Formation of a large polaron crystal from a homogeneous, dilute polaron gas

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We introduce a very simple method to study the phase transition from the homogeneous dilute large polaron gas toward the formation of a cubic crystal within the framework of the Vlasov [*Many-Particle Theory and its Applications to Plasma* (Gordon and Breach, New York, 1962)] nonlinear kinetic equation and the equations for the Bogolyubov [*Problems of Dynamic Theory in Statistical Physics. Selected Works on Statistical Physics* (Moscow State University, Moscow, 1979)] distribution functions. Two different critical temperatures T_1^{cr} and T_2^{cr} are introduced, defining the range of stability of the crystal phase ($T_2^{cr} < T < T_1^{cr}$). The existence and properties of the crystal phase are discussed as a function of the ionicity parameters of the medium, the electron-phonon Fröhlich coupling constant and the density of the dilute polaron gas. In particular, the lattice parameter is found to increase when the ionicity of the medium decreases whereas it is independent of the Fröhlich constant α and the polaron density. Furthermore, it increases upon decreasing the temperature from T_1^{cr} toward T_2^{cr}, showing a behavior different from that observed for common solids. We find also that a drift velocity of the polaron gas tends to reduce the stability of the crystal. To illustrate the simplicity of the calculation scheme, we apply the same technique to study the formation of the argon (Ar) crystal starting from the atomic gas interacting through a reliable Lennard-Jones potential. We calculate the crystallization temperature and the Ar atom distribution. The lattice parameter is an increasing function of the temperature and the second critical temperature is not defined. We try to relate the different dependence on the temperature of the lattice parameter to the features of the polaron-polaron and atom-atom interactions.

I. INTRODUCTION

The formation of a polaron lattice concerns the most general problem of the phase transition from the homogeneous to the periodic phase of interacting particles (the well known solidification and sublimation processes). This is a very old and important problem of the statistical physics which has been treated with a variety of techniques. We note that, even today, there are attempts to show analytically or numerically the phase transition from the homogeneous to the crystalline phase in the case of the hard sphere model[1,2] and that there are many methods to treat this problem.[3–9] In all the cases, analytical or numerical calculations are based on the knowledge of the interactions between the particles or of the static structure factor of the homogeneous phase or of the correlation function.[10–12] Phonon dispersion frequencies near the melting point have been an object of investigation as well.[13,14] Finally, a renewed interest in this problem has been stimulated by studies on photoinduced phase transitions.[15–21]

The crystallization of the large polaron gas has already been studied in specific models: interacting electrons in polar medium with isotropic and anisotropic structures,[22] extended in a recent work;[23] dielectric function models;[24,25] and formation of linear strings[26] in the Pekar polaron theory.[27,28] Furthermore, the combined effect of the electron-phonon interaction and the double- and superexchange magnetic effects determines in the manganites, such as $La_{1-x}Ca_xMnO_3$, the appearance of antiferromagnetic or paramagnetic domains with small polarons and ferromagnetic domains with large polarons.[29] Finally, the quantum lattice fluctuations in the ground state of the half-filled electron band are the source

of the Peierls instability of the one-dimensional molecular crystals.[30–33]

In a previous work,[34] we studied the instabilities of the homogeneous large polaron system versus the formation of a periodic phase. We used two different approaches to describe this problem: the Bogolyubov method of the equilibrium distribution functions[35] to find the features of the thermodynamical transition and the kinetic Vlasov nonlinear equation to determine the mechanical instabilities of the polaron system.[36] Both methods apply to dilute systems in which the correlation contributions are taken into account and the exchange terms neglected. The main input of the theory is the knowledge of the effective interaction between two polarons and this quantity is calculated *a priori* with the best sophisticated field theory methods.[37] The main results can be summarized as follows.

(1) Upon decreasing the temperature, the transition from the homogeneous to the periodic phase occurs at a critical temperature T_1^{cr}. The periodic phase can exist only for temperatures $T < T_1^{cr}$, being thermodynamically unstable otherwise. It turns out that T_1^{cr} decreases if the medium becomes less polar [namely, if $\varepsilon^*/\varepsilon_\infty = (1 - \varepsilon_\infty/\varepsilon_s)^{-1}$ increases, where ε_∞ and ε_s are the high frequency and static dielectric constants], whereas it increases if the electron-phonon Fröhlich coupling constant α increases. Furthermore, in the dilute limit, T_1^{cr} becomes larger if the polaron density n of the homogeneous phase increases. The phenomenon shows other features, such as the existence of an upper limit $(\varepsilon^*/\varepsilon_\infty)_{cr}$, for $\varepsilon^*/\varepsilon_\infty$, and a lower limit α_{cr}, for α. Both conditions $\varepsilon^*/\varepsilon_\infty < (\varepsilon^*/\varepsilon_\infty)_{cr}$ and $\alpha > \alpha_{cr}$ must be fulfilled for the existence of the periodic phase. Both α_{cr} and $(\varepsilon^*/\varepsilon_\infty)_{cr}$ depend on n. Fur-

thermore, α_{cr} depends on $\varepsilon^*/\varepsilon_\infty$ and $(\varepsilon^*/\varepsilon_\infty)_{cr}$ on α. This limits the range of the material parameters compatible with the formation of the periodic polaron lattice.

(2) At small temperatures, a mechanical instability of the periodic phase shows up. Thus, the existence of this phase is also limited by a lower critical temperature T_2^{cr}. The temperature range of existence $\Delta T_c = T_1^{cr} - T_2^{cr}$ depends on n, α, and $\varepsilon^*/\varepsilon_\infty$ and it tends to zero if either $\alpha \to \alpha_{cr}^+$ or $\varepsilon^*/\varepsilon_\infty \to (\varepsilon^*/\varepsilon_\infty)_{cr}^-$.

It is important pointing out that our previous results[34] were obtained within a semianalytical scheme, allowing us to only explore a small region around the transition points. An alternative scheme will be presented in this work, leading to the exact calculation of the same quantities. The polaron gas will be shown to crystallize as a simple cubic lattice. We study as function of T, $\varepsilon^*/\varepsilon_\infty$, and n, some crystal features as the lattice parameter, the particle distribution function along fixed directions, and the influence of the particle oscillations and of the polaron velocity in the homogeneous phase on the phase transition. We consider densities n up to 10^{19} cm^{-3}.

The same theoretical framework of the polaron crystallization is also applied to the formation of the Ar crystal starting from the atomic homogeneous gas phase and a suitable Lennard-Jones atomic potential. In this case there is only one critical temperature T_1^{cr} and the temperature T_2^{cr} cannot be defined.

The physical mechanism explaining the above phenomena is related to the specific form of the polaron-polaron and Lennard-Jones interactions. The former is repulsive and finite at $r=0$, attractive at distances r of the order of the polaron radius, and repulsive for higher distances, with a long range tail for $r \to \infty$; the latter is repulsive and divergent if $r \to 0$, and attractive at intermediate distances, with a (negative) r^{-6} tail as $r \to \infty$. The critical temperatures depend on the effective potentials that contain terms due to the correlation effects depending on the details of the bare polaron-polaron or argon-argon interactions, on the temperature T and on the density n.

The work is organized as follows: In Sec. II the theoretical framework, already discussed in a different form in Ref. 34, is outlined. In Sec. III A the simple cubic polaron crystal formation is discussed, whereas in Sec. III B our approach is applied to the Ar crystallization. Finally, in Sec. IV we summarize our conclusions.

II. THEORETICAL SCHEME

In the cited previous work[34] the polaron-polaron potential $\phi(r)$, calculated to describe the bipolaron formation, was used as a starting point to derive the interaction between polarons $K(r)$ (see the Appendix), including correlations terms and neglecting exchange terms, for a dilute many-polaron system. The polarons move in a rigid background of positive charges.

As already mentioned, both a kinetic (mechanical) and a thermodynamic instability can hinder the formation of the crystal phase. The two approaches needed for a full assessment of the problem are shortly summarized in the following. More details can be found in Ref. 34.

A. Thermodynamic instability

In the framework of the linearized nonstationary Vlasov kinetic equation, the effect of a small perturbation is described through the variation $f(\mathbf{r}, \mathbf{v}, t) = F(\mathbf{r}, \mathbf{v}, t) - F_0(\mathbf{v})$ of the distribution function $F(\mathbf{r}, \mathbf{v}, t)$ with respect to the stationary one $F_0(\mathbf{v})$. It can be calculated from the integral equation

$$f(\mathbf{r}, \mathbf{v}, t) = \frac{1}{2} \int_{-\infty}^t \Psi(\tau, \mathbf{r} - \mathbf{v}(t - \tau), \mathbf{v}) d\tau$$
$$+ \frac{1}{2} \int_\infty^t \Psi(\tau, \mathbf{r} - \mathbf{v}(t - \tau), \mathbf{v}) d\tau, \quad (1)$$

where

$$\Psi(t, \mathbf{r}, \mathbf{v}) = \frac{1}{M} \nabla_\mathbf{v} F_0(\mathbf{v}) \cdot \nabla_\mathbf{r} \int K(|\mathbf{r} - \mathbf{r}'|) f(\mathbf{r}', \mathbf{v}', t) d\mathbf{r}' d\mathbf{v}'. \quad (2)$$

The perturbation induces a variation of the electron density

$$\varrho(\mathbf{r}, t) = \int f(\mathbf{r}, \mathbf{v}, t) d\mathbf{v}. \quad (3)$$

If we write $\varrho(\mathbf{r}, t) = \Sigma_\mathbf{k} \varrho_\mathbf{k}(t) \exp(i\mathbf{k} \cdot \mathbf{r})$ we obtain

$$\varrho_\mathbf{k}(t) = \frac{1}{2} \int_{-\infty}^t G_\mathbf{k}(t - \tau) \varrho_\mathbf{k}(\tau) d\tau + \frac{1}{2} \int_\infty^t G_\mathbf{k}(t - \tau) \varrho_\mathbf{k}(\tau) d\tau, \quad (4)$$

where the kernel of the integral equation is

$$G_\mathbf{k}(t) = \frac{\sigma(k)}{M} \int \exp(-i\mathbf{k} \cdot \mathbf{v}t)[i\mathbf{k} \cdot \nabla_\mathbf{v} F_0(\mathbf{v})] d\mathbf{v} \quad (5)$$

and

$$\sigma(k) = \int K(r) \exp(-i\mathbf{k} \cdot \mathbf{r}) d\mathbf{r}. \quad (6)$$

The spherical symmetry of $K(r)$ and $F_0(v)$ implies that $G_\mathbf{k}(t) = G_k(t)$ and the existence condition for the solution of Eq. (4) is[37]

$$\int_0^\infty G_k(t) dt \geqslant 1. \quad (7)$$

We see that $G_k(t)$ depends on the distribution function of the velocity $F_0(v)$ of the homogeneous phase that we assume given by the Maxwell function.

If the whole homogeneous polaron phase has a drift velocity v_x along the x axis, $F_0(v)$ must be replaced with $F_0(|\mathbf{v} - \mathbf{v}_x|)$ and the condition of existence for the solution of Eq. (4) becomes

$$\int_0^\infty G_k(t) \cos(k_x v_x t) dt \geqslant 1. \quad (8)$$

The previous equation can be rewritten in a simpler form as

$$\mu_1 = -\frac{2\sigma(k)n}{\theta}\int_0^\infty x\exp(-x^2)\cos(\Omega_x x)dx \geqslant 1, \qquad (9)$$

with $k=(k_x^2+k_\varrho^2)^{1/2}$, $k_\varrho=(k_y^2+k_z^2)^{1/2}$, $u=(2\theta/M)^{1/2}$, and $\Omega_x=2v_x/u$ the adimensional parameter linking the drift velocity of the polaron gas to the thermal velocity. The corrections to the polaron effective mass M due to v_x could also be taken into account,[27] but their contribution is small,[28] if the velocity is so small that the polaron state corresponds to a cloud of electrons and virtual phonons.

If $v_x=0$, the condition to be satisfied to have a periodic phase (taking into account screening effects) is[34]

$$\mu = -\frac{n\sigma(k)}{\theta\left[1+\dfrac{4\pi ne^2}{\varepsilon_s(k^2+\kappa^2)\theta}\right]} \geqslant 1, \qquad (10)$$

where $\kappa=\left(\frac{4\pi ne^2}{\varepsilon_s\theta}\right)^{1/2}$ is the reciprocal Debye screening length, $\sigma(k)$ the Fourier transform of $K(r)$, and $\theta=k_BT$. The highest critical temperature T_1^{cr} is determined by the value of θ satisfying the equation $\mu=1$ with $k=k_{opt}$ [such that $\sigma(k_{opt})$ is the minimum negative value of $\sigma(k)$]. At this temperature, the system crosses from the homogeneous to the periodic phase, with periodicity $d=\frac{2\pi}{k_{opt}}$. The phase transition is determined by the combined action of the correlation and screening effects. In the range of densities we consider here (up to 10^{19} and 10^{22} cm^{-3} for the polaron and the argon gas, respectively)[34] the correlation enhances $K(r)$ with respect to $\phi(r)$. At higher densities the screened interaction $K(r)$ gets lower.

If $\Omega_x\neq 0$, the x axis becomes the anisotropy axis. We will assume that k_ϱ is the same as in the isotropic case and k_x is calculated through the equation $\mu_1=1$. In this case, the critical temperature T_1^{cr} is found by first taking the values of k_x giving the lowest negative value of σ and then solving the equation $\mu_1=1$ as function of θ.

The same stability problem can be approached within the stationary nonlinearized Bogolyubov scheme,[34] describing the polaron gas through the equilibrium distribution functions $F_s(\mathbf{r}_1,\mathbf{r}_2,\ldots,\mathbf{r}_s)$ $(s=1,2,\ldots)$. They satisfy a set of equations in which $F_s(\mathbf{r}_1,\mathbf{r}_2,\ldots,\mathbf{r}_s)$ can be calculated if $F_{s+1}(\mathbf{r}_1,\mathbf{r}_2,\ldots,\mathbf{r}_{s+1})$ is known. Each function $F_s(\mathbf{r}_1,\mathbf{r}_2,\ldots,\mathbf{r}_s)$ gives the probability of finding in the configuration space with s dimensions, s particles in the unit volume. When the method is applied to dilute systems, neglecting the three-particle and higher order correlations, the single particle distribution function $F_1(\mathbf{r})$ is given by the nonlinear integral equation

$$\log[\lambda F_1(\mathbf{r})]+\frac{\psi(\mathbf{r})}{\theta}+\frac{n}{\theta}\int K(|\mathbf{r}-\mathbf{r}'|)F_1(\mathbf{r}')d\mathbf{r}' = 0, \qquad (11)$$

where $\psi(\mathbf{r})$ is the electrostatic energy due to the polaron charge $-eF_1(\mathbf{r})$ plunged in the homogeneous background of the ionic positive charge and λ is a Lagrange multiplier introduced to take into account the normalization condition

$$F_1(\mathbf{r}) = \int F(\mathbf{r},\mathbf{v})d\mathbf{v}, \quad \lim_{V\to\infty}\frac{1}{V}\int F_1(\mathbf{r})d\mathbf{r}=1. \qquad (12)$$

Since $\psi(\mathbf{r})$ is a linear functional of $F_1(\mathbf{r})$, Eq. (11) is a non-linear integral equation of the Hammerstein type.[38] This equation can present the bifurcation phenomenon, namely, two independent solutions can occur for the same physical parameters of the system. Such solutions describe in our case the crossover from the homogeneous phase to the polaron lattice formation. In Ref. 34, we solved Eq. (11) with standard mathematical methods,[38] to find the critical temperatures at which the periodic phase appears. Such an approach gives quantitatively accurate results only near the bifurcation point, because it is based on series expansions of F_1, λ, θ^{-1}, and ψ around the critical temperature. To gain insight on the formation of the polaron crystal, in the present work we find exact solutions of Eq. (11), written in the form

$$F_1(\mathbf{r}) = \frac{1}{\lambda}\exp\left[-\frac{\psi(\mathbf{r})}{\theta}-\frac{n}{\theta}\int K(|\mathbf{r}-\mathbf{r}'|)F_1(\mathbf{r}')d\mathbf{r}'\right]. \qquad (13)$$

This allows us to calculate the temperature T_1^{cr} and other parameters that characterize the formation of the polaron crystal as function of n, α, ε_s, and ε_∞.

B. Kinetic instability

As previously reported,[34] it turns out that a single temperature T_1^{cr} does not allow to completely describe the existence and stability of the periodic phase. A careful analysis of the linearized Vlasov equation shows that a mechanical instability in the density fluctuation motion appears if

$$-\frac{\sigma_0(k)n}{\theta} > 1. \qquad (14)$$

Here, $\sigma_0(k)$ is the Fourier transform of the polaron-polaron interaction potential $\phi(r)$. As a consequence, a lower critical temperature $T_2^{cr} < T_1^{cr}$ must be introduced, such that the crystalline polaron phase can exist only if $T_2^{cr} < T < T_1^{cr}$. This odd behavior may be related to the temperature and density dependence of $K(r)$.

The dependence on T of $K(r)$ occurs through the term $\Delta\phi(r)$ (and n_0) of Eq. (A2). While this equation applies to both the polaron and argon gas, the features of $\Delta\phi(r)$ (and n_0) may be rather sensitive to the details of the bare particle-particle interaction $\phi(r)$. It turns out that, in the case of the polaron gas, upon reducing the temperature below a given threshold the corrections to $\phi(r)$ due to the correlations, responsible for the periodic phase, become negligible. In particular, as $T\to 0$, the attractive part of $\phi(r)$ gives the largest contribution to n_0, which becomes positive and large. Since the quantity n_0 balances the repulsive and the attractive part of $\phi(r)$ through T, $\Delta\phi(r)\to 0^-$ and $K(r)\simeq\frac{\phi(r)}{1+\varepsilon_0}$ (ε_0 is the dilution parameter that increases on increasing n, see the Appendix). We conclude that in this limit the correlation term $\Delta\phi(r)$ becomes negligible, $K(r) < \phi(r)$, and consequently the periodic phase cannot be present. Thus, suffi-

ciently small temperatures tend to destroy the ordered phase, at variance with the argon gas. On the other hand, the increase of the density n with fixed T produces an increase of the weight of the correlation term $\Delta\phi(r)$ with respect to the bare interaction $\phi(r)$.

The competition between the correlation and screening effects also plays a role in determining the critical value α_{cr} of α. As reported elsewhere (Fig. 4 of Ref. 34), α_{cr} is nearly independent of n for low polaron densities, whereas increasing with n for higher densities.

III. RESULTS

A. Polaron lattice

Firstly, we discuss the features of the solution of Eqs. (13) in the absence of a drift velocity of the polaron gas ($\Omega_x = 0$). We fix $k = k_{opt}$ (the optimal wave vector corresponds to the polaron crystallization with lowest lattice parameter) and assume cubic symmetry. Therefore, the distribution of polarons in the periodic phase can be written as

$$F_1(\mathbf{r}) = \sum_{|s|=0}^{+\infty} a_s \exp(is\mathbf{k} \cdot \mathbf{r}), \quad (15)$$

with $|\mathbf{k}| = k_{opt}$. By inserting Eq. (15) into Eq. (13), we obtain the following transcendental equations for the coefficient a_s:

$$a_s = \frac{C_0}{\pi} \int_0^\pi \exp\left[-\frac{n}{\theta} \sum_{|p|=0}^{+\infty} a_p \xi(pk) \exp(ip\eta) - is\eta \right] d\eta,$$

$$s = 0, \pm 1, \pm 2, \ldots, \quad (16)$$

with $\eta = \mathbf{k} \cdot \mathbf{r}$, and

$$\xi(k) = \frac{\int K(r)\exp(i\mathbf{k} \cdot \mathbf{r}) d\mathbf{r}}{1 + \dfrac{4\pi e^2 n}{\varepsilon_s(k^2 + \kappa^2)\theta}},$$

$$C_0 = \frac{1}{\pi} \int_0^\pi \exp\left[-\frac{n}{\theta} \sum_{n=1}^\infty 2a_n \xi(nk)\cos(n\eta) d\eta \right]. \quad (17)$$

The quasiexact solution of Eqs. (16) is made possible because it turns out that $|\xi(k_{opt})| > |\xi(2k_{opt})| > |\xi(3k_{opt})| > \ldots$, so that we can limit the number of equations to be solved. We find that in all the cases we can consider only the terms p, $s = 0, \pm 1, \pm 2, \pm 3$, whose self-consistent solutions give the coefficients a_1, a_2, and a_3. They are shown in Fig. 1 as function of T for $n = 10^{18}$ cm^{-3}, $\varepsilon^*/\varepsilon_\infty = 1.00$, and $\alpha = 15$. The critical temperature T_1^{cr} is the point at which the three coefficients become zero. The same T_1^{cr} was found in Ref. 34. We also find that T_1^{cr} is an increasing function of α for fixed $\varepsilon^*/\varepsilon_\infty$ and n and a decreasing function of $\varepsilon^*/\varepsilon_\infty$ for fixed α and n, as in Ref. 34. As a new result, we show in Fig. 2 the distribution function $\rho(x) = F_1(x, 0, 0)$ (a) with fixed α, n, and $T < T_1^{cr}$ for different values of $\varepsilon^*/\varepsilon_\infty$, (b) with fixed $\varepsilon^*/\varepsilon_\infty$, n, and $T < T_1^{cr}$ for different values of α, and (c) with fixed α,
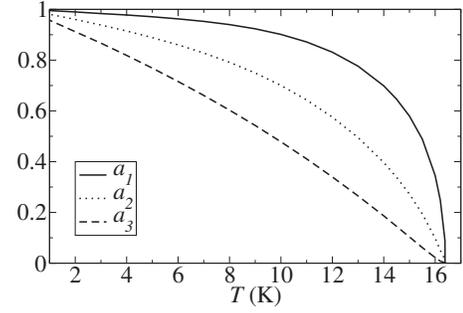

FIG. 1. The coefficients a_1, a_2, and a_3 [Eq. (16), $k = k_{opt}$] are shown as function of T for a polaron gas with $\varepsilon^*/\varepsilon_\infty = 1.00$, $n = 10^{18}$ cm^{-3}, and $\alpha = 15$. The critical temperature T_1^{cr} is found when a_1, a_2, and a_3 become zero.

$\varepsilon^*/\varepsilon_\infty$, and $T < T_1^{cr}$, for different values of n. Several aspects can be highlighted here: (i) the decrease of the ionicity of the medium has both effects of widening and lowering the peak and increasing the polaron lattice parameter [Fig. 2(a)]; (ii) the increase of α or n makes the distribution function more peaked [Figs. 2(b) and 2(c)]; (iii) upon decreasing the temperature $T < T_1^{cr}$, the lattice parameter $d = \frac{2\pi}{k_{opt}}$ (unexpectedly) increases in the case of the polaron gas (see Fig. 5, curve $\Omega_x = 0$), while (as expected) increases for the argon gas (see Fig. 10). Since in both cases the same procedure is applied, the features of the effective polaron-polaron and the atomic argon interactions are expected to play a key role in determining the temperature dependence of d. In particular, we
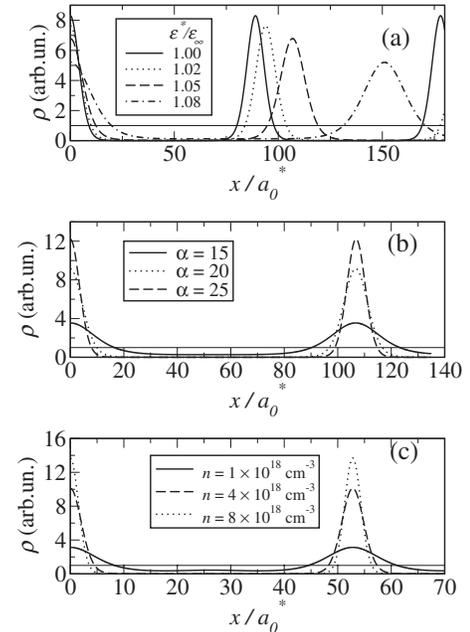

FIG. 2. The position dependent density $\rho(x) = F_1(x, 0, 0)$ for different parameters of the polaron gas: (a) $\alpha = 20$, $n = 10^{18}$ cm^{-3}, $T = 13$ K $< T_1^{cr}$, and different values of $\varepsilon^*/\varepsilon_\infty$; (b) $\varepsilon^*/\varepsilon_\infty = 1.05$, $n = 10^{18}$ cm^{-3}, $T = 10$ K $< T_1^{cr}$, and different values of α; (c) $\alpha = 25$, $\varepsilon^*/\varepsilon_\infty = 1.02$, $T = 50$ K $< T_1^{cr}$, and different values of n. The horizontal lines ($\rho(x) = 1$) correspond to the homogeneous gas. a_0^* is the effective Bohr radius (see the Appendix).

point out that the polaron-polaron interaction is finite and repulsive as $r \to 0$, attractive in a range of distances of the order of the polaron radius, and decays to zero at large distances, with a long range repulsive tail. On the other hand, the argon-argon interaction is repulsive and divergent as $r \to 0$, attractive in a range of distances around 3.8 Å, and decaying to zero with a short range attractive tail at larger distances.

To clarify the physical mechanism explaining the features of the polaron crystal, we introduce simple partial criteria to calculate α_{cr} and T_1^{cr}. By analogy with the electron Wigner crystal, the occurrence of a crystal phase is marked by the condition that the single-particle kinetic energy E_c is much lower than the potential energy E_p.[39] If $\phi(r)$ is the effective polaron-polaron potential, we can write $E_c = \frac{9}{8}\hbar\left[\frac{Z\phi''(r_0)}{M}\right]^{1/2}$ and $E_p = Z|\phi(r_0)|$ where r_0 has been already defined and Z is the coordination number of the crystal.[39] The equation $E_c = E_p$ defines α_{cr} as function of $\varepsilon^*/\varepsilon_\infty$, because it turns out that if $\alpha > \alpha_{cr}$, then $E_c < E_p$. This simple remark allows us to conclude that the formation of the polaron crystal is driven by the same physical mechanism that determines the formation of the electron Wigner crystal. Nonetheless, at variance with the electron Wigner crystal, the temperature dependent correlation effects introduce the second (lower) critical temperature T_2^{cr}.

The analogy with common crystals can be made even tighter by introducing the Lindemann criterion, well known in the theory of the phase transition. The crossover from the homogeneous to the periodic phase can be characterized[40] through the parameter $\zeta = (\langle x^2 \rangle / a^2)^{1/2}$, with a the crystal lattice parameter and $\langle x^2 \rangle^{1/2}$ the fluctuation length around the equilibrium position. The Lindemann criterion, applied to the polaron crystal, leads to the conclusion that the periodic phase can exist only if $\zeta \ll 1$ (for example, we can choose $\zeta \lesssim 0.1$). In Figs. 3(a) and 3(b) we show ζ as function of $\varepsilon^*/\varepsilon_\infty$, for fixed T and n and α and as function of T for fixed α, n, and $\frac{\varepsilon^*}{\varepsilon_\infty}$, respectively. In the first case we see that ζ decreases by increasing α or the polarity of the medium; in the second case we see that the lines are broken when the system crosses the lower temperature T_2^{cr}. Finally, in Fig. 4 we show α_{cr} as function of n and for different values of $\varepsilon^*/\varepsilon_\infty$, when we require that the Lindemann's criterion $\zeta \lesssim 0.1$ be satisfied (this makes the result qualitatively different from that shown in Fig. 4 of Ref. 34). We notice that each line does not span the entire range of densities. After the ending point no value of α satisfying all the required conditions can be found. Therefore, the ending point defines the lower critical temperature T_2^{cr}. The obtained values of T_2^{cr} are the same as in our previous work.[34] For each given value of $\varepsilon^*/\varepsilon_\infty$, Fig. 4 can be seen as a phase diagram in the α-n plane, the periodic phase existing only above the given curve. The strong Lindemann's criterion $\zeta \lesssim 0.1$ (small fluctuation of the polaron about the equilibrium position) requires that the screening and correlation effects act in a cooperative way. We remark also that, as shown in Figs. 3(a) and 3(b), the condition $\zeta < 1$ is fulfilled for a large range of values of α and $\varepsilon^*/\varepsilon_\infty$. This indicates that the specific values of T_1^{cr} and T_2^{cr} depend on the particular criterion adopted, but the qualitative description of the phenomenon is not modi-
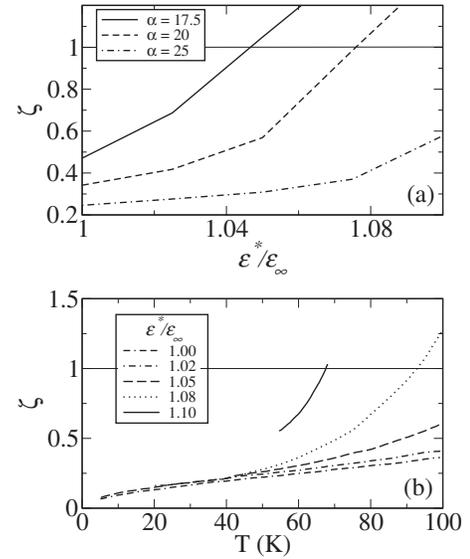

FIG. 3. (a) Dependence of the dimensionless parameter $\zeta = \langle x^2 \rangle^{0.5}/a$ on $\varepsilon^*/\varepsilon_\infty$ (we fix $T = 13$ K and $n = 10^{18}$ cm^{-3}), for different values of α (let us note that the periodic phase is absent if $\alpha = 17.5$ and $\varepsilon^*/\varepsilon_\infty > 1.05$ or $\alpha = 20$ and $\varepsilon^*/\varepsilon_\infty > 1.08$). The region $\zeta \geq 1$ (limited by the thin solid line) corresponds to the absolute instability of the periodic phase. (b) Dependence of ζ on the temperature, for different values of $\varepsilon^*/\varepsilon_\infty$ (we fix $\alpha = 25$ and $n = 5 \times 10^{18}$ cm^{-3}).

fied. The issue of the Wigner crystallization in a polarizable medium is also discussed in Ref. 23.

We now discuss how the previous results get modified in presence of a drift velocity of the polaron gas, which we assume directed along the x axis (we use the x subscript to label the calculated quantities). In Fig. 5 we show $k_{opt,x}$ as function of T for fixed $\varepsilon^*/\varepsilon_\infty$, n, α, and different values of Ω_x. The temperature dependence of $\sigma(k_x, k_\varrho)$ is taken into account. The critical temperature $T_{1,x}^{cr}$ corresponds to the end point of each curve and is found to decrease as a function of Ω_x. On the other hand, for a given drift velocity, a lower temperature bound is found (defined by the occurrence of $k_{opt,x} = 0$), which increases with Ω_x. This implies that, for fixed $\varepsilon^*/\varepsilon_\infty$, n, and α, a critical velocity $\Omega_{cr,x}$ exists, such that for $\Omega_x > \Omega_{cr,x}$ the periodic phase cannot form. As stated above, the occurrence of the polaron lattice corresponds to

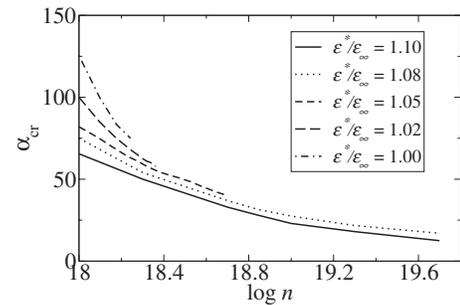FIG. 4. α_{cr} as function of n, for different values of $\varepsilon^*/\varepsilon_\infty$. We require the Lindemann criterion $\zeta \lesssim 0.1$ be satisfied. The ending point of each line defines T_2^{cr} (see text).
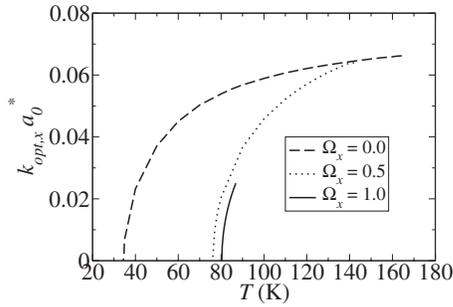
FIG. 5. $k_{\text{opt},x}$ as function of T [the temperature dependence of $\sigma(k_x, k_\varrho)$ is taken into account] for different values of Ω_x. We fix $\varepsilon^*/\varepsilon_\infty = 1.05$, $n = 10^{19}$ cm^{-3}, and $\alpha = 20$. a_0^* is the effective Bohr radius (see the Appendix).

periodic solutions of Eq. (13). Nonetheless, the presence of kinetic instabilities can drive the loss of the oscillatory character of such solutions, in favor of an exponentially decaying behavior.[34] We have already pointed out that a lower critical temperature $T_2^{\text{cr}} < T_1^{\text{cr}}$ is the signature of the appearance of such instabilities. It can be inferred from Eq. (13) that also T_2^{cr} depends on the distribution function of the homogeneous phase and, consequently, on the drift velocity of the polaron gas, in agreement with the findings of Fig. 5. The dependence of the critical temperatures on the drift velocity is well highlighted in Figs. 6 and 7. In Fig. 6 we show $T_{1,x}^{\text{cr}}$ as function of Ω_x for fixed n and $\varepsilon^*/\varepsilon_\infty$ and several values of α (as expected, we find that $T_{1,x}^{\text{cr}}$ is an increasing function of α). In Fig. 7 we show the phase diagram of the polaron gas in the plane (Ω_x, T), where the region of existence of the periodic phase is shown for $\alpha = 20$, $\varepsilon^*/\varepsilon_\infty = 1.05$, and $n = 10^{19}$ cm^{-3}.

As a final result, we show in Fig. 8 the polaron distribution function $\rho(x) = F_1(x, 0, 0)$ for (a) fixed T, α, $\varepsilon^*/\varepsilon_\infty$, n, and several values of Ω_x and (b) for fixed T, α, Ω_x, n, and several values of $\varepsilon^*/\varepsilon_\infty$. From Fig. 8(a) we can see that the lattice parameter increases upon increasing Ω_x, with the distribution function becoming lower and wider. The same occurs in Fig. 8(b), upon decreasing the medium polarity.

B. Argon crystallization

To check the goodness of the theory, we apply Eqs. (15)–(17) to study the crystallization of the Ar in a simple
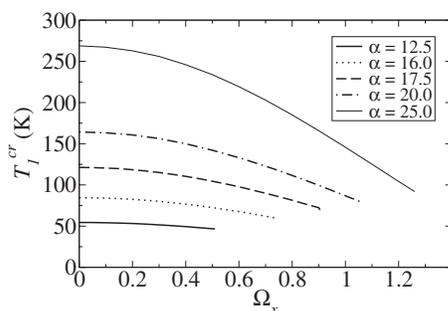

FIG. 6. T_1^{cr} as function of Ω_x for $n = 10^{19}$ cm^{-3}, $\varepsilon^*/\varepsilon_\infty = 1.05$, and several values of α.
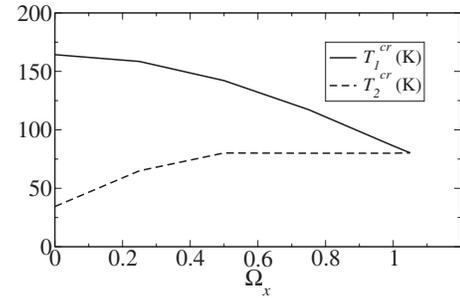

FIG. 7. The phase diagram of the polaron gas in the plane (Ω_x, T). The two curves enclose the region of existence of the periodic phase. We fix $\alpha = 20$, $\varepsilon^*/\varepsilon_\infty = 1.05$, and $n = 10^{19}$ cm^{-3}.

cubic crystal. The atomic interaction can be suitably modelled using the well known Lennard-Jones potential

$$\phi_a(r) = 4\varepsilon \left[\left(\frac{r_0}{r} \right)^{12} - \left(\frac{r_0}{r} \right)^6 \right], \tag{18}$$

with $r_0 = 3.408$ Å and $\varepsilon = 0.0103$ eV.[43] As in the case of the polaron, we define the effective argon-argon interaction (see Ref. 34 and Appendix).

If we adopt the Bogoliubov approach (in analogy with the polaron gas, see Fig. 1), we can obtain the critical temperature T^{cr} from the plot of the coefficients a_1, a_2, and a_3, shown in Fig. 9. All three coefficients become zero at $T = T^{\text{cr}}$. We get $T^{\text{cr}} = 107$ K for $n = 2.1 \times 10^{22}$ cm^{-3}. In Fig. 10 we show k_{opt} as function of T. We see that the lattice parameter $d = \frac{2\pi}{k_{\text{opt}}}$ is an increasing function of T (in contrast with what is shown for the polaron lattice parameter, see Fig. 5, curve $\Omega_x = 0$) and
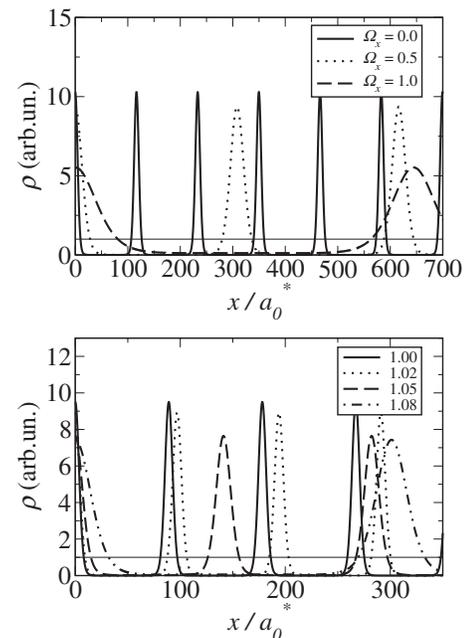

FIG. 8. Polaron distribution function for (a) $T = 80$ K, $\alpha = 20$, $\varepsilon^*/\varepsilon_\infty = 1.05$, $n = 10^{19}$ cm^{-3}, and several values of Ω_x and (b) $T = 105$ K, $\alpha = 20$, $\Omega_x = 0.25$, $n = 10^{19}$ cm^{-3}, and several values of $\varepsilon^*/\varepsilon_\infty$. a_0^* is the effective Bohr radius (see the Appendix).
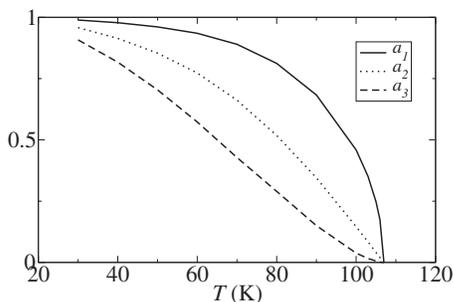
FIG. 9. The coefficients a_1, a_2, and a_3 [see Eq. (16)] as function of T calculated for the Lennard-Jones potential [Eq. (18)] with r_0 =3.408 Å and ε=0.0103 eV. The critical temperature T_{cr} is found at the point where a_1, a_2, and a_3 become zero.

that no lower critical temperature T_2^{cr} shows up. In Fig. 11 the atomic distribution function $\rho(x)=F_1(x,0,0)$ is calculated for several values of T, showing how the peaks of $F_1(x,0,0)$ get lower and wider on increasing the temperature.

As for the polaron gas, the problem can also be approached within the kinetic Vlasov approach. If we assume that the medium has a specific vibration frequency and if we look for solutions of the form $\varrho_k(t)\sim q_k(\omega)\exp(i\omega t)$ in Eq. (4), we find that the following condition [analog of Eq. (8)] must be satisfied:

$$\mu_2 = -\frac{2n\sigma(k)}{\theta}\int_0^\infty x\exp(-x^2)\cos\left(\frac{2\omega x}{k}\sqrt{\frac{m}{2\theta}}\right) \geqslant 1$$

(19)

to have the periodic phase. Following the route traced in the previous section, the solution of the equation $\mu_2=1$ allows us to determine the adimensional frequency of the oscillation $W=\frac{\omega}{k}\sqrt{\frac{m}{2\theta}}$ as function of k and θ. We find the critical temperature T^{cr} by first taking the values of k giving the lowest negative value of μ_2 and then solving the equation $\mu_2=1$ as function of θ. We calculate $k_{opt}=0.956a_0^{-1}$ ($a_0=\frac{\hbar^2\varepsilon^*}{e^2m}$ is the effective Bohr radius) and $T^{cr}=107$ K if $W=0$ (in agreement with the above result), whereas $k_{opt}=0.959a_0^{-1}$ and T^{cr} =96.05 K if $W=0.5$.

We stress that the same procedure applied to the formation of the polaron and argon crystal gives results that are
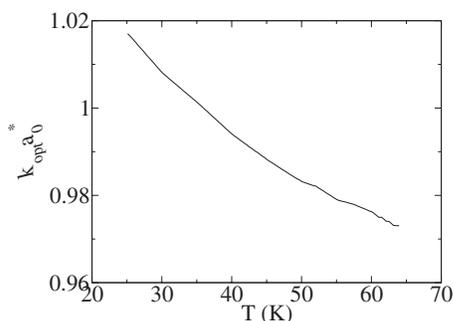

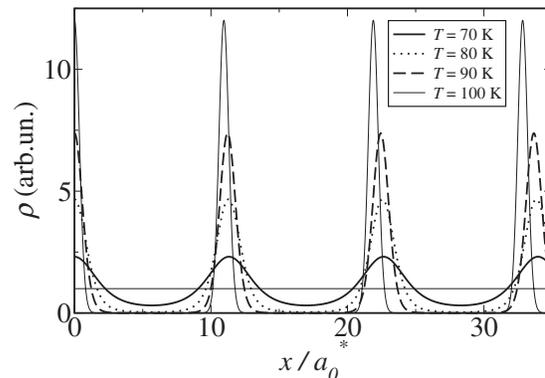FIG. 10. The dependence of the wave vector k_{opt} on the temperature for the argon crystal.

FIG. 11. The distribution function of the Ar atoms in the crystal for several values of T. We fix $n=2.1\times10^{22}$ cm^{-3}. The horizontal line ($\rho(x)=1$) corresponds to the homogeneous gas. a_0^* is the effective Bohr radius (see the Appendix).

very similar for what it concerns the existence of the periodic phase, but opposite for what it concerns the behavior of the lattice parameter as function of T. Moreover in the formation of the argon crystal there is only the first critical temperature, indicating that when $T\rightarrow 0$, the correlation terms survive to assure the existence of the periodic phase.

Finally, we conclude that a huge number of theoretical calculations can be found in the literature, concerning both the fluid and solid phases. Several approaches have been pursued, from analytical methods,[44,45] to Monte Carlo numerical approaches,[43,46] to molecular dynamics calculations.[47,48] Our result for T^{cr} for the simple cubic argon crystal are coherent with the face-centered cubic structure calculation of Ref. 43 done using the Monte Carlo numerical approach. Nevertheless, we point out that a precise, numerical assessment of the argon gas properties is out of the scope of the present work. The method presented here, applied to both the polaron and the argon gas, has allowed us to bring out the combined effect of correlation and temperature in differently correlated systems.

IV. DISCUSSION AND CONCLUSIONS

In this work an exact formulation of the transition from a dilute large polarons gas ($n\leqslant 10^{19}$ cm^{-3}) to the simple cubic polaron lattice has been shown. The same theoretical scheme as that developed in a previous work[34] has been adopted but, at variance with that case, the equation for the Fourier coefficients of the single-particle distribution function has been exactly solved. The features of the polaron-polaron interaction allow us to limit our problem to the solution of a small number of transcendental algebraic equations. The results previously reported[34] can be retrieved. The definition of α_{cr} is connected also to the formation of the Wigner crystal for the electrons and that of T_2^{cr} is due to the peculiar features of the correlation part of the interaction. We have also calculated the polaron distribution function in the crystal phase, showing that it depends on the ionicity parameter of the medium $\varepsilon^*/\varepsilon_\infty$, the electron-phonon Fröhlich constant α, the polaron density n, and the temperature T. In particular, we

have found that the lattice parameter increases upon decreasing the temperature, showing a behavior in contrast with what is expected for common crystals.

To check the goodness of our theoretical scheme, we have calculated also the transition temperature for the formation of the simple cubic Ar crystal, using a suitable Lennard-Jones potential to model the interaction between two atoms. We have found that the transition temperature is 107 K (the experimental one is 85 K for a face-centered cubic crystal) and the lattice parameter is an increasing function of the temperature. We notice the following.

(i) For both systems (polaron and Ar lattice) the calculation method includes the anharmonic terms.

(ii) The different behavior of the lattice parameter as function of T is due to the different features of $\phi(r)$ and $\phi_a(r)$: the first one is finite at $r=0$, has a central attractive part, and goes to zero with a repulsive tail as $r \to \infty$. The second one is infinite at $r=0$, has a central attractive part, and goes to zero with an attractive tail as $r \to \infty$. Furthermore, the Grüneisen constant is different as well.

(iii) The electron-phonon Fröhlich constant α and the ionicity parameter of the medium $\varepsilon^*/\varepsilon_\infty$ do not modify the lattice parameter, but only the height and the width of the peaks in the distribution function.

We have also calculated the same quantities when the polaron gas has a fixed drift velocity. Our main finding is that the system becomes nonisotropic in the direction of the collective motion. Our final conclusion is that the drift velocity makes the solid phase less stable. Furthermore, a critical velocity Ω_x^{cr} exists, for fixed values of n, α, and $\varepsilon^*/\varepsilon_\infty$, such that for $\Omega_x > \Omega_x^{cr}$ the solid phase cannot form. This case seems of academic interest, but it could be important to show the behavior of the polaron lattice in a flow of free polarons or in the formation of the polaron lattice on a surface of an ionic material.

ACKNOWLEDGMENTS

APPENDIX: INTERPOLARON POTENTIAL

The polaron-polaron interaction has been calculated in the strong coupling Pekar theory adapted to give reliable results also in the intermediate coupling regime.[34,37] This potential is coherent with those obtained within the Lee-Low-Pines[41] and path-integral techniques.[42] It can be approximated by the following analytical form:[34,37]

$$\frac{\phi(r)}{2\alpha^2\hbar\omega_0} = \{d + cr^2[a + b(r - \varrho_0)^2][1 - \exp(-\gamma r)]\}\exp(-\delta r)$$

$$+ \left(\frac{\varepsilon^*}{\varepsilon_\infty} - 1\right)[1 - \exp(-\delta r)]\frac{a_0^*}{r}, \qquad \text{(A1)}$$

where $a_0^* = \frac{\hbar^2\varepsilon^*}{e^2 M}$ is the effective Bohr radius and the coefficients a, b, c, d, ϱ_0, γ, and δ depend on $\varepsilon^*/\varepsilon_\infty$.[34] Furthermore $\hbar\omega_0$ is the energy of the longitudinal optical phonon and $\alpha = \left(\frac{1}{2\varepsilon^*}\right)\left(\frac{e^2}{\hbar\omega_0}\right)\left(\frac{2M\omega_0}{\hbar}\right)^{1/2}$. Neglecting three-particle correlation effects and using a suitable ansatz for the two-particle distribution function $F_2(\mathbf{r}_1, \mathbf{r}_2)$, we find an explicit form for the effective polaron-polaron interaction $K(r)$ (Ref. 34) given by

$$K(r) = \frac{1}{1 + \varepsilon_0}(\phi(r) + \Delta\phi(r))$$

with

$$\Delta\phi(r) = \frac{\theta\varepsilon_0}{n_0}\left[1 - \exp\left(-\frac{\phi(r)}{\theta}\right) - \frac{\phi(r)}{\theta}\right] \qquad \text{(A2)}$$

and $\varepsilon_0 = r_0^3/v_1$ ($v_1 = V/N$ is the average volume per particle). ε_0 is the dilution parameter, r_0 (of the order of the polaron radius) is the point at which $\phi(r)$ has its minimum value, and

$$n_0 = \frac{4\pi}{V}\int_0^\infty\left\{\exp\left[-\frac{\phi(r)}{\theta}\right] - 1\right\}r^2 dr. \qquad \text{(A3)}$$

We see that $\Delta\phi(r)$ is due to correlation effects and depends on the details of $\phi(r)$, n, and T.

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