ground-state and the asymptotic energy of the two free polarons has been subtracted. Throughout the paper, the values 1.10, 1.08, 1.05, 1.02 and 1.00 are used for the ratio $\epsilon^*/\epsilon_{\infty}$, i.e. the ratio $\epsilon_s/\epsilon_{\infty}$ varies from 10 to infinity.

The potential $K$ obtained within the Pekar strong coupling theory can be approximated by the following analytical expression

$$K(r) = 2\alpha^2 \hbar \omega_0 \left[ \frac{(\epsilon^*/\epsilon_{\infty} - 1)a^*_0}{r} + K_1(r)e^{-\delta r} \right].$$

where $K_1(r)$ is given by

$$K_1(r) = d + cr^2 + [a + b(r - \rho_0)^2](1 - e^{-\gamma r}) - \frac{(\epsilon^*/\epsilon_{\infty} - 1)a^*_0}{r}.$$ \hspace{1cm} (7)

In Eq. (6) $\alpha = (1/2\epsilon^*)(\epsilon^2/\hbar \omega_0)(2m^*\omega_0/\hbar)^{1/2}$ is the dimensionless electron-phonon coupling constant, $m^*$ is the effective mass at the bottom of the conduction band, $\omega_0$ is the longitudinal optical phonon frequency in the long wave-length approximation, and $a^*_0 = \alpha^{-1}(h/2m^*\omega_0)^{1/2}$ is the effective Bohr radius. The parameters $a$, $b$, $c$, $d$, $\gamma$, and $\delta$ of the potentials in Eq. (6) and (7) have been obtained by an accurate fit of the polaron-polaron potential in the Pekar theory.\textsuperscript{8,11,12,24} and are listed in Table I. In the numerical calculations it is furthermore assumed $\epsilon_{\infty} = 2$, $m^* = m$ with $m$ electron mass, and $\hbar \omega_0 = 0.03 eV$.

The Vlasov equations in Eqs. (1) and (2) are valid in the classical limit and the use of polaron-polaron interaction (6) is accurate for a dilute system. Therefore the temperature $T$ has to be high compared with the degeneracy temperature of polarons: $T > h^2 N_p^{3/2}/m_p k_B$, with $N_p$ polaron density and $k_B$ Boltzmann constant. This condition is verified at reasonable temperatures if $N_p < 5 \times 10^{18} cm^{-3}$. We note that for these densities some energy scales, for example the polaron plasmon frequency, are smaller or of the same order than the optical phonon frequency. Clearly, for the temperatures considered above, quantum effects in the statistics can be neglected and the Boltzmann-Maxwell distribution function can be used at the thermodynamic equilibrium.

III. COLLECTIVE EXCITATIONS OF THE POLARON SYSTEM

In this section we analyze the collective excitations of the polaron system. As discussed in the following subsection $A$, the polaron plasmon is obtained neglecting the role of the collective potential $U$ in the Vlasov equations (1) and (2). On the contrary in subsection $B$ we will examine the collective excitations induced by the potential $U$ in absence of the electrostatic potential $\Phi$. These density oscillations are completely different from the polaron plasmons, since at small values of the momentum $k$ they have a dispersion relation approximately proportional to $k$. 

\[ U(\vec{r}, t) = \int d\vec{r}' d\vec{v}' K(|\vec{r} - \vec{r}'|)f_p(\vec{r}', \vec{v}', t), \]
The procedure of calculation of these two types of excitations is the same. Indeed only the role of the polarons is mainly considered and the Vlasov equations are linearized taking

\[ f_p(\vec{r}, \vec{v}, t) = f_0(\vec{v}) + \phi(\vec{r}, \vec{v}, t), \]  

where \( f_0(\vec{v}) \) is the Maxwell distribution function

\[ f_0(\vec{v}) = N_p \left( \frac{m_p}{2\pi k_B T} \right)^{3/2} e^{-\frac{m_p v^2}{2k_B T}}, \]

associated to the homogeneous spatial distribution of the particles and \( \phi(\vec{r}, \vec{v}, t) \) is strongly smaller than \( f_0(\vec{v}) \). Therefore it is assumed that the perturbations induced by the time-dependent potentials are weak.

### A. Polaron plasmons

The polaron plasmons are the collective excitations in the limit of collective potential \( U_{zero} \). In this case the external force affecting the polaron distribution can be simply related to an electrical field \( \vec{E}(\vec{r}, t) \) defined as \( \vec{E}(\vec{r}, t) = -\vec{\nabla} \Phi(\vec{r}, t) \). Neglecting second order terms, the equation (1) becomes

\[ \frac{\partial \phi(\vec{r}, \vec{v}, t)}{\partial t} + \vec{v} \cdot \vec{\nabla}_r \phi(\vec{r}, \vec{v}, t) = \frac{e}{m_p} \vec{E}(\vec{r}, t) \cdot \vec{\nabla}_v f_0(\vec{v}). \]

Fourier transforming in space and time, one obtains

\[ \phi(\vec{k}, \vec{v}, \omega) = \frac{e \vec{E}(\vec{k}, \omega)}{im_p(\vec{k} \cdot \vec{v} - \omega)} \cdot \vec{\nabla}_v f_0(\vec{v}), \]

where the coefficient of \( \vec{\nabla}_v f_0(\vec{v}) \) represents the amplitude of momentum that the polaron acquires under the field \( \vec{E} \). Clearly this quantity has to be small compared with the mean momentum obtained through the equilibrium distribution \( f_0(\vec{v}) \).

Using Eq. (5), the Fourier transform of particle density \( \rho \) can be evaluated. This last quantity is connected to the polarization \( \vec{P} \) of the system since \( i\vec{k} \cdot \vec{P} = -\varepsilon_s \rho \). Employing the pole-rule defined by Landau, we obtain the relation

\[ i\vec{k} \cdot \vec{P}(\vec{k}, \omega) = -\frac{\varepsilon^2}{\varepsilon_s} \vec{E}(\vec{k}, \omega) \cdot \int d\vec{v} \frac{\vec{\nabla}_v f_0(\vec{v})}{im_p(\vec{k} \cdot \vec{v} - \omega) - i\eta}, \]

where \( \eta \) is infinitesimal. If the field \( \vec{E} \) and \( \vec{P} \) are directed along \( \vec{k} \), then the longitudinal dielectric constant \( \varepsilon_l(\vec{k}, \omega) \) can be derived by means of the equation \( 4\pi \vec{P} = (\varepsilon_l - 1)\vec{E} \), yielding

\[ \varepsilon_l(\vec{k}, \omega) = 1 - \frac{4\pi e^2}{\varepsilon_s k^2} \int d\vec{v} \frac{k \cdot \vec{\nabla}_v f_0(\vec{v})}{im_p(k \cdot \vec{v} - \omega) - i\eta}. \]

The dielectric constant of Eq. (13) is a complex quantity implying that the energy of the electrical field can be dissipated in the medium (Landau damping). Hence longitudinal electrical waves can propagate through the system and their dispersion relation is obtained by the equation \( \varepsilon_l(\vec{k}, \omega) = 0 \). Supposing \( \omega \gg kv_T \), with \( v_T = (k_B T/m_p)^{1/2} \) mean quadratic velocity along the direction of propagation, the zeros of the equation can be derived. At low order in momentum the real part of the frequency is

\[ \omega = \omega_{pp}(1 + \frac{3}{2} k^2 a_p^2), \]

with \( a_p = (\varepsilon_s k_B T/4\pi N_p e^2)^{1/2} \) and \( \omega_{pp} \) polaron plasma frequency defined as

\[ \omega_{pp} = \frac{v_T}{a_p} = \sqrt{\frac{4\pi N_p e^2}{\varepsilon_s m_p}}, \]
while the imaginary part is exponentially small. As expected in the limit $\omega_{pp} \leq \omega_0$, the plasma frequency is screened by the static dielectric constant $\varepsilon_s$.\textsuperscript{29}

In this derivation we have taken into account only the polaron contribution. Within the same approach it would be possible to consider also the role of the ionic plasmons through Eq. (2) and the interplay between polaronic and ionic oscillations.\textsuperscript{28} However, it is more interesting to focus on the collective excitations due to the polaron collective potential $U$.

**B. Excitations due to the collective potential $U$**

In this subsection we consider the time-dependent kinetic equations (1) for the polaron distribution function neglecting the contribution from the electrostatic potential $\Phi$. We investigate the propagation of longitudinal waves with lengths larger than the polaron-polaron distance in the bipolaron. Therefore our aim will be the calculation of the dispersion relationship linking frequency $\omega$ with wave vector $k$ in the limit $k \to 0$.

If one neglects second order terms, the Vlasov equation (1) becomes

$$\frac{\partial \phi(\mathbf{r}, \mathbf{v}, t)}{\partial t} + \mathbf{v} \cdot \nabla \phi(\mathbf{r}, \mathbf{v}, t) = \frac{1}{m_p} \nabla_v f_0(\mathbf{v}) \cdot \nabla_r \int d\mathbf{v}^\prime d\mathbf{r}^\prime K(|\mathbf{r}^\prime - \mathbf{r}|) \phi(\mathbf{r}^\prime, \mathbf{v}^\prime, t).$$

The solution of the integro-differential equation (16) can be written in the following form\textsuperscript{22}

$$\phi(\mathbf{r}, \mathbf{v}, t) = \frac{1}{2m_p} \nabla_v f_0(\mathbf{v}) \cdot \nabla_r \int d\mathbf{v}^\prime \left[ \int_{t_0}^{t} d\tau K(|\mathbf{r}^\prime - \mathbf{v}(t - \tau) - \mathbf{v}^\prime|) \rho(\mathbf{r}^\prime, \tau) + \int_{t_1}^{t} d\tau K(|\mathbf{r}^\prime - \mathbf{v}(t - \tau) - \mathbf{v}^\prime|) \rho(\mathbf{r}^\prime, \tau) \right],$$

with $t_0 \leq t \leq t_1$ and $\rho(\mathbf{r}, t)$ defined in Eq. (5). Integrating with respect to the velocity, one obtains

$$\rho(\mathbf{r}, t) = \frac{1}{2m_p} \int d\mathbf{v} \nabla_v f_0(\mathbf{v}) \cdot \nabla_r \int d\mathbf{v}^\prime \left[ \int_{t_0}^{t} d\tau K(|\mathbf{r}^\prime - \mathbf{v}(t - \tau) - \mathbf{v}^\prime|) \rho(\mathbf{r}^\prime, \tau) + \int_{t_1}^{t} d\tau K(|\mathbf{r}^\prime - \mathbf{v}(t - \tau) - \mathbf{v}^\prime|) \rho(\mathbf{r}^\prime, \tau) \right].$$

Considering the spatial and temporal Fourier transform of the density $\rho$, Eq. (18) becomes

$$\rho(\mathbf{k}, \omega) = \frac{1}{2} \int_{-\infty}^{\infty} d\tau e^{-i\omega(t-\tau)} G(\mathbf{k}, t - \tau) \rho(\mathbf{k}, \omega) + \frac{1}{2} \int_{0}^{\infty} d\tau e^{-i\omega(t-\tau)} G(\mathbf{k}, t - \tau) \rho(\mathbf{k}, \omega),$$

where $G(\mathbf{k}, t)$ is defined by

$$G(\mathbf{k}, t) = \frac{i\sigma(k)}{m_p} \mathbf{k} \cdot \int d\mathbf{v} e^{i\mathbf{k} \cdot \mathbf{v}} \nabla_v f_0(\mathbf{v}),$$

with $\sigma(k)$ Fourier transform of the polaron-polaron potential shown in Fig. 2 for different values of the ratio $\varepsilon^*/\varepsilon_\infty$. The condition of existence of the nontrivial solutions of the equation (19) is the following

$$\int_{0}^{\infty} dt G(\mathbf{k}, t) \cos(\omega t) = 1,$$

that links implicitly the frequency $\omega$ to the momentum $\mathbf{k}$. We obtain the dispersion for small $k$ in the form

$$\omega = \left( \frac{v_T}{2} \right) k \left( 1 + \frac{k_B T}{N_p\sigma(k)} \right)^{1/3},$$

where $v_T = (k_B T/m_p)^{1/2}$ is the mean quadratic velocity along the direction of propagation. Therefore the system exhibits a collective mode sustained by the coherent self-consistent interaction arising from neighboring particles. Clearly these excitations are well defined if

$$1 + \frac{k_B T}{N_p\sigma(k)} > 0.$$
As deduced from Fig. 2, the collective mode can certainly propagate for values of \( k \) around 0 where \( \sigma(k) \) is positive. The Fourier transform \( \sigma \) at \( k = 0 \) is given by the spatial integral of the potential \( K \) that, as shown in Fig. 1, becomes completely negative as the ratio \( \epsilon^*/\epsilon_\infty \) approaches the unity. By fixing the ratio \( \epsilon^*/\epsilon_\infty \) and increasing the electron-phonon coupling constant \( \alpha \), the potential \( \sigma(k) \) deepens implying that the region of stability in \( k \) is reduced. So there is a range of values of the momentum where Eq. (23) is violated. This suggests the possibility that the particles in equilibrium are not longer single polarons, but, due to the attractive effect of the interaction, a polaron of the system can bind another one in order to form a bipolaron. Clearly two particles could form with a third a cluster of more than two particles. Therefore it is important to study directly the formation of polaron clusters induced by the collective potential \( U \).

IV. POLARON CLUSTERS

In this section we will study the solutions of the Vlasov equations (1) and (2) in the temporal stationary regime. Clearly these equations are satisfied if the polaron \( f_p \) and ion \( f_i \) distribution functions are independent of position. Our aim is to study the solutions of equations (1) and (2) near to the homogeneous ones.

In stationary conditions, we write for the polaron and ion distribution function

\[
f_j(\vec{r}, \vec{v}) = \rho_j(\vec{r}) w_j(\vec{v}),
\]

where \( j \) stands for \( p \) or \( i \), \( \rho_j(\vec{r}) \) and \( w_j(\vec{v}) \) the spatial and velocity distribution functions, respectively. If the velocity distribution function is that of the equilibrium, then from equations (1) and (2) the spatial distribution functions of polarons and ions can be deduced as

\[
\rho_p(\vec{r}) = N_p e^{-\frac{U(\vec{r}) - \Phi(\vec{r})}{\kappa_B T}},
\]

and

\[
\rho_i(\vec{r}) = N_i e^{-\frac{\Phi(\vec{r})}{\kappa_B T}},
\]

where \( N_i \) is the ion concentration, such that \( N_p = N_i = N_0 \) since the system has charge neutrality. Substituting (25) and (26) in (3) and (4), we obtain the coupled equations

\[
U(\vec{r}) = \int d\vec{r}' K(|\vec{r} - \vec{r}'|) \rho_p(\vec{r}')
\]

and

\[
\Delta \Phi(\vec{r}) = \left( \frac{4\pi e}{\epsilon_\infty} \right) [\rho_p(\vec{r}) - \rho_i(\vec{r})],
\]

that allow to determine self-consistently both the collective polaron \( U(\vec{r}) \) and electrostatic \( \Phi(\vec{r}) \) potentials.

The exact solution of Eqs. (27) and (28) is a formidable task. Therefore, considering the dependence of the potential \( K \) on the relative distance, we iteratively build a solution for a spherical symmetric cluster of radius \( R \) obtaining at the lowest order \( \Phi_0(r) = 0 \) and

\[
U_0(r) = \begin{cases} N_0 \int d\vec{r}' K(|\vec{r}' - \vec{r}|), & r \leq R, \\ N_0 \int d\vec{r}' K(|\vec{r}' - \vec{r}|), & r > R. \end{cases}
\]

We note that the collective potential \( U_0(r) \) is directly proportional to the particle density \( N_0 \) and through \( K \) it depends on the electron-phonon coupling constant \( \alpha \). Through the use of the coordinate transformation

\[
s^2 = r^2 + x^2 - 2xr \cos(\theta), \quad ds = xr \sin(\theta) d\theta,
\]

the potential inside the sphere \( U^{(in)}_0(r) \) is written as

\[
U^{(in)}_0(r) = \frac{2\pi N_0}{r} \left[ \int_0^r dx \int_{r-x}^{r+x} ds K(s) + \int_r^R dx \int_{R-x}^{R+x} ds K(s) \right], r \leq R,
\]

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and connects with continuity to that outside $U^{(\text{out})}(r)$

$$U_0^{(\text{out})}(r) = \frac{2\pi N_0}{r} \int_0^R dx \int_{r-x}^{r+x} ds K(s), r > R.$$  \hspace{1cm} (32)

The local modifications of the spatial distribution function due to the attractive forces are described by the polaron spatial density $N_1(r)$

$$N_1(r) = N_0 \left( -\frac{U_0(r)}{k_B T} \right)$$  \hspace{1cm} (33)

showing that the distribution of the polarons is determined by the collective potential $U_0(r)$. Actually the charge neutrality is locally perturbed and the increase of the polaron density can be consistent with a bound cluster of particles.

In Figs. 3(a) and 3(b) we show the collective potential for different radii $R$ and for the value of $\epsilon^*/\epsilon_\infty = 1.05$. The qualitative behaviours are similar in all the considered cases except for $\epsilon^*/\epsilon_\infty = 1.00$. For a fixed ratio $\epsilon^*/\epsilon_\infty$, $U_0(r)$ is negative in a region around $r = 0$, it assumes the minimum value at $r = 0$ and becomes positive at large values of $r$. The quantity $U_0(0)$ is first decreasing and then increasing as function of $R$, so that it exists a value of $\bar{R}$ which gives the minimum value of $U_0(0)$. Only in the case $\epsilon^*/\epsilon_\infty = 1$ (i.e. $\epsilon_\infty = \infty$) $U_0(0)$ is always decreasing as function of $R$. In Fig. 4 we show the quantity $U_0(0)$ as function of $R$ for all the indicated values of $\epsilon^*/\epsilon_\infty$, except for $\epsilon^*/\epsilon_\infty = 1$. It occurs that the decrease of $\epsilon^*/\epsilon_\infty$ implies the increase of $\bar{R}$.

It is important to calculate the minimum values of $\alpha$ for which the cluster begins to form. We have evaluated the critical values $\alpha_c$ within the full quantum mechanical approach of a particle in the collective potential $U_0(r)$ calculating when the first bound level develops. Hence the quantity $\alpha_c$ indicates the minimum value for which the bipolaron forms. It has been checked that these values are only slightly smaller than those obtained in the next subsection through the statistical model that can be generalized at arbitrary levels. In particular we will investigate the resulting shell structure in the cluster.

A. Shell structure of the polaron cluster

In analogy with the structure of nuclei and metal clusters, we try now to calculate the conditions for existence of the polaron clusters and the related shell structure. For the spherically symmetric collective potential $U_0(r)$, we use the same criterion of the atomic physics regarding the quantum numbers to introduce in order to characterize the state of a single electron in the atoms. In other words we introduce the quantum numbers of single particle states without considering neither the electrostatic corrections nor the relativistic ones. In the statistical model, the shells with the orbital quantum number $l$ ($l = 0, 1, 2, 3, \ldots$) begin to form when $N_1$ defined by

$$N_i = \frac{4}{\pi \hbar} \left( l + \frac{1}{2} \right) \int_{R_1}^R dr \left[ -2m_p U_0(r) - \frac{\hbar^2}{l(l+1/2)^2} \right]^{1/2} = \frac{4}{\pi \hbar} \left( l + \frac{1}{2} \right) \int_{R_1}^R dr \left[ P^2 - \frac{\hbar^2}{r^2} \right]^{1/2}$$  \hspace{1cm} (34)

becomes larger than 1. In the above formula $R$ is the cluster radius, $R_1$ is the lower value of $r$ for which the function to integrate is zero, $P$ is the maximum polaron momentum. In the statistical approximation the maximum momentum $P$ is connected with the local polaron density $N_1(r)$ given in (33) through the relation

$$P(r) = 2\pi \hbar \left( \frac{3N_1(r)}{8\pi} \right)^{1/3},$$  \hspace{1cm} (35)

so that, writing $N_1(r) = m\rho_0(r)$, where $m$ is the number of the particles involved in the cluster, we have to ensure that $\int d\vec{r}\rho_0(r) = 1$. Taking into account Eq. (35), we find the following equation

$$\frac{1}{r} = -\frac{1}{3} \frac{d}{dr} \ln \rho_0(r),$$  \hspace{1cm} (36)

which allows to determine explicitly the value $R_1$.

In table II we have reported the calculated values of the electron - phonon coupling constants $\alpha_{c,l}$ from which the shell with the indicated value of $l$ begins to be filled. We find that, increasing the polaron concentration, the collective
potential $U_0(r)$ deepens, so that the values of $\alpha_{c,l}$ decrease. For example, taking $\epsilon^* / \epsilon_\infty = 1.05$, for $N_0 = 10^{18} \text{cm}^{-3}$ the first shell $l = 0$ starts to be filled as soon as $\alpha_{c,0} = 10.2$, while for $N_0 = 10^{17} \text{cm}^{-3}$ we have $\alpha_{c,0} = 18.2$. Furthermore, since the increase of the number $l$ reflects a higher binding energy of the particles in the cluster, in table II the values of $\alpha_{c,l}$ get enhanced as a function of $l$.

Finally we can calculate the sequence of the shell formation in a polaron cluster. In analogy to the filling of states for nuclear matter and metal clusters, we obtain the sequence $(1s)^2(2p)^6(3d)^{10}(2s)^2(4f)^{14}$ for the polaron cluster. This order differs from the known order of filling of electron levels in atoms: in fact shells with 2, 8, 18, 20 polarons are stable. Then it is possible that in the system stable clusters can form becoming the basic units in equilibrium at a given temperature.

Our calculation scheme based on the strong coupling Fröhlich electron-phonon theory is coherent with the results obtained in Eq. (37) is a function of the polaron density also through the constants $\alpha_{c,l}$ of the coupling constant. In the table III the critical temperatures $T_{cr}$ are shown. We note that the critical temperature $T_{cr}$ obtained in Eq. (37) is a function of the polaron density also through the constants $\alpha_{c,l}$ that, as reported in tab. II, are strongly dependent on $N_0$. Since the collective potential responsible for the cluster formation is proportional to $N_0$, we expect that the critical temperatures strongly increase as a function of the polaron concentration, as confirmed by the results of tab. III. Clearly it is possible to define the critical temperatures for condensation of polarons for different shells. Increasing the quantum number $l$, the binding energies becomes larger, the cluster becomes more stable, so that the critical temperatures are enhanced.

In this section we have realized that, at the lowest order of the iterative procedure used for solving equations (27) and (28), the electrostatic potential $\Phi$ defined in Eq. (4) does not affect the cluster formation. However, at higher orders, the difference between the density of polarons and ions could perturb the states of the cluster. The frequency scale of such perturbation is close to the frequency $\omega_{pp}$ of the polaron plasma oscillation given in Eq. (15). Such fluctuations can contribute to the broadening of the states determined in the cluster. Obviously the broadening is small if $\omega_{pp} < \omega_t$, where $\omega_t$ is the frequency of motion of the particle in the collective potential at the level with a quantum number $l$. From this inequality it is possible to find the highest value of the electron-phonon coupling constant $\tilde{\alpha}$, such that for $\alpha < \tilde{\alpha}$ the cluster is unstable against these perturbations. For example, at the concentrations $N_0 = 10^{17} \text{cm}^{-3}$ and $N_0 = 10^{18} \text{cm}^{-3}$ for $l = 0$ and $\epsilon^* / \epsilon_\infty = 1.08$, we have $\tilde{\alpha} = 16.6$ and $\tilde{\alpha} = 12.5$, respectively. These results do not contradict the data listed in the table II. Therefore when the polaron cluster is formed in the system, it is also stable against the energy fluctuations of the bound states of the collective potential $U_0$.

\section{Conclusion}

Using the statistical model, we have found that clusters can form in a dilute polaron gas. We have calculated the critical values of the electron-phonon interaction for which the ground and excited state shells can be filled. The found sequence of the shells is analogous to that of the nuclei and of the metal clusters rather than that of the electron states in atoms. We have also calculated the stability of the polaron clusters against the fluctuations of the collective potential. We have found that the values for which the cluster can form are sufficiently large to assure the stability of the system. Finally the critical temperature for the condensation of the polarons in the cluster has been calculated. Our calculation scheme based on the strong coupling Fröhlich electron-phonon theory is coherent with the results since all critical values for the formation of the clusters are found in the regime of large coupling. Clearly this implies that the theoretical results can be discussed in connection with real systems only in situations of poorly screened strong electron-phonon coupling.

The system with polaron clusters is characterized by collective modes different from those of the homogeneous phase, for example that induced by perturbations which tend to deform the cluster. In such a case the difficulty is to solve the time dependent equations starting at the zero order from the spatially perturbed polaron distribution function calculated in the previous section. Actually vibronic modes have been discussed in electronic bound configurations showing that their frequency is of the order $10^{14} - 10^{15} \text{Hz}$ for typical parameters of metallic oxides. Finally we note...
that, in the quantum case of high density and low temperature characteristic of perovskite oxides, the system can exhibit a true phase transition toward a clustered state that in the one-dimensional case can be a string.\footnote{G. Verbist, F.M. Peeters, and J.T. Devreese, Phys. Rev. B 11.}

\section*{FIGURE CAPTIONS}

Fig.1 Polaron-polaron potential $K$ (in units of $2a^2\hbar\omega$) as a function of the distance $\rho$ (in units of $a_0^*$) for different values of the ratio $\epsilon^*/\epsilon_\infty$: solid ($\epsilon^*/\epsilon_\infty = 1.00$), large dot ($\epsilon^*/\epsilon_\infty = 1.02$), dash ($\epsilon^*/\epsilon_\infty = 1.05$), dash-dot ($\epsilon^*/\epsilon_\infty = 1.08$), small dot ($\epsilon^*/\epsilon_\infty = 1.10$).

Fig.2 Fourier transform $\sigma$ (in units of $2a^2\hbar\omega$ $a_0^3$) of the polaron-polaron potential $K$ as a function of the momentum $k$ (in units of $a_0^{*-1}$) for different values of the ratio $\epsilon^*/\epsilon_\infty$: 1-solid ($\epsilon^*/\epsilon_\infty = 1.10$), 2-dot ($\epsilon^*/\epsilon_\infty = 1.08$), 3-dash-dot ($\epsilon^*/\epsilon_\infty = 1.05$), 4-dash ($\epsilon^*/\epsilon_\infty = 1.02$), 5-solid ($\epsilon^*/\epsilon_\infty = 1.00$).

Fig.3 (a) The collective polaron potential $U_0$ (in units of $2a^2\hbar\omega/N_0$) as a function of the distance $r$ (in units of $a_0^*$) for $\epsilon^*/\epsilon_\infty = 1.05$: 1-solid (radius of the cluster $R = 7a_0^*$), 2-dash (radius of the cluster $R = 11a_0^*$), 3-dash-dot (radius of the cluster $R = 15a_0^*$). Optimal radius of the cluster is $15a_0^*$. The dot curve defines the boundaries of the cluster.

(b) The collective polaron potential $U_0$ (in units of $2a^2\hbar\omega/N_0$) as a function of the distance $r$ (in units of $a_0^*$) for $\epsilon^*/\epsilon_\infty = 1.05$: 1-solid (radius of the cluster $R = 16a_0^*$), 2-dash (radius of the cluster $R = 20a_0^*$), 3-dash-dot (radius of the cluster $R = 22a_0^*$). Optimal radius of the cluster is $15a_0^*$. The dot curve defines the boundaries of the cluster.

Fig.4 The collective polaron potential $U_0$ (in units of $2a^2\hbar\omega/N_0$) at $r = 0$ as a function of the cluster radius $R$ (in units of $a_0^*$) for different values of the ratio $\epsilon^*/\epsilon_\infty$: 1-dot ($\epsilon^*/\epsilon_\infty = 1.10$), 2-dash-dot ($\epsilon^*/\epsilon_\infty = 1.08$), 3-dash ($\epsilon^*/\epsilon_\infty = 1.05$), 4-solid ($\epsilon^*/\epsilon_\infty = 1.02$).

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TABLE I. Parameters of the polaron-polaron potential $K$

| $\epsilon / \epsilon_\infty$ | $a$          | $b (a_0^{-2})$ | $c (a_0^{-2})$ | $d$  | $\gamma (a_0^{-2})$ | $d (a_0^{-2})$ | $\rho_0 (a_0)$ |
|-----------------------------|--------------|----------------|----------------|------|-------------------|----------------|---------------|
| 1.10                        | $-7.95 \times 10^{-7}$ | $6.875 \times 10^{-7}$ | $-6.821 \times 10^{-7}$ | $1.4 \times 10^{-3}$ | 0.2475                          | 0.2047                          | $7.95 \times 10^{-7}$ |
| 1.08                        | $-5.175 \times 10^{-7}$ | $6.885 \times 10^{-7}$ | $-6.857 \times 10^{-7}$ | 0.001 | 0.245                           | 0.20                    | $8.17 \times 10^{-7}$ |
| 1.05                        | $-1.907 \times 10^{-7}$ | $6.855 \times 10^{-7}$ | $-6.852 \times 10^{-7}$ | $8.583 \times 10^{-3}$ | 0.25                             | 0.19                    | $8.81 \times 10^{-7}$ |
| 1.02                        | $-6.9 \times 10^{-7}$   | $6.9188 \times 10^{-7}$ | $-6.887 \times 10^{-7}$ | $-3.097 \times 10^{-3}$ | 0.286                            | 0.166                   | $9.25 \times 10^{-7}$ |
| 1.00                        | $-7.92 \times 10^{-7}$  | $6.709 \times 10^{-7}$ | $-6.677 \times 10^{-7}$ | $-7.75 \times 10^{-2}$ | 0.32                             | 0.15                     | 0.1087          |

TABLE II. The critical values of the electron-phonon coupling constant when the shell with momentum $l$ is filled

| $\epsilon / \epsilon_\infty$ | $N_0 = 10^{16} \text{ cm}^{-3}$ | $N_0 = 10^{17} \text{ cm}^{-3}$ | $N_0 = 10^{18} \text{ cm}^{-3}$ |
|-----------------------------|---------------------------------|---------------------------------|---------------------------------|
| $a$                | $l = 0$  | $l = 1$  | $l = 2$  | $l = 3$  | $l = 0$  | $l = 1$  | $l = 2$  | $l = 3$  | $l = 0$  | $l = 1$  | $l = 2$  | $l = 3$  |
|-----------------------------|---------------------------------|---------------------------------|---------------------------------|
| 1.10                        | $76.0$                           | $89.8$                           | $110.7$                          | $129.4$                           | $42.7$                           | $50.5$                           | $62.3$                           | $72.7$                           |
| 1.08                        | $51.5$                           | $59.8$                           | $73.7$                           | $86.1$                           | $29.0$                           | $33.6$                           | $41.5$                           | $48.4$                           |
| 1.05                        | $32.2$                           | $35.0$                           | $42.2$                           | $48.9$                           | $18.2$                           | $19.7$                           | $23.7$                           | $27.5$                           |
| 1.02                        | $23.7$                           | $25.4$                           | $30.4$                           | $35.1$                           | $9.8$                            | $10.3$                           | $12.2$                           | $13.9$                           |
| 1.00                        | $17.5$                           | $18.3$                           | $21.6$                           | $24.7$                           | $5.6$                            | $5.8$                            | $6.8$                            | $7.8$                            |

TABLE III. Critical temperatures (in units of $2\alpha^2\hbar\omega_0/k_B$) corresponding to the filling of the cluster shell with momentum $l$.

| $\epsilon / \epsilon_\infty$ | $N_0 = 10^{16} \text{ cm}^{-3}$ | $N_0 = 10^{17} \text{ cm}^{-3}$ | $N_0 = 10^{18} \text{ cm}^{-3}$ |
|-----------------------------|---------------------------------|---------------------------------|---------------------------------|
| $l = 0$                      | $l = 1$  | $l = 2$  | $l = 3$  | $l = 0$  | $l = 1$  | $l = 2$  | $l = 3$  | $l = 0$  | $l = 1$  | $l = 2$  | $l = 3$  |
|-----------------------------|---------------------------------|---------------------------------|---------------------------------|
| 1.10                        | $2.4$                            | $3.1$                            | $4.7$                            | $6.5$                            | $7.0$                            | $9.8$                            | $15.0$                           | $28.4$                           |
| 1.08                        | $1.6$                            | $2.0$                            | $3.0$                            | $4.1$                            | $4.9$                            | $6.2$                            | $9.5$                            | $12.9$                           |
| 1.05                        | $0.91$                           | $1.1$                            | $1.6$                            | $2.1$                            | $2.9$                            | $3.4$                            | $4.9$                            | $6.7$                            |
| 1.02                        | $0.72$                           | $0.83$                           | $0.6$                            | $0.8$                            | $2.3$                            | $2.6$                            | $3.8$                            | $5.0$                            |
| 1.00                        | $0.84$                           | $0.92$                           | $1.2$                            | $1.7$                            | $2.6$                            | $2.9$                            | $4.1$                            | $5.3$                            |
|-----------------------------|---------------------------------|---------------------------------|---------------------------------|
| 1.10                        | $22.2$                           | $31.1$                           | $47.2$                           | $64.4$                           | $15.6$                           | $19.6$                           | $29.8$                           | $40.6$                           |
| 1.08                        | $15.6$                           | $19.6$                           | $29.8$                           | $40.6$                           | $9.2$                            | $10.8$                           | $15.8$                           | $21.1$                           |
| 1.05                        | $7.2$                            | $8.2$                            | $11.8$                           | $15.8$                           | $7.2$                            | $8.2$                            | $11.8$                           | $15.8$                           |
| 1.02                        | $8.6$                            | $9.3$                            | $12.7$                           | $16.7$                           | $8.6$                            | $9.3$                            | $12.7$                           | $16.7$                           |
