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by

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Using the Feynman path integral method and a theory of polarizable fluids, I evaluate properties of nondegenerate Fröhlich polarons interacting in the strong coupling limit. At large enough densities and temperatures these properties are found to be mainly governed by the dispersion forces, i.e. attractive van-der-Waals interactions, which are no attributed to any permanent electric multipoles. Neglecting short-range correlations in the polaron gas, I have obtained an explicit expression for the dispersion contribution to the free energy of the system. The analysis of this contribution indicates that the dispersion effect is nonlinear and strongly cooperative at large enough densities of the polaron gas. The quasiparticles attract due to these forces leading to softening of the absorption peak, negativity of the dielectric function, and divergence of compressibility of the system. The main consequence of the dispersion forces is a quantum transition which results in a dielectric catastrophe considered as the onset of metallization. A possible excitonic phase consisting from quasiparticles with a nonzero dipole momentum is also examined. Comparing experimental data for metal-ammonia solutions, alkali-halide molten salts, and high-T_c superconducting cuprates, I find that dispersion forces may govern the behavior of self-trapped carries in these compounds.

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I. INTRODUCTION

London dispersion forces, i.e. induced dipole-dipole van-der-Waals interactions, are quite important in soft condensed matter. They play a significant role both in chemical and biological systems.[1] At the same time, their role in charged systems is not revealed and they are usually ignored with respect to the Coulomb interactions. Indeed, the estimates of their effect obtained by perturbation methods indicate that the dispersion interactions are usually much weaker than Coulomb interactions. However, despite of recent progresses,[2] the theory of dispersion forces in quantum systems is still incomplete, while its application is restricted to the study of small atomic/molecular dimers or layered systems (linked by van-der-Waals attractions). The origin of this difficulty mainly resides on the fact that dispersion forces are not additive and must be collectively treated, whereas coupling between short- and long-range correlations of electrons complicates the treatment of these collective effects.

These forces have been proposed to play a crucial role for quantum quasiparticles.[3–8] First, in the case of doped ionic solids with strong electron-phonon coupling and at low enough densities, they result in a new metal-to-insulator transition (MIT) for a 2D or 3D Wigner crystal of large polarons,[3–5] namely, a polarization catastrophe is caused by these dipolar interactions, yielding the onset of metallization of the polaronic Wigner crystal. It has been shown recently[6–8] that the same ideas can be applied to explain the origin of the MIT and a phase separation in metal-ammonia solutions (MAS). Furthermore, an analogy between the MAS and the superconducting cuprates has been proposed.[9,11] Following this analogy, there are three regions[10] in the phase diagram of such polar materials: the low density region where the Coulomb forces lead to the formation of bound states like as polarons or solvated electrons; the highest density region where the Coulomb interactions are completely screened, preventing the formation of such bound states (only free carriers may exist), and finally an intermediate region where the Coulomb forces may be overscreened, resulting in either a superconducting state either a phase separation.[9,10] As it has been shown,[6] this new MIT picture radically contradicts the usual Mott transition scheme, opening the road for considering the possibility of new exotic electronic phases in doped polar substances.[8]

The formation of polarons and their interactions is a major problem in the physics of doped dielectrics. Being an old problem, it still carries a lot of mysteries. Polarons are usually believed to play an important role in determining the properties of several compounds,

such as high-T_c superconducting cuprates,[12] manganites,[13] doped oxides and also conjugated polymers.[14] It is little known beyond a single polaron or bipolaron state, although many specific situations have been considered to investigate the state of a homogeneous polaron gas and especially its stability. A general theory is not complete due to the complexity of the problem. The fundamental reason resides on the fact that a single polaron is already a many-body problem, whereas Coulomb and short-range interactions between polarons still enhance one step beyond the difficulty of the problem. Besides the low density limit of Fröhlich polarons in the crystallized state discussed above,[3–5] many groups have recently improved our knowledge in different limits of the problem,[15–17] including the possibility of electron strings and stripes,[18] or even more complicated situations as in the coupled boson-fermion model.[19]

In the present paper, I will generalize my previous results to the case of the 3D Fröhlich polaron gas interacting at finite temperatures. Moreover, I will provide analytical evaluations of the dispersion forces in the strong electron-phonon coupling limit corresponding to a large Fröhlich coupling constant $\Omega = ce^2(m^*/2\hbar^3\omega_{lo})^{1/2}$,[21] where e and m^* are the electron charge and the effective band mass, $c = \epsilon_\infty^{-1} - \epsilon_0^{-1}$ is the Pekar factor, while ϵ_∞ and ϵ_0 are respectively the dielectric constants of the host medium at high ($\omega >> \omega_{lo}$) and low ($\omega << \omega_{lo}$) frequencies, and ω_{lo} is the longitudinal optical phonon frequency. I should emphasize that the strong electron-phonon coupling ($\Omega > 7$) is hardly realized in real 3D solids. However, the 3D results will serve as a robust basis to better understand 2D, or layered quasi-2D systems of polarons, which are believed to occur in cuprates, since the strong coupling limit is easily reached at $\Omega > 4$ for these layered systems[20] (see, also Ref.[4]).

First, I focus on the statistical behavior of the polarons, i.e. if they may be considered as *classical* (nondegenerate) or *quantum* (degenerate) gas. This behavior depends on the dimensionless parameter $\theta = n\Lambda(T)^3$, where n is the density of polarons, while $\Lambda(T) = (2\pi\hbar^2/M_P k_B T)^{1/2}$ is the de Broglie wavelength and M_P is the polaron mass. The system remains classical if parameter θ is small with respect to unity. Hence, I obtain the temperature T_0 below which the gas is to be degenerate:

$$T_0 \sim \left(\frac{m^*}{M_P}\right) \frac{0.4}{r_s^2} \frac{m^* e^4}{\hbar^2}, \tag{1}$$

where $r_s = (4\pi n/3)^{-1/3} m^* e^2/\hbar^2$. Therefore, under the conditions $r_s > 20$ ($n < 2 \cdot 10^{20}\mathrm{cm}^{-3}$) and $M_P/m * (\Omega > 7) > 50$ corresponding to the strong coupling case, I have $T_0 = 2 \cdot 10^{-5}$

a.u., i.e. the degeneracy temperature is lower than few Kelvins.

Thus, the polaron gas is not degenerate at $T > T_0$ and behaves mainly as a classical diluted electrolyte. Starting from this point, I evaluate the Debye electrostatic screening length for this gas, which is given by $\ell_D = (4\pi n e^2/k_B T\epsilon_0)^{-1/2}$. Taking $T \sim 100$K, $\epsilon_0 \sim 30$ and a density of $n \sim 10^{20}\text{cm}^{-3}$, one obtains $\ell_D \sim 1$Å. This indicates a strong screening of the *electrostatic* interactions in the nondegenerate polaron gas. However, there are other correlations in the system, due to the composite nature of the polarons. Indeed, although a polaron behaves classically as a whole, the electron self-trapped in the polarization cloud remains quantum. The fluctuations due to electronic transitions in localized excited states, occurring at a characteristic frequency ω_0 (typically of the order of $0.1 - 0.2$ eV), induce dipolar interactions between polarons, i.e. dispersion forces. Since I consider the strong coupling case, these electronic transitions are of Franck-Condon type because the transition time duration ω_0^{-1} is much lower than the phonon relaxation time ω_{lo}^{-1}. The difference of behavior between the two kinds of correlations, i.e. the classical (elestrostatic) correlations in one hand, and the quantum (dipolar) correlations in the other hand, allows me to treat them separately. My strategy exactly follows that already used for solvated electrons in MAS,[6–8] and the reader may find there details and complementary discussions. Basically, the main idea is to consider the classical motion of the charged polarons in the framework of the theory of classical one-component plasmas (OCP),[22] while the quantum degrees of freedom are treated with the help of Feynman path integrals,[23] together with the known results of the theory of polarizable fluids.[24–27] This allows me to obtain semi-analytical expressions for the free energy of the system, and evaluate its thermodynamical behavior.

The layout of the paper is as follows. Starting from the linear electron-phonon coupling between N interacting electrons, I derive in Sec. II the partition function of the system and then factorize it by separating the quantum and the classical contributions. In Sec. III I obtain an analytical expression for the free energy of the polaron gas at large coupling constants. Then I will analyze this expression in Sec. IV to reveal a role of the dispersion forces for the polarons. The physical consequence of these forces on the behavior of the quantum quasiparticles is discussed in Sec. V. Finally, I give an evidence of the essential role of these dispersion forces for several compounds such as alkali-halide molten salts (AMHS), MAS, and cuprates. Below I will use the effective atomic units ($\hbar^2/m^*e^2 = 1$) to simplify all the analytical expressions throughout.

II. PARTITION FUNCTION OF THE SYSTEM.

To begin with, I consider a system of N interacting electrons in a 3-dimensional space. The electrons are immersed in a neutralizing jellium background and coupled to longitudinal optical phonons. The partition function Z of the system can be presented as

$$Z = \frac{1}{N!}\int d\mathbf{R}^{\{N\}} d\mathbf{Q}^{\{N\}} Tr\{\exp[-\beta H]\}, \tag{2}$$

where $d\mathbf{R}^{\{N\}}d\mathbf{Q}^{\{N\}}$ means $d\mathbf{R}_1 d\mathbf{R}_2 \dots d\mathbf{R}_N d\mathbf{Q}_1 d\mathbf{Q}_2 \dots d\mathbf{Q}_N$, while $\mathbf{R}_i$ and $\mathbf{Q}_i$ are the coordinates and the momenta corresponding to the translational motion of polarons, β is the inverse temperature, and H is the Hamiltonian of the system, whereas symbol Tr means trace over quantum degrees of freedom. I generalize the Pekar model[28] to the many-polaron case and define the Hamiltonian as

$$H(t) = -\sum_{i=1}^{N}\frac{\nabla_i^2}{2} + \int [\frac{2\pi}{c}(P^2 + \omega_{lo}^{-2}\dot{P}^2) - \mathbf{P}\cdot\mathbf{D}]d\mathbf{r} + \int\int \frac{(\widehat{n}(\mathbf{r},t) - n_))(\widehat{n}(\mathbf{r}_1,t) - n_))d\mathbf{r}d\mathbf{r}_1}{2\epsilon_\infty|\mathbf{r}-\mathbf{r}_1|}, \tag{3}$$

where $\mathbf{P}(\mathbf{r},t)$ is the longitudinal polarization of the medium. In the above relation I have used the notation n for the average density of excess electrons, while $\mathbf{D}(\mathbf{r},t)$ is the induction induced by excess charges:

$$\mathbf{D}(\mathbf{r},t) = \mathbf{D}_- + \mathbf{D}_+, \quad \mathbf{D}_-(\mathbf{r},t) = \nabla\int \frac{\widehat{n}(\mathbf{r}_1,t)d\mathbf{r}_1}{|\mathbf{r}-\mathbf{r}_1|}, \quad \mathbf{D}_+ = -\nabla\int\frac{nd\mathbf{r}_1}{|\mathbf{r}-\mathbf{r}_1|}, \tag{4}$$

whereas $\widehat{n}(\mathbf{r},t)$ is the operator of electron density given by

$$\widehat{n}(\mathbf{r}) = \sum_{i=1}^{N} n_i(\mathbf{r}-\mathbf{r}_i - v_i t) = \sum_{i=1}^{N}\delta(\mathbf{r}-\mathbf{r}_i - v_i t), \tag{5}$$

where I take into account that each polaron moves with velocity $\mathbf{v}_i = \partial\mathbf{R}_i/\partial t$. The main problem to treat (2) is that the classical and the quantum degrees of freedom are coupled due to interactions between polarons and phonons, therefore my task in this section is to separate the respective degrees of freedom by factorizing the partition function into the classical and the quantum contributions.

Since the jellium is assumed to be rigid, I introduce the polarization field which responds only to the electron motion by making the following transformation:

$$\mathbf{P}_-(\mathbf{r},t) = \mathbf{P}(\mathbf{r},t) - \frac{c}{4\pi}\mathbf{D}_+. \tag{6}$$

Then, the Hamiltonian reads

$$H(t) = -\sum_{i=1}^{N}\frac{\nabla_i^2}{2} + \int[\frac{2\pi}{c}(P_-^2+\omega_{lo}^{-2}\dot{P}_-^2) - \mathbf{P}_-\cdot\mathbf{D}_-]d\mathbf{r} + \int\int\frac{\widehat{n}(\mathbf{r},t)\widehat{n}(\mathbf{r}_1,t)d\mathbf{r}d\mathbf{r}_1}{2\epsilon_\infty|\mathbf{r}-\mathbf{r}_1|} + \int\int\frac{n(\widehat{n}(\mathbf{r},t)-n)d\mathbf{r}d\mathbf{r}_1}{2\epsilon_0|\mathbf{r}-\mathbf{r}_1|}. \quad (7)$$

The translational motion of polarons seems to be slow, i.e.

$$|\mathbf{v}_i| \ll \omega_{lo}r_p. \quad (8)$$

where $r_p = \langle r_i^2\rangle^{1/2}$ is the mean polaron radius, and can be treated by perturbation methods. Moreover, I assume the density of polaron gas to be small and ignore exchange effects and possibility of formation of multi-electron states. Then, expanding (7) with respect to the small parameter up to the second order, I find

$$H(t) \approx H_0 = \sum_{i=1}^{N}(h_i + \frac{M_p v_i^2}{2}) + \int\int\frac{\widehat{n}(\mathbf{r})\widehat{n}(\mathbf{r}_1)d\mathbf{r}d\mathbf{r}_1}{2\epsilon_\infty|\mathbf{r}-\mathbf{r}_1|} + \int\int\frac{n(\widehat{n}(\mathbf{r})-n)d\mathbf{r}d\mathbf{r}_1}{2\epsilon_0|\mathbf{r}-\mathbf{r}_1|}, \quad (9)$$

and h_i is one-polaron hamiltonian:

$$h_i = -\frac{\nabla_i^2}{2} + \int[\frac{2\pi}{c}(P_{-i}^2+\omega_{lo}^{-2}\dot{P}_{-i}^2) - \mathbf{P}_{-i}\cdot\mathbf{D}_i]d\mathbf{r}, \quad (10)$$

while $\mathbf{D}_i = \nabla\int\langle n_i(\mathbf{r}_1)\rangle\, d\mathbf{r}_1/|\mathbf{r}-\mathbf{r}_1|$ is the induction induced by i-th polaron, $\langle n_i(\mathbf{r}_1)\rangle$ is the averaged one-electron density, and the effective polaron mass M_p is related with $\mathbf{D}_i$ as[28]

$$M_p = \frac{c}{4\pi\omega_{lo}^2}\int(\frac{\partial\mathbf{D}_i}{\partial\mathbf{x}_i})^2 d\mathbf{r} = \frac{4\pi c}{3\omega_{lo}^2}\int\langle n_i(\mathbf{r})\rangle^2 d\mathbf{r}, \quad (11)$$

where $\mathbf{x}_i$ is a vector coinciding with the direction of polaron velocity $\mathbf{v}_i$.

Introducing de Broglie wavelength $\Lambda = (2\pi\beta/M_p)^{1/2}$ and providing integration over the momenta corresponding to the translational motion of polarons:

$$\int d\mathbf{Q}^{\{N\}}\exp[-\frac{\beta M_p}{2}\sum_i v_i^2] = \Lambda^{-3N} = (2\pi\beta/M_p)^{-3N/2}, \quad (12)$$

I write the partition function of the system in terms of the density matrix ρ as:

$$Z = \int\frac{d\mathbf{R}^{\{N\}}}{V^N}\exp[-N(\ln(n\Lambda^3)-1)]\rho(\mathbf{R}^{\{N\}}), \quad (13)$$

while density matrix $\rho(\mathbf{R}^{\{N\}})$ is expressed by path integrals:

$$\rho = \int\cdots\int_{\mathbf{r}_i(0)=\mathbf{r}_i(\beta)}\prod_i D\mathbf{r}_i(\tau)\exp[-S], \quad (14)$$

where $\int\cdots\int_{\mathbf{r}_i(0)=\mathbf{r}_i(\beta)}$ means the functional integration over all space-time paths $\mathbf{r}_i(\tau)$ of the particles, S is the action of the system:

$$S = \frac{1}{2}\sum_i \int_0^\beta \dot{r}_i^2(\tau)d\tau + \sum_{i,j}\sum_{\mathbf{k}} \frac{c_{\mathbf{k}}^2}{2\beta}\int_0^\beta\int_0^\beta \exp[i(\mathbf{k}\mathbf{r}_i(\tau)-\mathbf{k}\mathbf{r}_j(\sigma))]G_{\omega_{lo}}(\tau-\sigma)d\tau d\sigma$$
$$+ \frac{1}{2\beta\epsilon_\infty}\sum_{i\neq j}\int_0^\beta\int_0^\beta \frac{d\tau d\sigma}{|\mathbf{r}_i(\tau)-\mathbf{r}_j(\sigma)|} + \frac{n}{2\epsilon_0}\int\{\sum_i\int_0^\beta \frac{d\tau}{|\mathbf{r}_i(\tau)-\mathbf{r}|} - \frac{\beta N}{|\mathbf{r}|}\}d\mathbf{r}, \quad (15)$$

and $G_{\omega(\mathbf{k})}(\tau-\sigma)$ is the phonon propagator given by

$$G_{\omega(\mathbf{k})}(x) = \frac{\exp[(\beta-|x|)\omega_{lo}]+\exp[x\omega_{lo}]}{\exp[\beta\omega_{lo}]-1}. \quad (16)$$

To separate the classical and the quantum motions of polarons, I introduce new variables $\mathbf{u}_i(\tau)$ related as

$$\mathbf{r}_i(\tau) = \mathbf{R}_i(\tau) + \mathbf{u}_i(\tau). \quad (17)$$

The variables $\mathbf{R}^{\{N\}} = \{\mathbf{R}_1, \mathbf{R}_2, ..., \mathbf{R}_N\}$ are the coordinates of the centers of mass of polarons, and related with the translational (classical) motion of polarons. On the contrary, the variables $\mathbf{u}_i(\tau)$ correspond to highly oscillating quantum fluctuations. Since I consider the polaron gas at large coupling constants Ω, the electrons are well localized:

$$|\mathbf{u}_i(\tau)| \ll |\mathbf{R}_i(0)|. \quad (18)$$

Therefore I can expand the Hamiltonian with respect to the small parameter $|\mathbf{u}_i/\mathbf{R}_i|$ and neglect in the expansion the terms higher than the second order. As a result, I obtain

$$\rho = \exp[-S_{cl}(\mathbf{R}^{\{N\}}) - S_{mix}(\mathbf{R}^{\{N\}}\mathbf{u}^{\{N\}})]\cdot\rho_q, \quad (19)$$

where S_{cl} is the classical action

$$S_{cl} = \int\int \frac{\widehat{n}_{cl}(\mathbf{r})\widehat{n}_{cl}(\mathbf{r}_1)d\mathbf{r}d\mathbf{r}_1}{2\epsilon_0|\mathbf{r}-\mathbf{r}_1|}, \quad (20)$$

while $\widehat{n}_{cl}(\mathbf{r}_1)$ is the density operator determined the distribution of classical charges, it is given by

$$\widehat{n}_{cl}(\mathbf{r}) = \sum_{i=1}^N \delta(\mathbf{r}-\mathbf{R}_i) - n. \quad (21)$$

On the other hand, the density matrix ρ_q is related with quantum degrees of freedom and expressed as

$$\rho_q = \int\cdots\int_{\mathbf{u}_i(0)=0}^{\mathbf{u}_i(\beta)=\mathbf{0}} \prod_i D\mathbf{u}_i(\tau)\exp[-\sum_{i=1}^N S_i - \sum_{i\neq j}^N S_{ij}], \quad (22)$$

where S_i and S_{ij} are the one- and the two- electron contributions presented as

$$S_i(\mathbf{u}_i) = \frac{1}{2}\int_0^\beta \dot{u}_i^2(\tau)d\tau - \frac{\omega_{lo}c}{4\beta}\int_0^\beta\int_0^\beta \frac{d\tau d\sigma G_{\omega_{lo}}(\tau-\sigma)}{|\mathbf{u}_i(\tau)-\mathbf{u}_i(\sigma)|}, \tag{23}$$

$$S_{ij}(\mathbf{u}_i,\mathbf{u}_j) = \frac{1}{2\beta\epsilon_\infty}\int_0^\beta\int_0^\beta \mathbf{u}_i^\perp(\tau)\cdot\mathbf{T}_{ij}\cdot\mathbf{u}_j(\sigma)\widetilde{G}(\tau-\sigma)d\tau d\sigma, \tag{24}$$

whereas $\widetilde{G}(\tau-\sigma)$ is the modified phonon propagator given by

$$\widetilde{G}(x) = \delta(x) - \frac{\omega_{lo}c\epsilon_\infty}{2}G_{\omega_{lo}}(x), \tag{25}$$

and $\mathbf{T}_{ij}(\mathbf{R}_{ij})$ is the dipolar tensor depending on the distance $\mathbf{R}_{ij}=\mathbf{R}_i-\mathbf{R}_j$ between centers of mass of polarons, which takes the form:

$$T_{ij}^{\alpha\gamma}(\mathbf{R}_{ij}) = \frac{\delta_{\alpha\gamma}\mathbf{R}_{ij}^2 - 3\mathbf{R}_{ij}^\alpha\mathbf{R}_{ij}^\gamma}{|\mathbf{R}_i-\mathbf{R}_j|^5}. \tag{26}$$

Apart from the classical and the quantum contributions, the density matrix ρ depends on the mixing part $S_{mix}(\mathbf{R}^{\{N\}}\mathbf{u}^{\{N\}})$, but this action includes only the terms which are linearly proportional to $\mathbf{u}_i(\tau)$ or $\widehat{n}_{cl}(\mathbf{r})$, corresponding to permanent-dipole-charge and permanent dipole-dipole interactions between polarons. However, I have $\langle\widehat{n}_{cl}\rangle = \langle\mathbf{u}_i\rangle = 0$ due to neutrality of polaron gas and spherical symmetry of the polaron ground state. Therefore, these terms do not yield any contribution to the partition function of the system. Therefore, I can factorize the partition function:

$$\begin{aligned} Z &= Z_{cl}Z_q, \qquad Z_{cl} = \int\frac{d\mathbf{R}^{\{N\}}}{V^N}\exp[-N(\ln(n\Lambda^3)-1) - \beta\int\int\frac{\widehat{n}_{cl}(\mathbf{r})\widehat{n}_{cl}(\mathbf{r}_1)d\mathbf{r}d\mathbf{r}_1}{2\epsilon_0|\mathbf{r}-\mathbf{r}_1|}], \\ Z_q &= \int\cdots\int_{\mathbf{u}_i(0)=0}^{\mathbf{u}_i(\beta)=\mathbf{0}}\prod_i D\mathbf{u}_i(\tau)\exp[-\sum_{i=1}^N S_i - \sum_{i\neq j}^N S_{ij}], \end{aligned} \tag{27}$$

where the effective actions S_i and S_{ij} are determined by Eqs. (23) and (24), respectively.

III. EVALUATION OF THE FREE ENERGY OF THE SYSTEM

A. Classical contribution

The classical part Z_{cl} corresponds to the partition function of the one-component plasma, i.e. classical point charges with mass M_p immersed in a jellium. This part gives the following contribution to the free energy:

$$\beta f_{ocp}(n,T) = -N^{-1}\ln Z_{cl} = \big[\ln(n\Lambda^3)-1\big] + \beta f_{ex}(\Gamma), \tag{28}$$

where the first term in (28) is the ideal part, while the second one is the excess free energy due to electrostatic interactions between point charges, it can be expressed in terms of dimensionless parameter $\Gamma = \beta(4\pi n/3)^{1/3}/\epsilon_0$.[22] There are available analytical expressions for $f_{ex}(\Gamma)$, for instance,[29] in the range $1 < \Gamma < 160$ it can be written as:

$$\beta f_{ex}(\Gamma > 1) = -0.89752\Gamma + 3.620172\Gamma^{1/4} - 0.75824\Gamma^{-1/4} - 0.81487 \ln \Gamma - 2.58274. \quad (29)$$

The first term in this expression represents the Madelung energy of polarons, while the rest is a temperature-dependent correction due to the thermal motion of polarons. I note that the degeneracy parameter θ is determined by the value $n\Lambda^3$, whereas the polaron gas is nondegenerate until the parameter is small, i.e. $\theta = n\Lambda^3 << 1$.

B. Quantum contribution in the ultra-low density limit

When the average density of the gas tends to zero, i.e., $n \to 0$, polaron interactions are infinitely small and I can ignore S_{ij} with respect to S_i. Therefore, I have a system of noninteracting polarons, while the quantum contribution is given by

$$Z_q = \int \cdots \int_{\mathbf{u}_i(0)=0}^{\mathbf{u}_i(\beta)=0} D\mathbf{u}_i(\tau) \exp[-NS_i]. \quad (30)$$

To estimate this partition function, I can use the variational method with the Feynman trial action S_0:[23]

$$S_0 = \frac{1}{2}\int_0^\beta \dot{u}_i^2(\tau)d\tau + \frac{(\omega_0^2 - \omega_1^2)\omega_1}{8}\int_0^\beta \int_0^\beta d\tau d\sigma G_F(\tau - \sigma)|\mathbf{u}_i(\tau) - \mathbf{u}_i(\sigma)|^2, \quad (31)$$

where ω_1 and ω_0 are the variational parameters, while $G_F(\tau)$ is the propagator defined by:

$$G_F(x) = \frac{\cosh[(\beta/2 - |x|)\omega_1]}{\sinh[\beta\omega_1/2]}. \quad (32)$$

Then, the variational estimate of the free energy is obtained by a cumulant expansion of (30) with respect to the difference $\Delta S = S_i - S_0$, ([23], see also[30]) and the quantum part of the free energy is expressed as

$$\beta f_{pol} = -N^{-1} \ln Z_q = \beta f_0 + \langle \Delta S \rangle_0 + ... \quad (33)$$

where f_0 is the free energy associated with the trial action, while symbol $\langle .. \rangle_0$ means the mean value obtained with the use of the trial action S_0. I remark that the main advantage

of the choice of the Feynman trial action is that the corresponding free energy is calculated explicitly in terms of the variational parameters. As $\beta \to \infty$, it reads[23]

$$f_{pol} = \frac{3(\omega_0 - \omega_1)^2}{4\omega_0} - \frac{\Omega\omega_0}{\sqrt{\pi}} \int_0^\infty e^{-x}[x + (\frac{\omega_0}{\omega_1} - \frac{\omega_1}{\omega_0})(1 - \exp[-\frac{\omega_0 x}{\omega_1}])]^{-1/2} dx, \qquad (34)$$

Moreover, it can be evaluated analytically in the weak and the strong coupling limits. When $\Omega >> 1$, I have $\omega_1/\omega_{lo} = 1$, whereas $\omega_0/\omega_{lo} = 4\Omega^2/9\pi - (4\ln 2 - 1)$.

C. Dispersion contribution

The quantum part Z_q deviates from $\exp\{-\beta N f_{pol}\}$ at moderate density n of polarons due to their interactions. In the case of the Feynman trial action, it can be presented as

$$Z_q = Z_d \exp[-\beta N f_{pol}], \qquad Z_d = \int \cdots \int_{\mathbf{u}_i(0)=0}^{\mathbf{u}_i(\beta)=\mathbf{0}} \prod_i D\mathbf{u}_i(\tau) \exp[-S_{dd}]. \qquad (35)$$

where Z_d is the dispersion contribution,while S_{dd} is the effective action of the induced dipole-dipole interactions between polarons:

$$\begin{aligned} S_{dd} \;=\; & \frac{1}{2}\sum_i^N [\int_0^\beta \dot{u}_i^2(\tau) d\tau + \frac{(\omega_0^2 - \omega_1^2)\omega_1}{4} \int_0^\beta \int_0^\beta d\tau d\sigma G_F(\tau - \sigma)|\mathbf{u}_i(\tau) - \mathbf{u}_i(\sigma)|^2] \qquad (36) \\ & + \sum_{i\neq j}^N \int_0^\beta \int_0^\beta \mathbf{u}_i^\perp(\tau) \cdot \mathbf{T}_{ij} \cdot \mathbf{u}_j(\sigma) \frac{\widetilde{G}(\tau - \sigma)}{2\beta\epsilon_\infty} d\tau d\sigma. \end{aligned}$$

As it is seen, this action is quadratic with respect to $\mathbf{u}_i$ and corresponds to a set of Drude oscillators interacting by induced dipolar forces. The most difficult part of the free energy comes from this contribution, because the dispersion forces should be collectively treated. Moreover their evaluation requires data on the two-electron density distribution $n_2(\mathbf{r}, \mathbf{r}') = \langle\langle \widehat{n}\widehat{n} \rangle\rangle$. However the low-density of polaron gas $nr_p^3 << 1$ and different scales in quantum and classical motions allows me to simplify these contribution and represents the two-electron density as a product $n_2(\mathbf{r}, \mathbf{r}') \sim ng(\mathbf{R})n_1(r)$, where $g(\mathbf{R})$ is the correlation function responsible for the distribution of centers mass of polarons. Concerning the quantum contribution Z_q, I can treat polarons as polarizable particles in polar medium and consider only induced dipolar interactions between them, since the electrostatic Coulomb interactions are taken in account by (28), while other electrostatic interactions (like as permanent-dipole-charge and permanent dipole-dipole contributions) disappear due to spherical symmetry of the polaron ground state.

To begin with the dispersion forces, I use the fourier transform of the variables $\mathbf{u}_i(\tau)$:

$$\mathbf{u}_i(\omega) = \int \mathbf{u}_i(\tau) \exp[i\omega\tau] d\tau, \tag{37}$$

and define the polarizability $\alpha_F(\omega)$ of the Feynman quasiparticle

$$\alpha_F(\omega) = \frac{\omega^2 - \omega_1^2}{\omega^2[\omega_0^2 - \omega^2]}. \tag{38}$$

Then, using the dielectric frequency-dependent function of the host medium

$$\epsilon_h(\omega) = \frac{\epsilon_\infty(\omega_{lo}^2 - \omega^2)}{\omega_{to}^2 - \omega^2} = \epsilon_\infty + \frac{(\epsilon_0 - \epsilon_\infty)\omega_{to}^2}{\omega_{to}^2 - \omega^2}, \tag{39}$$

which has pole at $\omega = \omega_{to} = \omega_{lo}\sqrt{\epsilon_\infty/\epsilon_0}$ and equals zero at $\omega = \omega_{lo}$, I arrive at

$$S_{dd} = \frac{1}{2}\sum_{ij}^{N} \int \mathbf{u}_i(\omega) \cdot [\frac{\mathbf{I}_{ij}}{\alpha_F(\omega)} + \frac{\mathbf{T}_{ij}}{\epsilon_h(\omega)}] \cdot \mathbf{u}_j(\omega) d\omega. \tag{40}$$

where $\mathbf{I}_{ij}$ is the tensor, whose elements equal to δ_{ij}. Thus, when the polaron gas is subjected to an external frequency-dependent field $\mathbf{E}_\ell(\omega)$, the later induces the instantaneous moment $\mathbf{u}_i(\omega)$ given by

$$\mathbf{u}_i(\omega) = [\mathbf{I}_{ij}/\alpha_F(\omega) + \mathbf{T}_{ij}/\epsilon_h(\omega)]^{-1} \cdot \mathbf{E}_\ell(\omega), \tag{41}$$

where symbol $[\mathbf{I}_{ij}/\alpha_F(\omega) + \mathbf{T}_{ij}/\epsilon_h(\omega)]^{-1}$ means matrix inverse to $[\mathbf{I}_{ij}/\alpha_F(\omega) + \mathbf{T}_{ij}/\epsilon_h(\omega)]$. At the same time, the average moment $\langle \mathbf{u}_i(\omega) \rangle$ is related with the effective polarizability $\alpha(\omega)$ of the polaron gas

$$\langle \mathbf{u}_i(\omega) \rangle = \alpha(\omega)\mathbf{E}_\ell(\omega)/\epsilon_h(\omega). \tag{42}$$

Thus, the effective polarizability is formally expressed as

$$\alpha(\omega)/\epsilon_h(\omega) = \left\langle [\mathbf{I}_{ij}/\alpha_F(\omega) + \mathbf{T}_{ij}/\epsilon_h(\omega)]^{-1} \right\rangle. \tag{43}$$

However the computation of the polarizability is not simple. To perform it, I should calculate the matrix $[\mathbf{I}_{ij}/\alpha_F(\omega) + \mathbf{T}_{ij}/\epsilon_h(\omega)]^{-1}$ and then average this matrix. Formally, the relation for effective polarizability $\widetilde{\alpha}(\omega) = \alpha(\omega)/\epsilon_h(\omega)$ can be rewritten as Dyason's equation[31]

$$\widetilde{\alpha}(\omega) = \frac{\widetilde{\alpha}_F(\omega)}{[1 - \widetilde{\alpha}_F(\omega)U(\widetilde{\alpha}(\omega), n)]}, \tag{44}$$

where $\widetilde{\alpha}_F(\omega) = \alpha_F(\omega)/\epsilon_h(\omega)$ and $U(\widetilde{\alpha}(\omega), n)$ is the self-energy. Using suitable approximations for $U(\widetilde{\alpha})$, I should solve (44) to find a complex solution $\widetilde{\alpha}(\omega)$ and calculate the density

of states $D(\omega, n)$, which defines the number of eigen-states with frequency ω in a small interval $[\omega; \omega + d\omega]$.

With the use of the fluctuation-dissipation theorem I relate the imaginary part $\widetilde{\alpha}_i$ of the polarizability and the density of states (DOS):

$$D(\omega, n) = 6\omega\widetilde{\alpha}_i(\omega)/\pi. \tag{45}$$

I remark that the polarizability has an imaginary part at a finite range $\omega_- < \omega < \omega_+$, where ω_- and ω_+ are the edge eigen-frequencies. To reveal the role of these eigen-frequencies, I note that $\epsilon_h(\omega \to \omega_{lo}) \to 0$, and there are no nontrivial real solutions for $\mathbf{u}_i(\omega)$ in the range $\omega_{to} < \omega < \omega_{lo}$. Hence electrons can not move in the polarizable medium subjected to the field altering with frequency $\omega_{to} < \omega < \omega_{lo}$. This is a consequence of the formation of phonon polaritons which are stationary electro-magnetic waves in the polarizable medium. The presence of polaritons results in a stopgap at the range $\omega_{to} < \omega < \omega_{lo}$ where polaritons decay. Therefore, if the low-edge frequency $\omega_-(n)$ is to be equal to the phonon frequency ω_{lo} under a certain critical density n_c, an instability of eigen-modes takes place,[3] and the behavior of the polaron gas changes sufficiently. This critical density plays a central role in behavior of quantum polarizable particles, while the condition of this transition can be formulated as

$$\omega_-(n_c) = \omega_{lo}. \tag{46}$$

Then, using the conventional formulas[2] for the set of harmonic oscillators, I arrive at

$$\beta f_d(n, T) = -\frac{\ln Z_d}{N} = \int_0^\infty [D(\omega, n) - 3\delta(\omega - \omega_0 + \omega_1)] \ln(2\sinh[\frac{\beta\omega}{2}])d\omega, \tag{47}$$

in which I take into account that the free energy of the Feynman trial action is equal to $f_0(T \to 0, \Omega \to \infty) = 3(\omega_0 - \omega_1)/2$. The expression for dispersion contribution f_d can be written in terms of a dimensionless function $d(\eta, \zeta, \overline{\omega}, \overline{\omega}_1)$ depending on the dimensionless parameters $\zeta = 2\beta c^2/9\pi >> 1$, $\eta = n/n_c \leq 1$, and on the variational frequencies $\overline{\omega} = 9\pi\omega_0/2c^2 = \omega_0/\gamma\omega_{lo}$, $\overline{\omega}_1 = \omega_1/\omega_{lo}$, and $\gamma = 4\Omega^2/9\pi$:

$$\begin{aligned} &9\pi f_d/2c^2 = \zeta^{-1} d(\eta, \zeta, \overline{\omega}, \overline{\omega}_1) = \\ &\frac{1}{\zeta}\int_0^\infty [D(x, \eta, \overline{\omega}, \overline{\omega}_1) - 3\delta(x - \overline{\omega} + \gamma^{-1}\overline{\omega}_1)] \ln(2\sinh[\frac{\zeta x}{2}])dx. \end{aligned} \tag{48}$$

Introducing the dimensionless free energy $\overline{f} = 9\pi f(n, T)/2c^2$, I have finally:

$$\overline{f} = \frac{3(\overline{\omega} - \gamma^{-1}\overline{\omega}_1)^2}{4\overline{\omega}} - \frac{3(\overline{\omega}_1\overline{\omega})^{1/2}}{2}\int_0^\infty F(\overline{\omega}/\overline{\omega}_1, x)dx + \zeta^{-1}[d(\eta, \zeta, \overline{\omega}, \overline{\omega}_1) + \ln\theta + f_{ex}(\Gamma)], \tag{49}$$

where $F(z,x) = \exp(-x/z)/\sqrt{(x+[z^2-1])(1-\exp[-x])}$, while $f_{ex}(\Gamma)$ and $d(\eta,\zeta)$ are calculated by (29) and (48), respectively, whereas $\Theta(\eta,\overline{\omega},\overline{\omega}_1) = n\Lambda^3$. Therefore, the complete behavior of the nondegenerate polaron gas is described by (49) with the dimensionless free energy $\overline{f}(\overline{\omega},\overline{\omega}_1,\zeta,\Gamma,\eta,\gamma)$ depending on dimensionless parameters ζ,Γ, γ, and η. The variational frequencies $\overline{\omega}$ and $\overline{\omega}_1$ are obtained by the minimization of the free energy:

$$\frac{\partial\overline{f}}{\partial\overline{\omega}} = \frac{\partial\overline{f}}{\partial\overline{\omega}_1} = 0. \tag{50}$$

They depend on the dimensionless density η and the dimensionless inverse temperature ζ. This means that the frequency $\overline{\omega}$ and the mean polaron radius should be calculated self-consistently by the extremum (50). Thermodynamic properties such as pressure p, chemical potential μ, and compressibility κ are calculated by the usual relations:

$$p = n^2\frac{\partial f}{\partial n}, \qquad \mu = f + n\frac{\partial f}{\partial n}, \qquad \kappa^{-1} = n\frac{\partial p}{\partial n}. \tag{51}$$

Therefore, the set of Eqs. (29), (48), and (49) is my final result for the free energy, it describes completely the behavior of the nondegenerate polaron gas, though additional approximations for $U(\tilde{\alpha})$ are required to solve this set. Below I will consider a model, which allows me to treat semi-analytically these relations.

IV. ANALYSIS

Although the results described above are valid not only for large coupling constants Ω but also at intermediate coupling, to provide semi-analytical analysis, I consider the strong coupling limit $\Omega \to \infty$. In this case my formulas are simplified since $\overline{\omega}_1/\overline{\omega} \to 0$ and I have the well known results[23] when $\beta \to \infty$ and $n \to 0$:

$$\frac{9\pi f_{pol}}{2c^2} = \frac{3\overline{\omega}}{4} - \frac{3\overline{\omega}^{1/2}}{2}, \qquad M_p = \overline{\omega}^2, \qquad r_p = \frac{3\sqrt{3\pi}}{2c}. \tag{52}$$

Finite-temperature corrections to these relations and next-order terms with respect to Ω are well documented in literature.[32]

With the same accuracy I can put $\overline{\omega}_1 = 0$ in the relations for the dispersion contribution and ignore the difference between phonons and polaritons, furthermore I consider the low-temperature asymptotic $\beta \to \infty$ ignoring in (48) the terms proportional to $exp[-\beta\omega_{lo}]$. Then, the condition for the polarization catastrophe reads:

$$\omega_-(n_c) = 0, \tag{53}$$

while the polarizability of an isolated polaron is given by

$$\alpha_F(\omega) = \frac{1}{\omega_0^2 - \omega^2}. \tag{54}$$

and the dispersion contribution is expressed as

$$\zeta^{-1} d(\eta, \zeta, \overline{\omega}, \overline{\omega}_1 = 0) = \frac{1}{2} \int_0^\infty x[D(x, \eta, \overline{\omega}) - 3\delta(x - \overline{\omega})]dx. \tag{55}$$

The next level of the consideration requires information on $D(x, \eta, \overline{\omega})$ and, respectively, an approximation for the self-energy $U(\widetilde{\alpha}(\omega), n)$. I note the physical meaning of the self-energy, i.e. the value $U(\widetilde{\alpha})$ is related with the average dipolar energy U_d of an effective dipolar liquid, while the later can be presented in terms of the pair distribution function $g(\mathbf{r}\Psi_1\Psi_2, \widetilde{\alpha})$ of induced dipoles with an effective momentum $d = (3\widetilde{\alpha}/\beta)^{1/2}$:

$$U(\widetilde{\alpha}, n) = -\frac{2\beta U_d}{3\widetilde{\alpha}} = n \int \frac{\mathbf{d} \cdot \mathbf{T} \cdot \mathbf{d}}{d^2} g(\mathbf{r}\Psi_1\Psi_2, \widetilde{\alpha}) \frac{d\mathbf{r} d\Psi_1 d\Psi_2}{(4\pi)^2}, \tag{56}$$

where Ψ_1 and Ψ_2 are the Euler angles of the interacting dipoles. In general, the required information on $g(\mathbf{r}\Psi_1\Psi_2, \widetilde{\alpha})$ can be obtained by the integral equation theory[33] or directly by approximating function $U(\widetilde{\alpha}, n)$.[24,34] In our case the function $U(\widetilde{\alpha}, n)$ as well as $g(\mathbf{r}\Psi_1\Psi_2, \widetilde{\alpha})$ depend on the two dimensionless parameters: $n\sigma^3$ and $\widetilde{\alpha}_F(0)\sigma^{-3}$, where σ is the characteristic size of short-range correlations in the effective liquid. The first of these parameters means the relative fraction of the volume occupied by the dipoles, while the second one indicates a strength of an isolated dipole. Dependencies of the functions on these parameters are quite complicated and well parameterized only in the case when $\widetilde{\alpha}_F\sigma^{-3} << 1$ corresponding to a weakly polarizable classical liquid. Since I consider polarons as distinguishable quasiparticles, what means $\sigma \gtrsim 2r_p$. Hence, taking into account the relation between r_p and ω_0, I have $\widetilde{\alpha}_F(0)\sigma^{-3} \approx r_p/18\epsilon_\infty = 1/4(1 - \epsilon_\infty/\epsilon_0)$, which more than an order exceeds the values typical for classical liquids. At the same time, as I indicated below, the parameter $n\sigma^3$ is less than 1/2 at $n = n_c$. Therefore, it is reasonable to consider the low-density (LD) limit when $n\sigma^3 \to 0$ as an approximation for our case. Then, the dependency $U(\widetilde{\alpha}, n)$ can be easily found

$$U(\widetilde{\alpha}, n\sigma^3 \to 0) = \frac{8\pi n\widetilde{\alpha}}{3\sigma^3}, \tag{57}$$

while equation (44) becomes quadratic and may be solved analytically.

Analyzing the free energy (49), I note first that parameter $\eta < 1$ is small, while parameter $\zeta >> 1$ and parameter $\Gamma >> 1$ are large. Therefore, in the zero approximation the

asymptotic behavior of the polaron gas is described by the function $\overline{f}(\overline{\omega}, \zeta = \Gamma = \infty, \eta) = \overline{f}_{PC}(\overline{\omega}, \eta)$, but this limiting case corresponds exactly to the polaron crystal, which has been studied before.[3] Hence, my model recovers the formation of polaron crystals and I should estimate the influence of finite values of parameters η, ζ, and Γ for evaluating the behavior of the polaron gas.

To continue the analysis, I have to choose the cut-off distance σ. It is obvious that $\sigma(n \to 0) \to 2r_p$ due to the construction of dipolar interactions and inequality (18). However, the size can deviate from the twice mean polaron radius due to exchange effects in the concentrated regime. Nevertheless, with the same level of the accuracy as before, I ignore these deviations and assume $\sigma(n) = 2r_p(n)$. Then, all the required quantities are calculated analytically. The real ($\widetilde{\alpha}_r$) and the imaginary ($\widetilde{\alpha}_i$) parts of the polarizability are given by:

$$\widetilde{\alpha}_r(\omega < \omega_-) = \frac{2n_c[(\omega_0^2 - \omega^2) - (\omega_+^2 - \omega^2)^{1/2}(\omega_-^2 - \omega^2)^{1/2}]}{n\omega_0^4},$$
$$\widetilde{\alpha}_r(\omega > \omega_+) = \frac{2n_c[(\omega_0^2 - \omega^2) + (\omega_+^2 - \omega^2)^{1/2}(\omega_-^2 - \omega^2)^{1/2}]}{n\omega_0^4},$$
$$\widetilde{\alpha}_i(\omega_- < \omega < \omega_+) = \frac{2n_c(\omega_+^2 - \omega^2)^{1/2}(\omega^2 - \omega_-^2)^{1/2}}{n\omega_0^4}, \tag{58}$$

where $\omega_-$and ω_+ are the edge eigen-frequencies expressed as

$$\omega_\pm = \omega_0[1 \pm \sqrt{\eta}]^{1/2}, \tag{59}$$

whereas the critical density n_c, at which $\omega_-(n_c) = 0$, is given by

$$n_c = \frac{3r_p^3\omega_0^4\epsilon_\infty^2}{4\pi} = \frac{243\epsilon_\infty^2}{64\pi r_p^5(n)} = \frac{3^{1/2}9\epsilon_\infty^2\omega_0^{5/2}}{2^{1/2}8\pi}. \tag{60}$$

The expression for dispersion contribution $d(\eta, \zeta)$ reads:

$$\zeta^{-1}d(\eta, \zeta \to \infty) = \frac{3}{\pi}\int_0^\pi [(1 + \eta^{1/2}\cos y)^{1/2} - 1]\sin^2 y dy. \tag{61}$$

and expressed in terms of a hypergeometric function. Expanding the integrand function in series with respect to η, I find

$$\zeta^{-1}d(\eta, \zeta \to \infty) = -[\frac{3\eta}{64} + \frac{15\eta^2}{2048} + \cdots]. \tag{62}$$

Therefore, the dispersion contribution is negative and provide attractions between polarons. At low densities it gives a contribution $\propto n^2$ to the total free energy as it should be to provide

van-der-Waals tails $\propto r_s^{-6}$, (where $r_s = (4\pi n/3)^{1/3}$ is the inter-electron distance). However, the dispersion contribution deviates significantly from this asymptotic behavior at increased densities (see, Fig. 1), indicating a strong cooperative effect of the dispersion forces. It is approximately twice stronger than the estimate obtained by the linear contribution, i.e. the first term in (62). Therefore, the dispersion term is always small with respect to the free energy of polaron formation, i.e. $f_d/f_{pol} \leq \eta/16$ ($\eta \leq 1$), nevertheless this contribution has a pronounced effect on the polaron formation in the vicinity of n_c. The dispersion forces do not play a role at low densities, but become significant at intermediated densities and even dominant in the thermodynamic behavior of polaron gas in the vicinity of n_c.

The dispersion forces result not only in attractions between polarons, but increase also the mean polaron radius. Moreover, the spherically symmetrical state of polarons can disappear due to the dispersion forces. The simple estimates indicate that the dimensionless polaron radius $\overline{r}_p = \overline{\omega}^{-1/2}$ follows the relation:

$$\overline{r}_p(n) = 1 - 4\zeta^{-1}\overline{r}_p + \frac{3\eta\overline{r}_p}{32} + \frac{5\eta^2\overline{r}_p^2}{128} + ... \tag{63}$$

The second term in the right side of (63) is caused by classical pressure of the polaron gas due to the thermal motion of polarons. It decreases the polaron radius, but the effect is minor, because the term includes the small factor $\zeta^{-1} << 1$. The next terms in the right side of (63) are due to the dispersion contribution providing a negative pressure. At moderate temperatures they increase the mean polaron radius by several percents, while the localized spherically symmetrical solution disappears at low enough temperatures when the polaron density exceeds some critical value, i.e. $\eta > \eta_{ei}(T)$. Our estimates indicate that this value is less than unity at $\zeta > 32$ (Fig. 2) and decreases monotonically as temperature decreases, i.e. the solution disappears before the dielectric catastrophe takes place. Thus, the dispersion forces lead to a transition at low temperatures, since the localized electron states with zero dipole momentum can not exist at $n > n_{ei}(T)$.

In this paper I do not treat properly the absorption spectrum, since it requires to account of anharmonic contributions to the polaron self-trapped potential. I note only that the characteristic frequency is inversely proportional to the mean polaron radius, hence I have for the maximum frequency ω_m of the absorption spectrum

$$\omega_m \sim \omega_0(n) = \frac{2c^2}{9\pi}[1 - 4\zeta^{-1}\overline{r}_p + \frac{3\eta\overline{r}_p}{32} + \frac{5\eta^2\overline{r}_p^2}{128} + ...]^{-2} \tag{64}$$

Therefore, an increased temperature results in the blue shift of the absorption spectrum, whereas an increased radius leads to a decrease in the frequency (Fig. 2), which can be detected as a red shift of the maximum of the absorption spectrum.

Let us focus on the behavior of the polaron gas near the critical density n_c. Formally, my model is not applicable at $n > n_c$, since the particles can not stay in the same ground state, because the square of the lowest eigen-frequency ω_- becomes negative. Rigourously, such instability may be interpreted in two ways: either polarons escape from their self-trapped potentials and that corresponds to the onset of metallization; either the polaron gas becomes instable with respect to the formation of a state having a permanent dipole momentum $\langle \mathbf{u}(\omega = 0) \rangle \neq 0$. This possible phase arises in the vicinity of the metal-insulator transition and referred as an excitonic insulator.[35] It has been intensively studied[36,37] in semiconductors as a possible paring between electrons and holes. At the same time, the similar scenario in liquid mercury was first proposed by Turkevich and Cohen[38] for Frenkel excitons, and later studied by different authors[39–41] treated neutral atoms. I will argue below that the excitonic phase can arise in the polaron gas only at very low temperatures, and the critical density n_c is close to the onset of metallization.

For this purpose I deal with dielectric properties of the gas, which can be evaluated with the use of the data on the effective polarizability $\alpha(\omega)$. Treating the polaron gas as a set of polarizable quasiparticles with the effective polarizability $\alpha(\omega)$ in the medium with dielectric constant ϵ_0, I obtain the modified Maxwell-Garnett expression:[7]

$$\frac{\epsilon(\omega) - \epsilon_0}{\epsilon(\omega) + 2\epsilon_0} = \frac{4\pi n \alpha(\omega)}{3\epsilon_\infty}. \tag{65}$$

It is important that effective polarizability $\alpha(\omega)$ depends on the density of polarons, and hence the above relation accounts the interactions between quasiparticles in contrast to the original Herzfeld treatment.[42] Finally, I write the effective dielectric function $\epsilon(\omega)$ versus the polaron density n by inversion (65):

$$\epsilon(\omega) = \epsilon_0 \frac{3\epsilon_\infty + 8\pi n \alpha(\omega)}{3\epsilon_\infty - 4\pi n \alpha(\omega)}. \tag{66}$$

Figure 3 shows the real and imaginary parts of normalized dielectric function $\epsilon(\omega)/\epsilon_0$ of the polaron gas versus the the normalized frequency ω/ω_0 obtained with the use of (66). As it is seen, the real part rises sufficiently (more than 20 times) close to $n = n_c$. At the same time, the detailed study of dielectric function $\epsilon(\omega)$ indicates that this function becomes

negative in a wide range of frequencies (see inset in Fig. 3) at densities exceeding $\eta > 0.3$. Therefore, the dispersion forces result in a strong negativity of the dielectric function. At this stage, I have not extended the calculations to $k \neq 0$, but it is clear that the dielectric function $\epsilon(0, k \neq 0)$ should be also negative. The physical consequence of this effect has been discussed, for example, it could result in superconducting properties of polaron crystal.[3]

I note also the following effect. Formally, the real part of the dielectric constant diverges when denominator in (66) is equal to zero:

$$\frac{4\pi n_\infty \alpha_r(\omega = 0, n_\infty)}{3\epsilon_\infty} = 1, \tag{67}$$

which defines the second critical density n_∞ corresponding to a dielectric catastrophe in the system. This catastrophe may be interpreted as a locus of metallization. With the use of (60) and (58), I find

$$\sqrt{\frac{3}{\pi}} \frac{(1 - \epsilon_\infty/\epsilon_0)\omega_0^2(n_\infty)}{\overline{r}_p(n_c)\omega_0^2(n_c)} [1 - (1 - \frac{n_\infty}{n_c})^{1/2}] = 1. \tag{68}$$

This equation is valid only when the dimensionless radius $\overline{r}_p(n_c)$ is less than unity, because the value in the square brackets is always less than unity. Such situation takes place at high temperatures when $\overline{r}_p(n_c) < 1$ due to pressure of the polaron gas (see Fig. 1). On the other hand, I have $\overline{r}_p(n_c) > 1$ at low temperatures and hence the dielectric catastrophe occurs after the instability of eigen-modes, i.e. $n_\infty/n_c > 1$. Figure 4a shows these two cases corresponding to the high and the low temperatures. Therefore, within the framework of our assumptions, I have $n_\infty > n_c$ at low temperatures. This means that the MIT from the polaron states to metallic states occurs at large enough temperatures, whereas an excitonic insulator phase can arise at low temperatures. In this paper, I do not consider this phase, but indicate only that it can be formed from polarons trapped in a self-consistent nonspherical potential with $p-$symmetry. Such states have been numerically investigated in Ref.[43] (see, also review[44]). On the other hand, this state exhibiting phonon instability[45] can transit into a metallic state. Thus, at low temperatures the polaron gas can undergo a ferroelectric transition to an excitonic insulator phase and then transits to a metallic state.

The next important feature of dispersion interactions is that they provide a negative compressibility (Fig. 4b) like it takes place for classical fluids where the dispersion interactions compete with the short-range repulsions to drive a liquid-gas phase separation below a critical temperature. The same situation occurs in my model, however the phase separation

is frustrated due to neutralizing rigid background. Although the classical one-component plasma is not stable at $\Gamma \geq 3$,[46] the the dispersion forces enhance substantivally this instability. Using (51), I find the condition for the critical line $n_{vdW}(T)$ below which the compressibility is negative:

$$\frac{T}{\omega_0} = \frac{0.094\eta + 0.022\eta^2 + \cdots}{1 - 1.187\Gamma + 3.92\Gamma^{1/4} - 0.694\Gamma^{-1/4} + ...}. \tag{69}$$

Simple evaluations yield the dispersion contributions are dominant at moderate densities, for example the dispersion term gives the main effect on the compressibility at $\eta > 1/3$ at $\epsilon_\infty/\epsilon_0 = 0.1$. There is a critical temperature T_{cr} above which the polaron gas is always stable. Using (69), I find $T_{cr} \sim 0.1\omega_0$ that corresponds to several hundreds of Kelvins. Of course, the van-der-Waals instability caused by the dispersion forces does not immediately imply the thermodynamic instability of the polaron gas and can be realized only in the case of a finite compressibility of the ionic subsystem. Typically, the finite size of ions stabilizes the ocp, for example, the critical temperature T_{cr}^{DH} calculated within the framework of the Debye-Hückel model is about of $1/16\sigma\epsilon_0$,[47] while $n_{cr}^{DH} \sim 1/64\pi\sigma_i^3$ (where σ_i is characteristic diameter of ions), hence the ratios $T_{cr}^{DH}/T_{cr} \sim 0.36(\epsilon_\infty\sigma/\epsilon_0\sigma_i) << 1$ and $n_{cr}^{DH}/n_c \sim 10^{-2}(\sigma/\sigma_i)^3 << 1$ are small in strongly polar dielectrics and the finite-size effects can not stabilize the polaron gas, it remains unstable in a wide range of temperatures and densities.

Finally, I depict the phase diagram for the polaron gas (Fig. 5) at $\Omega \to \infty$, in which I indicate various phases and instabilities arising in the strong coupling case. The variable ζ^{-1} is the dimensionless temperature, while η is the dimensionless density. The thick dashed line η_∞ corresponds to the dielectric catastrophe, the solid line η_c to the instability of eigenmodes, whereas the thin dashed line shows schematically a transition from an excitonic insulator to a metallic state. All these line correspond to a MIT. In the phase diagram I indicate as a gas the state of the many-polaron system at which I can ignore the interactions between the polarons. This phase is separated from the polaron condensed phase by the critical line $\eta_{vdW}(T)$(dash-dotted curve), below which the system is not stable due to dispersion interactions and the inverse compressibility is negative, whereas the classical ocp is unstable below the line indicated by dotted curve $\Gamma = 3$. The ground state of polarons fails spherical symmetry below the line indicated by circles, while the system crystalizes at sufficiently low temperatures when $\Gamma > 179$ (the line depicted by triangles). The arising polaron crystal is to melt at high enough densities, indicating by the arrow corresponding to the quantum

melting following the Lindenmann criterion. Above this critical density the polaron crystal is an imperfect, however the spherically-symmetrical ground state of polarons disappears below η_{ei} and a ferroelectric phase consisting from self-trapped polarons having nonzero dipole moment can arise. Such excitonic insulator phase can undergo the MIT transition to a metallic state at increased densities due to the instability of eigen-modes. On the other hand, the polaron condensate consisting from spherical polarons can transit directly to a metallic phase caused by the dielectric catastrophe occurring at $\eta_\infty(T)$ which is quite close to the instability $\eta_c = 1$. I note that $\eta_\infty(T) \approx 1$ is due to account of dispersion interactions between polarons in the relation for the dielectric function. I should mentioned also that the temperature dependencies of all the critical lines can be sufficiently modified due to account of various short-range corrections (influence of acoustical phonons, finite-size of ions, etc). Nevertheless, I believe the proposed phase diagram to be rather general, it may be revealed in strongly polar dielectrics, where the condensed phase of polarons can arise. To estimate the required density, I rewrite (60) in the conventional units

$$n_c \approx 4.5 \cdot 10^{21} (\frac{m^*}{\epsilon_\infty})^3 (1 - \frac{\epsilon_\infty}{\epsilon_0})^5 \, \mathtt{cm}^{-3}. \tag{70}$$

Since the high-frequency dielectric constant ϵ_∞ varies typically between 1.5 and 5, the critical concentration is to be of the order $(10^{19} \div 10^{21})$ cm^{-3} that is not so extraordinary and corresponds to many practical cases for doped dielectrics. Therefore, the considered scenario can be realized the systems in which strongly coupled polarons can arise.

V. DISCUSSIONS

Thus, I have evaluated the effect of the dispersion forces on dielectric, optical, and thermodynamic properties of the many-polaron system in the strong coupling limit. Starting from the linear coupling between the electrons and the longitudinal polarization of the medium, I have derived the free energy of the system. The great difference in the times scales of the quantum and the classical degrees of freedom allows me to separate the relevant contributions and obtain semi-analytical estimates for these contributions. The classical term is evaluated with the use of the theory of the one-component plasma, whereas the quantum contribution by the methods of quantum polarizable liquids. Considering the diluted limit $nr_p^3 << 1$ I have obtained the explicit expression for the dispersion contribution. The

analysis of this contribution indicates that the dispersion effect is nonlinear and strongly cooperative at large enough densities of polarons. I have found the dispersion forces are to result in an increased radius of polarons and, hence, decrease in the characteristic frequency of absorption spectrum. It is interesting that similar shift can be obtained for polarons even in the weak coupling case.[48]

In addition to these peculiarities, there are two main consequences of the dispersion forces. The first one is the quantum phase transition at $n_\infty \approx n_c$ leading to a metal-insulator transition and revealed as the dielectric catastrophe, the second transition results is the classical van-der-Waals instability leading to possibility of a phase separation (PS). Although my analysis is restricted to the system with a neutralizing rigid background, the simple arguments evidence in favor of such separation in real systems. The detailed study of the phase separation requires a consideration of the metallic phase which has been beyond the scope of the current paper. I note that the presence of the metallic phase substantivally modifies the behavior of the polaron condensate close to the the polarization catastrophe, and details of this behavior will be investigated elsewhere. In the current treatment I have focused on the long-range correlations caused by dispersion forces and ignore completely the exchange effects due to short-range correlations. With the use of (63), I find that the parameter $n\sigma^3 = 8nr_p^3 \sim 0.4$ is not so small in the vicinity of n_c. A careful estimation of the influence of this parameter requires a more detailed model for dispersion effects nearly n_c, for instance, an advanced model for the density dependency of $U(\alpha, n)$. Various models of polarized liquids[24] or disordered lattice like as the effective medium approximation[49] or the coherent potential approximation (see, for example Ref.[31]) can be used to improve my simple evaluations. However, the main difficulty seems to provide self-consistent evaluations accounting changes in the polaron radius caused by both the short- and the long-range effects. But the later requires a proper account of exchange effect again.

On the other hand, the large value of the parameter $n\sigma^3$ indicates strong effects of association and a possibility of formation of multielectron states like as bipolarons, polaron clusters and so on. Of course, to model such aggregates, I should account short-range correlations which are completely ignored in my current model, since the short-range correlations are responsible for the stability of bipolarons in ionic systems[50] and polar dielectrics[51]. Nevertheless, my numerical analysis indicates that the criteria for stability of bipolarons and multielectron states should be sufficiently modified to account the role of the dispersion

forces. The proper treatment of both the types of the correlations (exchange and dispersion contributions) can be based on the explicit separation between them in the correlation potential[52] or by the construction a 'seamless' functional,[53] although additional efforts are required to separate explicitly these interactions in the case of polarons.

It has been believed so long that the dielectric catastrophe following the original Herzfeld model[42] is not realistic in doped dielectrics, since it occurs at densities so high that overlapping of orbitals is essential (see, for example, discussion in Ref.[54]). My calculations confirm it, since $\eta_\infty \approx 2$ and hence $\eta_\infty \sigma^3 \approx 1$ when I ignore the dispersion interactions as in the Herzfeld model.[42] However, the critical density decreases sufficiently (more than twice) due to the dispersion interactions, and the dielectric catastrophe can occur in a diluted regime where short-range correlations play a minor role. Thus, my study indicates the dispersion forces change completely the scenario of the metal-insulator transition. In contrast to the usual Mott mechanism focused on the screening of the long-range Coulomb potential by a stable electron gas, my scenario assumes the dominant role of the dispersion attractions for localized electrons. My model is also different from the Anderson transition, since disorder does not play a significant role in my treatment. It results only in a translational motion of polarons and weak temperature dependencies of the polaron characteristics due to this effect. On the other hand, the consequence of the dispersion attractions is the strong coupling between the MIT and phase separation.

The question arises in what systems the similar mechanism could realize? First, the systems should exhibit a significant difference between the dielectric constants. Next, the size of quasiparticles should neither so large nor so small, since $n_c \propto r_p^{-5}$. For large sized particles the critical concentration can be so low to be masked by Coulomb forces, whereas the dispersion effect disappears in the case of small sizes of particles due to a dominant role of short-range correlations. On the other hand, the dispersion effect plays the crucial role mainly for quasiparticles, because special conditions are required to obtain the polarization catastrophe for classical objects (high pressures an so on) since $n_c \propto \alpha^{-2}$, while the polarizability of classical molecules is quite low (for example, $\alpha_{NH_3} \sim 18.8$ (Ref.[55]) (in Born units $a_0 = \hbar^2/me^2$), $\alpha_{Na^+} \sim 1.34$ (Ref.[56]) (for sodium ion), at the same time the polarizability of polarons exceeds by two orders or even more, since $\alpha(0) \sim 184(m/m^*)^3/c^4\ a_0^3$.

Although my model of many-polaron system is so simplified, I believe that similar scenario occurs in the metal-ammonia solutions, alkali-halide molten salts, whose behavior is

controlled by self-trapped electrons and where the MIT is associated with the phase separation and the dielectric catastrophe. High-T_c superconducting cuprates (HTSC) can be another example of the compounds, where similar scenario may occur, however the phase separation is frustrated in these systems by layering of the material. As a result of such frustration, a new superconducting phase may arise. I have compared various properties of these compounds in Table 1. First, I have evaluated the critical density n_c in these compounds, for this purpose I apply $\epsilon_\infty = 1$, $\epsilon_0 = \infty$ for AHMS,[57,58] $\epsilon_\infty = 1.75$, $\epsilon_0 = 25$ for MAS,[7,8] and $\epsilon_\infty = 5$, $\epsilon_0 = 30$ for HTSC,[3] which have been used before to describe details of the absorption spectrum in the corresponding compounds. I also apply $m^*/m_e = 1$ for MAS and AHMS, but I use the two values for m^* for HTSC, since the information on the effective mass of carries is controversial in this case. Several authors estimate $m^*/m_e \approx 2$,[59,60] while others believe the mass to be higher and estimate it as $4 - 5m_e$.[61,62] I have derived available experimental data on the critical density corresponding to the MIT in these compounds,[63–66] although this transition continues and the critical density varies sufficiently as composition of the compounds or temperature change. I have estimated also the critical density n_∞ corresponding to the dielectric catastrophe,[67] using the data on dielectric enhancement in the relevant compounds.[60,63,68] The comparison between my results and the experimental values indicates that the estimates are quite close, while the deviations from this correspondence in the cases of HTSC and AHMS can be caused by peculiarities of these systems, i.e. the quasi-two dimensional structure of cuprates and finite size of ions in molten salts. The considered compounds reveal also similarities in the properties associated with the dispersion effect, namely, experimental observations exhibit a dielectric catastrophe,[59,63,68] softening of the absorption peak[68,69] as well as the possibility of phase segregation close to the MIT.[64,65,70–72] I remark also other interesting similarity, i.e. a strong spin-pairing of electrons in the considered compounds.[61,73,74] Perhaps, it is the one of the reasons why the high-T_c superconductivity of MAS has been debated during several decades,[75,76] and only the recent experiments have given an evidence[77] that a highly conducting (nonstationary) state arises instead of a superconducting phase. Thus, my analysis indicates that the dispersion effect is to be strong in these systems, though a detailed study of these quite different systems requires additional efforts and, perhaps, will be provided elsewhere.

A special question is the dispersion effect to be peculiarity of interacting polarons or it can be observed for other quasiparticles? The effect seems to take place for excitons also,

but the the critical density is much less in this case because it behaves as r^{-5} and size of excitons is much large than that of polarons, $r_{ex} >> r_p$. Hence, the critical density is low and it could be the origin of the existence of the second critical point in the phase diagram of excitons in semiconductors.[78] Therefore I believe that the effect of dispersion forces is quite important for quantum particles in strongly polar dielectrics at intermediate doping, while the study of the effect in the manner provided in this paper may give a new insight into collective properties of a condensate formed from quasiparticles like as excitons and polarons.

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Figure captions.

Fig. 1. Density dependency of the dimensionless dispersion contribution f_d to the free energy at $T = 0$. The solid line corresponds to the total contributions, while the dashed one to the low-density limit (the first term in (62).

Fig. 2. Density dependencies of the normalized polaron radius $\overline{r}_p$ (solid lines) and the normalized frequency $\overline{\omega}_m$ (dashed lines) at various temperatures. The curves corresponding to increased temperatures are indicated by thick lines.

Fig. 3. The real (a) and the imaginary (b) parts of the normalized dielectric function $\epsilon(\omega)/\epsilon_0$ versus dimensionless frequency ω/ω_0 at various densities of the polaron gas. The parameter ζ is equal to 30, while $\epsilon_\infty/\epsilon_0 = 0.1$. The inset shows the negativity of the real part of the dielectric function in the range $\omega_- < \omega < \omega_+$. The relevant densities of the polaron gas are depicted at each curve.

Fig. 4. Density dependencies of the normalized static dielectric function $\epsilon_s(\omega = 0)/\epsilon_0$ (a) and the dimensionless inverse compressibility $\overline{\kappa}^{-1} = \beta\kappa^{-1}/n_c$ (b) at various temperatures governed by parameter ζ. The symbols η_∞ and η_{vdW} corresponds to the densities at which dielectric catastrophe or van-der-Waals instability take place.

Fig. 5. Phase diagram of interacting polarons in the strong coupling limit and $\epsilon_\infty/\epsilon_0 = 0.08$ (see details in the text).

Table 1. Similarities between the behavior of self-trapped carriers in various compounds, indicating a strong effect of dispersion forces.

properties \ compound	AHMS	MAS	HTSC
$n_c/10^{21}$ cm^{-3} (Theory)	4.5	0.7	0.2 ÷ 1.2 $\frac{m^*}{m_e} = 2$ $\frac{m^*}{m_e} = 4$
$n_{MIT}/10^{21}$ cm^{-3} (Exp.)	$1 \div 2$ [63,64]	$0.5 \div 1$ [65]	0.5 ÷ 5 [66]
$n_\infty/10^{21}$ cm^{-3} (Exp.)	1.2 [63]	$0.3 \div 0.8$ [68]	0.2 ± 0.05 [60]
dielectric enhancement	✓[63]	✓[68]	✓[60]
softening of the absorption peak	not	✓[68]	✓[69]
possibility of PS close to MIT	✓[64,72]	✓[65,71]	✓[70]
spin pairing of electrons	✓[73]	✓[74]	✓[61]
high-T_c superconductivity	not	✓[75] not[77]	✓[79]

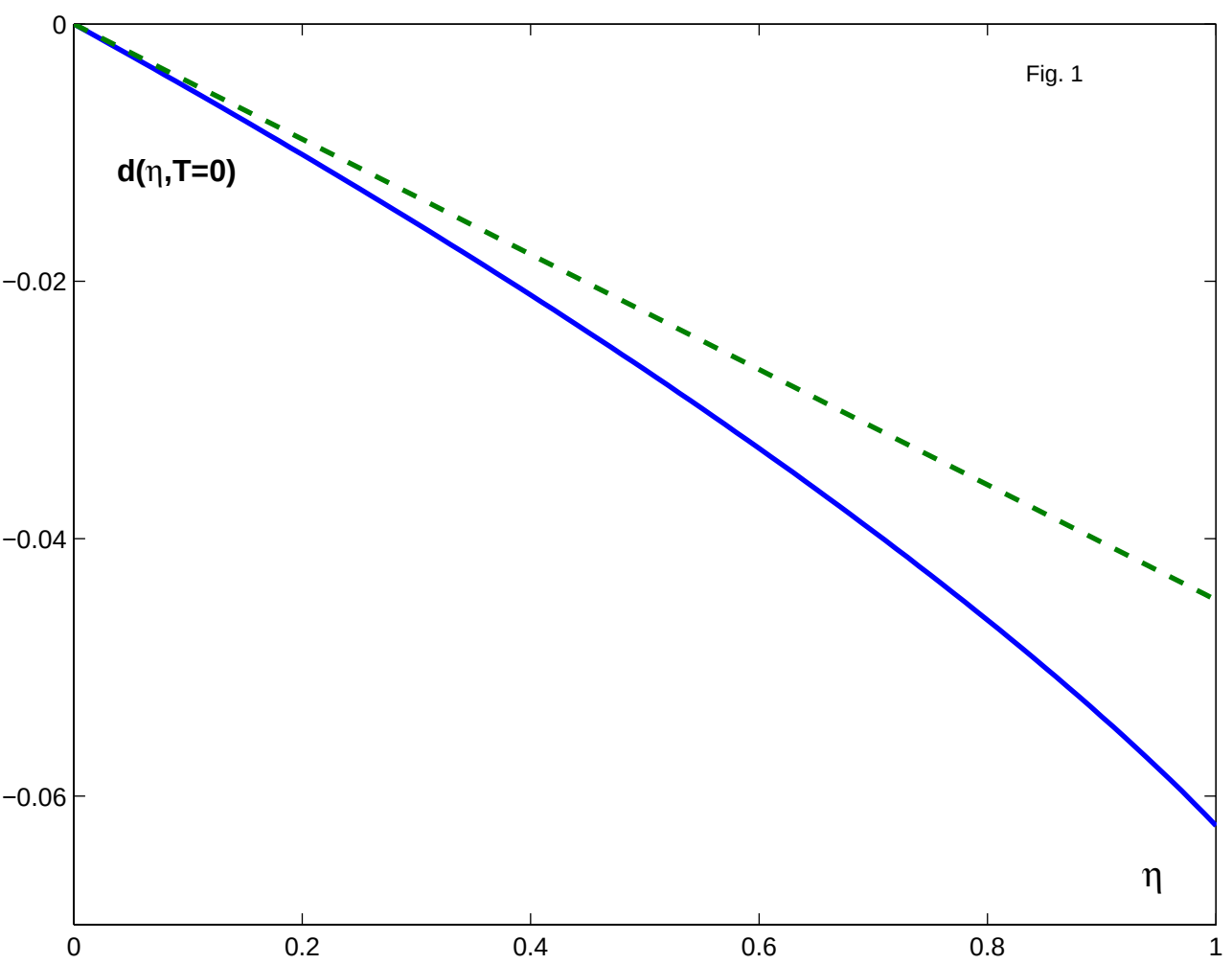
Fig. 1
d(η,T=0)
0
−0.02
−0.04
−0.06
η
0
0.2
0.4
0.6
0.8
1

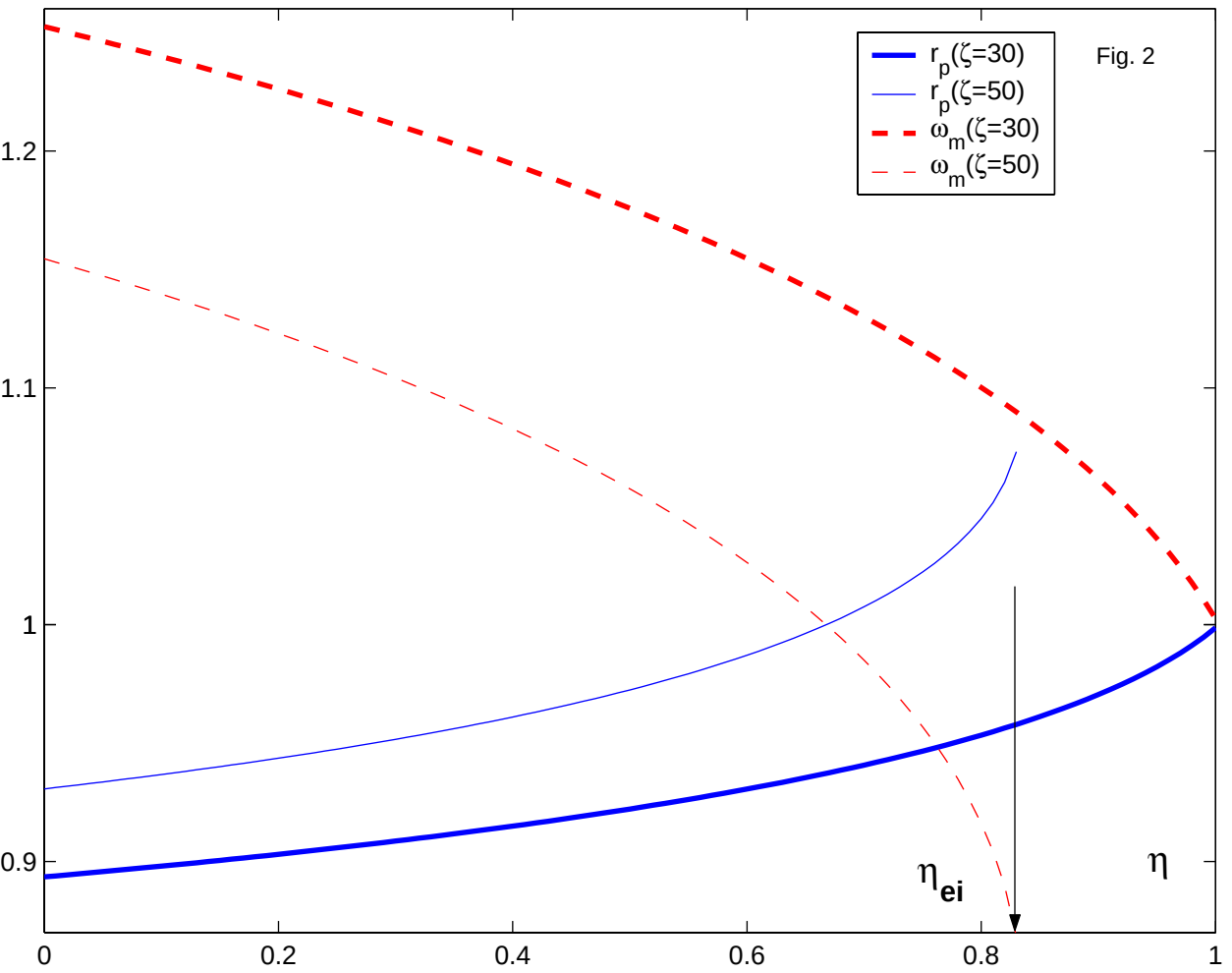
Fig. 2
$r_p(\zeta=30)$
$r_p(\zeta=50)$
$\omega_m(\zeta=30)$
$\omega_m(\zeta=50)$
1.2
1.1
1
0.9
0
0.2
0.4
0.6
0.8
1
η_{ei}
η

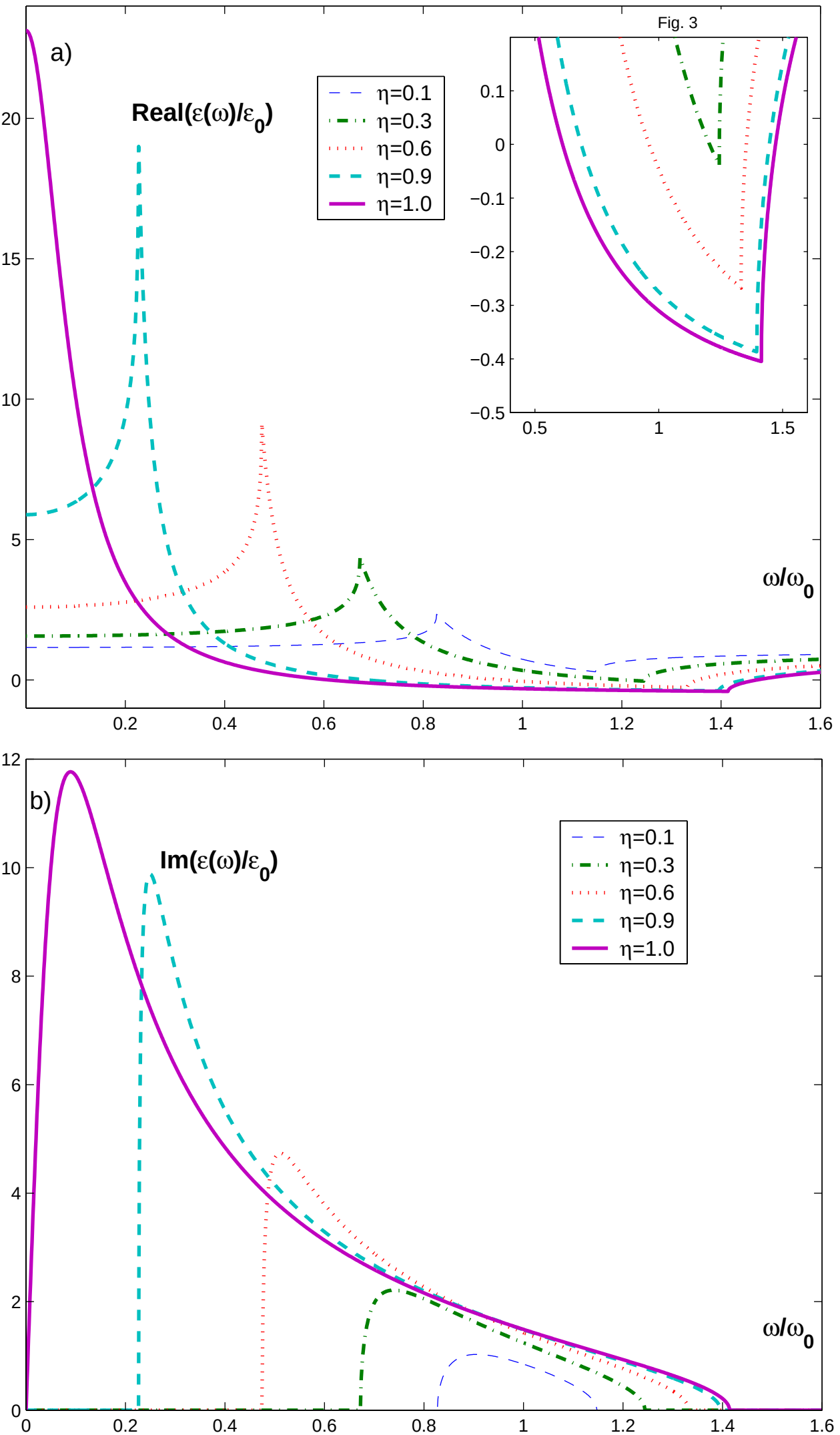
Fig. 3
a)
Real(ε(ω)/ε0)
η=0.1
η=0.3
η=0.6
η=0.9
η=1.0
ω/ω0
b)
Im(ε(ω)/ε0)
η=0.1
η=0.3
η=0.6
η=0.9
η=1.0
ω/ω0

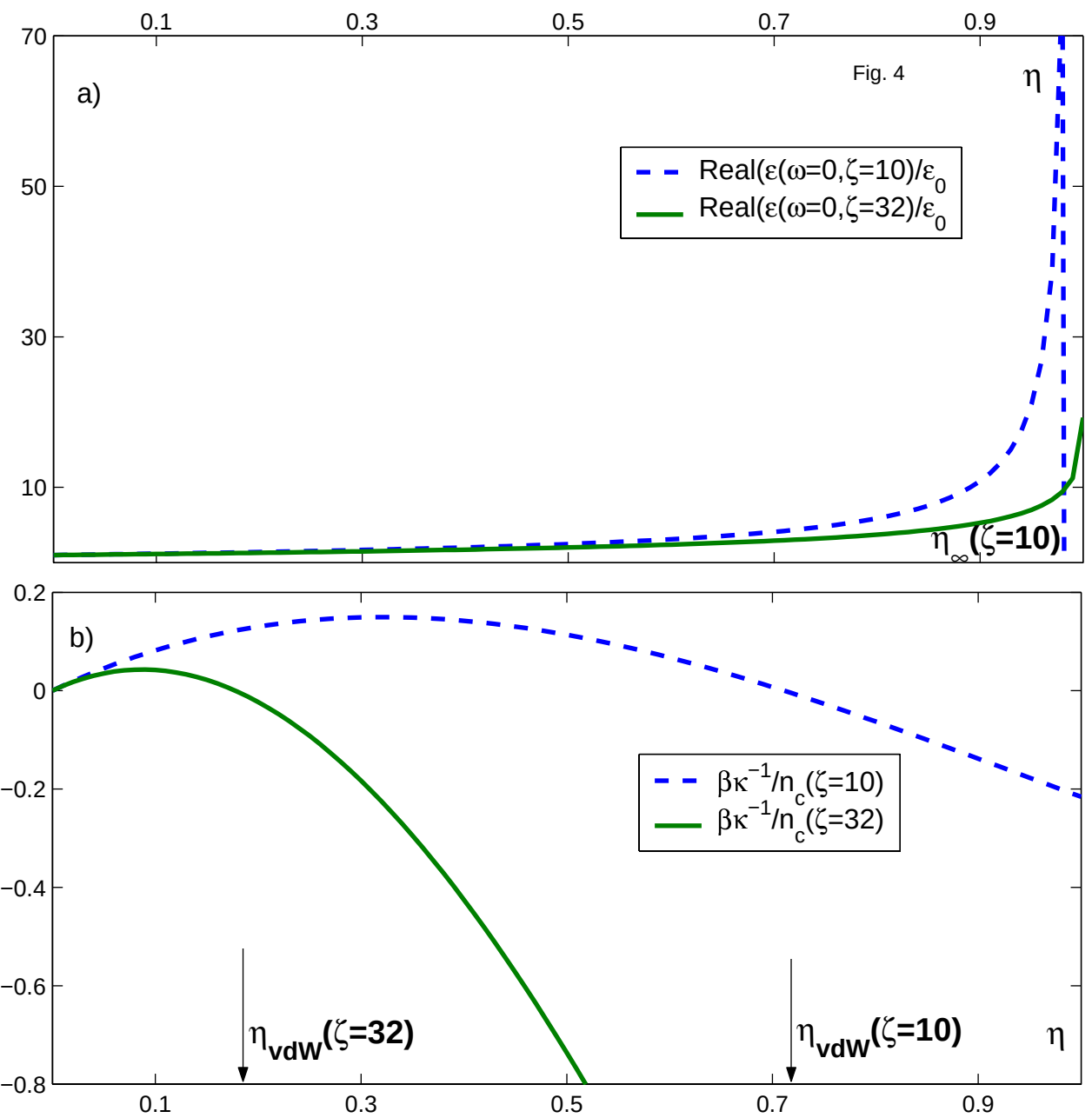
Fig. 4
a)
η
Real(ε(ω=0,ζ=10)/ε0
Real(ε(ω=0,ζ=32)/ε0
η∞(ζ=10)
b)
βκ−1/nc(ζ=10)
βκ−1/nc(ζ=32)
ηvdW(ζ=32)
ηvdW(ζ=10)
η

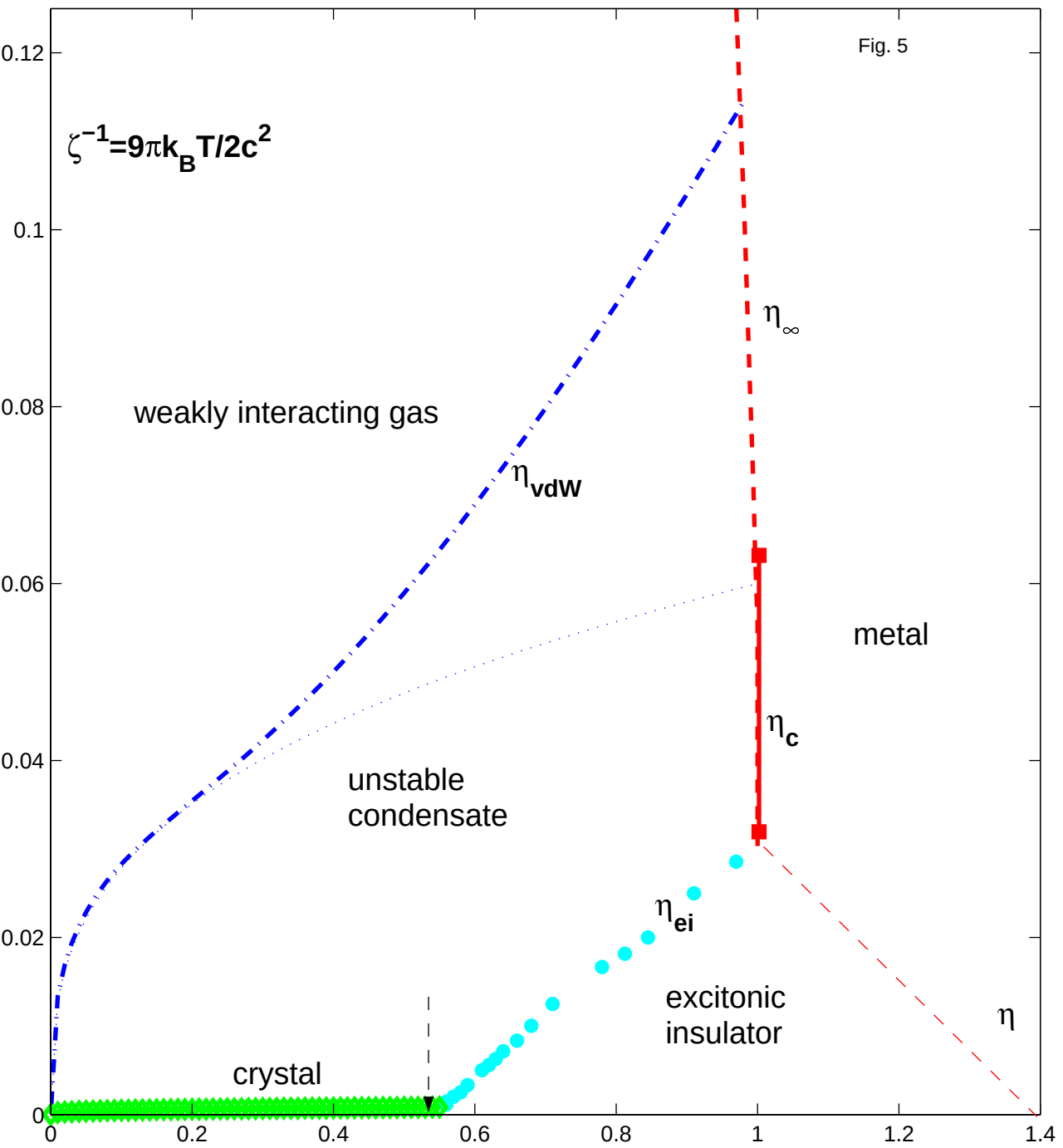
Fig. 5
$\zeta^{-1}=9\pi k_B T/2c^2$
weakly interacting gas
η_{vdW}
η_∞
metal
η_c
unstable
condensate
η_{ei}
excitonic
insulator
η
crystal
0.12
0.1
0.08
0.06
0.04
0.02
0
0
0.2
0.4
0.6
0.8
1
1.2
1.4