Non-metal-to-metal transition driven by van der Waals forces in an interacting polaronic gas

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Abstract. Using path integrals and the theory of polarizable fluids, we develop a model treating non-degenerate interacting Fröhlich polarons at low densities and temperatures. Starting from the dilute regime, we show that at strong electron–phonon coupling, the collective properties of polarons are mainly governed by the London dispersion forces, i.e. induced dipole–dipole van der Waals interactions. At a critical density, these forces provoke a non-metal-to-metal transition by means of a polarization catastrophe and a mechanical instability, which results in a polaron dissociation.
1. **Introduction**

London dispersion forces, i.e. induced dipole–dipole van der Waals (vdW) interactions, are very important in soft condensed matter. They actually play a significant role in many chemical and biological processes [1]–[3]. However, in the case of systems consisting of charged particles, their influence is generally neglected with respect to the Coulomb forces. Nevertheless, if one considers a finite density of particles, their effects may be predominant and should be carefully examined. Indeed, owing to their inherent highly dynamical and fully quantum nature, the dispersion forces are not screened in any piece of matter on the same grounds as the electrostatic interactions. Thus, there may exist situations where the electrostatic interactions are well screened, for example, by the usual Debye mechanism, whereas the dispersion forces are either not or only weakly screened, because they depend on the polarizability of the particles and not on their bare charges. Such a situation has been recently pointed out in alkali metal–ammonia solutions [4]. It was shown that the vdW interactions really drive the non-metal-to-metal transition (NMT) in this system by means of a polarization catastrophe [5]. That mechanism may be regarded as a quantum version of the old Goldhammer–Hersfeld scenario for insulator-to-metal transitions [6, 7].

Here, we consider the many-Fröhlich polaron gas at low densities, interacting by long-range Coulomb forces and at large enough electron–phonon coupling constant. Polarons, which are composite particles, are often believed to sustain an important role in determining the properties of several materials, such as high-$T_c$ superconducting cuprates [8], manganites [9], other doped oxides and conjugated polymers [10]. It is little known beyond a single polaron or bipolaron state (which is a bound state formed by two polarons), although many specific situations have been considered to investigate the homogeneous polaron gas and its stability. A general theory is still not achieved due to the complexity of this many-body problem. Most theoretical efforts have been recently performed by several groups in the intermediate...
and/or high densities limit, improving our current knowledge. In particular, depending on the strength of the electron–phonon coupling, many results were accumulated [11]–[14] including the possibility of various electron strings and stripes [15] or even more complicated situations as that in the coupled resonant boson–fermion model [16].

Our starting point is to consider interacting Fröhlich polarons [17, 18] at low but finite densities. As was stated previously [19], at $T = 0\,\text{K}$ the ground state is the Wigner crystal of polarons (PWC), which is formed owing to the long-range Coulomb interactions. The quantum melting of the polaronic crystal was examined carefully as a function of the density by path-integral calculations [20, 21]. It was shown that an insulator-to-metal transition takes place at a finite critical density and large enough electron–phonon coupling constant, resulting in the polaron dissociation beyond this density [22]. The complete mechanism was identified as a polarization catastrophe [21], due to dipolar interactions between localized polarons in the PWC. Interestingly, that scenario also opened the possibility to overscreen the Coulomb forces and thus the possibility of an insulator-to-superconductor transition [23]. As we will discuss in the next section, the PWC can also thermally melt into a gas state at a rather low melting temperature $T_m$ of about a few kelvins. The examination of its degeneracy temperature $T_0$ will also show that it is of the same order, i.e. of about a few kelvins at large enough electron–phonon coupling. As a result, at the finite temperatures of interest, the normal state is a non-degenerate gas of interacting polarons, i.e. the state that we are looking at in the present paper.

The layout of the paper is as follows. We discuss in section 2 the physical parameters controlling the behaviour of the polaron gas. In section 3 we derive our model. Taking advantage of the non-degeneracy of the polaron gas and of the different time scales of screening, we separate the classical degrees of freedom from the quantum ones. It is shown in section 4 that the former gives a classical contribution to the free energy, which may be treated in the framework of a classical one-component plasma (ocp). The quantum contributions are twofold: the free energy of the polaron formation and the contribution due to the collective vdW interactions. The first one will be treated by path-integral calculations, whereas the second one will be treated by a theory of simple polarizable fluids. The complete variational expression for the free energy is then derived. In section 5, we restrain ourselves to the strong electron–phonon coupling limit. We demonstrate that the vdW interactions are responsible for a polarization catastrophe leading to an NMT. These results generalize the ones obtained for the PWC at $T = 0\,\text{K}$ [20, 21] to the case of a polaronic gas at finite temperatures. Eventually, concluding remarks and possible extensions are discussed in the last section.

2. Physical parameters controlling the many-polaron state

The Fröhlich model consists of a set of interacting electrons of density $n$ together with a compensating rigid jellium of positive charges, both embedded in a host polar dielectric [17, 18]. The electrons are characterized by their effective band mass $m$, which may be different from the bare electron mass $m_e$. The density is related to their mean distance $2R$ by $n^{-1} = 4\pi R^3/3$ (and the usual Wigner–Seitz parameter is $r_s = R/a_0$, where $a_0$ is the Bohr radius). The host polar material is completely determined by the following three quantities: the frequency $\omega_{\text{LO}}$ of longitudinal optical phonons, and $\epsilon_s$ and $\epsilon_\infty$, respectively, the static and high-frequency dielectric constants of the host medium. For oxide compounds, the static dielectric constant exceeds, at least by an order of magnitude, the high-frequency dielectric constant that is of the order of unity ($\epsilon_\infty \approx 2–5$). This difference is a signature of two sources of polarization in the
medium: the ionic polarizability, which responds at any frequencies lower than typical values of the order of 1–2 eV, and the polarization carried by optical phonon modes, which only responds at frequencies lower than \( \omega_{\text{LO}} \). The range of frequencies considered in the paper will always be lower than 1 eV, so that the lower bound for the value of the dielectric constant \( \epsilon \) will be \( \epsilon_\infty \) (the total transparency \( \epsilon = 1 \) is never reached). Moreover, since the transverse phonon frequency \( \omega_{\text{TO}} \) satisfies the Lindanne–Sachs–Teller relation \( \epsilon_\infty \omega_{\text{TO}}^2 = (\epsilon_\infty - 1)^2 \omega_{\text{LO}}^2 \), the dielectric function of the host material may be written as

\[
\epsilon_\infty(\omega) = \epsilon_\infty - \frac{\omega_{\text{LO}}^2}{\omega^2 - \omega_{\text{TO}}^2}.
\] (2.1)

Basically, a polaron is a composite particle formed by an electron (or a hole) moving together with its surrounding phonon clouds. Although it has an internal structure, it may move as a whole. The properties of an isolated polaron are entirely determined by the electron–phonon dimensionless coupling: \( \Omega = \hbar^2 (m/2\hbar \omega_{\text{LO}})^{1/2} / \bar{\epsilon} \) and the dimensionless temperature \( T = k_B T / \hbar \omega_{\text{LO}} \), where \( \bar{\epsilon} = 1/(\epsilon_\infty^{-1} - \epsilon_s^{-1}) \) is the effective dielectric constant of the medium. The polaron is mainly characterized by three physical values: (i) an effective mass \( M_p \), (ii) a mean polaron radius \( R_p \) of the electron localization inside the potential created by the phonons and (iii) an internal frequency \( \omega_0 \) of the electron fluctuations inside the potential well. Depending on the strength of \( \Omega \) and \( T \), the ratio \( M_p / m \) may vary from unity to several dozens, whereas the internal frequency may vary from a few \( \omega_{\text{LO}} \) at low coupling and low temperatures, to several dozens of \( \omega_{\text{LO}} \) at strong coupling and/or large temperatures. Typical values for \( M_p \) and \( \omega_0 \) are well reported in [24]. At the same time, the polaron radius is directly related to \( M_p \) and \( \omega_0 \) (see the next section). In our case of low densities and strong coupling, we always have \( R_p \ll R_s \). Eventually, to conclude this paragraph, we emphasize that we neglect the possibility of creation of bipolarons in our system, because it is well known [25]–[27] that the condition to have repulsive interactions between polarons even at short distances is \( \epsilon_\infty / \epsilon_s > 0.1 \). We assume in our paper that this condition is satisfied.

The next step is to examine the degree of degeneracy of the polaron gas. The dimensionless degeneracy parameter is \( \Theta = k_b T / E_F \), where \( E_F \) is the Fermi energy of a non-interacting polaron gas (with mass \( M_p \)):

\[
\Theta(T) = 0.91 (k_B T) r_s^2 \left( \frac{M_p}{m} \right) \frac{a_0}{\epsilon^2}.
\] (2.2)

Numerical values of \( \Theta(T) \) are given in table 1. At low densities \( n < 10^{19} \text{ cm}^{-3} \) and strong electron–phonon coupling such that \( M_p / m > 10 \), the degeneracy parameter \( \Theta(T) \) is lower than unity only for temperatures below a few kelvin \( (T_0 < 10 \text{ K}, \text{where } T_0 \text{ is the degeneracy temperature}) \). The polaron gas is thus non-degenerate at these densities and behaves classically in a first approximation. We may now evaluate the coupling parameter for a classical ocp:

\[
\Gamma(T) = \frac{1}{\epsilon_s r_s (k_B T)} \left( \frac{e^2}{a_0} \right).
\] (2.3)

Numerical values are reported in table 1. The literature about the classical ocp indicates that it crystallizes when \( \Gamma(T_\text{m}) \sim 170 \). At \( n \sim 10^{19} \text{ cm}^{-3} \) and \( \epsilon_s = 30 \), one obtains \( T_\text{m} \sim 1 \text{ K} \), which is of the same order as \( T_0 \). We may draw the first statement: in the case of strong enough coupling and low densities, the PWC melts at a rather low temperature into a classical liquid (or gas) of polarons. For such a gas, the range of temperatures considered in the present paper is as follows:

\[
k_B T_\text{m} < k_B T < \hbar \omega_{\text{LO}}.
\] (2.4)
Table 1. The degeneracy parameter \( \Theta(T) \) and the plasma parameter \( \Gamma(T) \) at various polaron densities \( T = 100 \text{ K}, M_p/m = 10 \) and \( \varepsilon_s = 30 \). Note that \( r_s, \Theta \) and \( \Gamma \) are dimensionless parameters (see the definitions in the text).

| \( r_s \) | 20 | 50 | 100 | 200 |
|-----|-----|-----|-----|-----|
| \( n/10^{19} (\text{cm}^{-3}) \) | 25 | 1.6 | 0.2 | 0.025 |
| \( \Theta \) | 1.2 | 7.5 | 30 | 120 |
| \( \Gamma \) | 5.7 | 2.3 | 1.15 | 0.6 |

From this point, we may now evaluate the Debye electrostatic screening length for this classical gas, which is given by \( \ell_D(T, n) = (4\pi e^2 / k_B T \varepsilon_s)^{-1/2} \). Taking \( T \approx 100 \text{ K}, \varepsilon_s \approx 30 \) and \( n \approx 10^{19} \text{ cm}^{-3} \), one obtains \( \ell_D \approx 5 \text{ Å} \). Therefore, we have \( \ell_D \ll R_e \approx 30 \text{ Å} \) for the case under consideration. This essentially indicates strong screening of the electrostatic interactions.

Besides electrostatic correlations, there exists another type of correlations in the system due to the composite nature of the polarons. As already discussed, although a polaron behaves classically as a whole, the electron self-trapped in the polarization cloud remains quantum. Due to electronic transitions in a localized excited state, occurring at the characteristic frequency \( \omega_0 \) (typically of the order of 0.1 eV), the fluctuations induce dipolar interactions between polarons, i.e. dispersion forces. Moreover, at strong electron–phonon coupling, these electronic transitions are of Franck–Condon type because the transition time \( \omega_0^{-1} \) is much smaller than the phonon relaxation time \( \omega_1 \). Consequently, the vdw forces induced by these fluctuations are a priori only screened by the high dielectric constant \( \varepsilon_\infty \). Moreover, we may easily see that they will play an important role. Indeed, let us consider the polarons as particles with polarizability \( \alpha_0(0) \sim e^2 / \hbar m \omega_0^2 \). With typical values of \( \omega_0 \) (~0.1 eV), we obtain \( \alpha_0(0) \approx 10^3 a_0^2 \), which is a huge polarizability. For comparison, the polarizability of simple ions is only of the order of \( a_0^2 \). Now, a simple way to estimate the effect of this huge polarizability of the polarons at finite densities is to consider the total static dielectric function of the system approximated by the usual Maxwell–Garnett relation (see, for example, [28]):

\[
\frac{\epsilon(0)/\varepsilon_s - 1}{\epsilon(0)/\varepsilon_s + 2} = \frac{4\pi}{3} n\alpha_0(0)/\varepsilon_\infty.
\] (2.5)

We can easily see that a polarization catastrophe (i.e. \( \epsilon \to \infty \)) occurs when

\[
\omega_0^2 = \omega_p^2 / 3\varepsilon_\infty.
\] (2.6)

where \( \omega_p^2 = 4\pi n e^2 / m \) is the plasma frequency. This simple estimate, already proposed in the case of the PWC [29], shows that for \( \omega_0 \approx 0.1 \text{ eV}, m = m_e \) and \( \varepsilon_\infty = 4 \), the critical density is about \( n_e \sim 10^{20} \text{ cm}^{-3} \). Although formula (2.6) contains the main Lorentz local field effect of the dispersion forces in the case of a frozen system (such as a PWC in cubic symmetry) or in a dilute gas, it is a very crude approximation. It does not sufficiently take into account the details of the interactions and the disorder inherent in liquid or gas states. To improve (2.6), we need to use the results obtained in a theory of simple polarizable fluids [30]–[34], which mainly gives access to a renormalization \( \alpha(\omega) \) of the bare polarizability \( \alpha_0(\omega) \) in (2.5). As we will see, this may reduce by several times the magnitude of the critical density. In the following sections, we explicitly develop the model and the formalism able to describe accurately the present physics.
3. The model

The Fröhlich Lagrangian may be given in terms of electric and polarization fields:

\[
L = \sum_{i=1}^{N} \frac{m}{2} \dot{r}_i^2 - \frac{1}{8\pi \varepsilon_\infty} \int D^2 + \int \mathbf{P}_{ir} \cdot \mathbf{D} + \frac{2\pi \tilde{\varepsilon}}{\omega_{LO}^2} \int \left( \dot{P}_{ir}^2 - \omega_{LO}^2 P_{ir}^2 \right),
\]

where the integrals run for a space variable over the whole volume. Electrons are compensated for by positive charges with the same density, which are considered as a jellium. Thus, the total field is \( \mathbf{D} = \mathbf{D}^+ + \mathbf{D}^- \), where the + sign runs for the jellium, and the − sign for the electrons, with

\[
\mathbf{D}^- = \sum_{i=1}^{N} \mathbf{D}_i^-, \quad \mathbf{D}_i^- = -e \frac{\mathbf{r} - \mathbf{r}_i}{|\mathbf{r} - \mathbf{r}_i|^3}, \quad \mathbf{D}^+ = +en \int \frac{\mathbf{r} - \mathbf{r}'}{|\mathbf{r} - \mathbf{r}'|^3} d^3 r'.
\]

The charges are coupled in (3.1) to the polarization field \( \mathbf{P}_{ir} \equiv \mathbf{P}_{ir}(\mathbf{r}) \), which is induced by the optical longitudinal phonons of the medium. This polarization field is naturally related to the habitual creation and annihilation operators of phonons (see [35] for example). Since the Lagrangian (3.1) is quadratic in the polarization field, we may directly integrate it by path integrals. The exact partition function may be given in terms of path integrals

\[
Z = \int e^{\delta \partial(\text{path})},
\]

where we implicitly define \( \tau = i\beta \) as a complex time, \( \beta^{-1} \) being the temperature. The free energy of the system is then given by

\[
F = -\frac{1}{\beta} \log(Z).
\]

After integration on the polarization field in (3.1) and using (3.2), we directly obtain [20]

\[
S(\{\mathbf{r}_i\}) = \sum_i^m \frac{1}{2} \int_0^\beta \dot{r}_i^2(\tau) d\tau - \frac{e^2 n^2 \beta}{2\varepsilon_s} \int \int \frac{d^3 \mathbf{r} d^3 \mathbf{r}'}{|\mathbf{r} - \mathbf{r}'|}
\]

\[
+ \frac{e^2 n}{\varepsilon_s} \sum_i \int_0^\beta \frac{d^3 \mathbf{r} d\tau}{|\mathbf{r} - \mathbf{r}_i(\tau)|} - \frac{e^2}{2\varepsilon_\infty} \sum_{i\neq j} \int_0^\beta \frac{d\tau}{|\mathbf{r}_i(\tau) - \mathbf{r}_j(\tau)|}
\]

\[
+ \frac{\omega_{LO} e^2}{4\tilde{\varepsilon}} \sum_{i,j} \int_0^\beta \int_0^\beta \frac{d\tau d\sigma}{|\mathbf{r}_i(\tau) - \mathbf{r}_j(\sigma)|} G_{\beta,\omega}(\tau - \sigma),
\]

where the Green function of the phonons is given by

\[
G_{\beta,\omega}(\tau - \sigma) = \frac{\cosh(|\tau - \sigma| - \beta \omega/2)}{\sinh(\beta \omega/2)}.
\]

All the effects of the electron–phonon coupling are now contained in the last term of (3.5), including the retarded interaction of an electron with itself (\( i = j \)), which is nothing else than the polaron effect, whereas for \( i \neq j \) the electron \( i \) interacts with the electron \( j \) via phonons. The other terms of (3.5) represent the kinetic energy of the electrons and the diverse Coulomb interactions: jellium–jellium, electron–jellium and electron–electron.
3.1. Single polaron

The particular case of (3.5) with only one electron results in the one polaron problem for which the action reduces to

\[
S(\mathbf{r}) = \frac{m}{2} \int_0^\beta \tau^2(\tau) \, d\tau + \frac{\omega_{\text{LO}}^2 e^2}{4\varepsilon} \int_0^\beta \int_0^\beta \, d\tau \, d\sigma \frac{G_{\beta,\omega_0}(\tau - \sigma)}{|\mathbf{r}(\tau) - \mathbf{r}(\sigma)|}. \tag{3.7}
\]

By following the variational method of Feynman, the free energy is estimated by [24, 36, 37]

\[
f_{\text{pol}} = f_0 + (1/\beta) \langle S - S_0 \rangle_{S_0}, \tag{3.8}
\]

with the trial action \( S_0 \) given by

\[
S_0(\mathbf{r}) = \frac{m}{2} \int_0^\beta \tau^2(\tau) \, d\tau + \frac{(\omega_0^2 - \omega_1^2) \omega_1}{8} \int_0^\beta \int_0^\beta \, d\tau \, d\sigma G_{\beta,\omega_1}(\tau - \sigma)|\mathbf{r}(\tau) - \mathbf{r}(\sigma)|^2. \tag{3.9}
\]

Here, \( \omega_0 = (K/\mu)^{1/2} \) and \( \omega_1 = (K/M)^{1/2} \) are the two variational parameters. \( \mu \) is the reduced mass \( \mu = mM/(m + M) \) and \( M/m = (\omega_0^2/\omega_1^2) - 1 \), \( K = M\omega_1^2 \). The polaron mass is then defined as \( M_p/m = M + 1 \). The polaron radius is defined as \( R_p = \sqrt{3/2 \mu \omega_0} \). The free energy, which may be minimized with respect to \( \omega_0 \) and \( \omega_1 \), is

\[
f_{\text{pol}} = - \frac{3\hbar(\omega_0^2 - \omega_1^2)}{4\omega_0} \coth \left( \frac{\beta \omega_0}{2} \right) - \frac{\hbar \Omega}{\sqrt{\pi}(1 - e^{-\beta \omega_0})} \int_0^\beta \frac{e^u}{\sqrt{g(u)}}. \tag{3.10}
\]

with

\[
g(u) = \frac{\omega_0^2 - \omega_1^2}{\omega_0^3} \left[ \frac{1 - \cosh(\omega_0 u)}{\tanh(\beta \omega_0 / 2)} + \sinh(\omega_0 u) \right]. \tag{3.11}
\]

This well-known expression [24] will be a part of the total free energy of the many-polaron free energy. Let us note that in the strong coupling limit and at low temperature, we obtain the well-known result [36, 37]

\[
\omega_0/\omega_{\text{LO}} \approx 4\Omega^2/9\pi, \quad f_{\text{pol}}/\hbar \omega_{\text{LO}} \approx -\Omega^2/3\pi. \tag{3.12}
\]

In that case, the polaron radius is independent of the phonon frequency \( \omega_{\text{LO}} \) and may be expressed as

\[
R_p = \left[ 3\sqrt{3\pi}/2 \right] \varepsilon a_0. \tag{3.13}
\]

3.2. Many polarons at low finite densities

We now consider the polaron gas at finite densities. The electrons are sparse enough in volume and are localized in different polaronic wells, which are separated from each other. Our first approximation is to neglect the exchange between the electrons, which would give only a very weak contribution at the densities under consideration. Taking advantage of that point, we introduce the two different variables \( \{ \mathbf{R}_i(\tau) \} \) and \( \{ \mathbf{u}_i(\tau) \} \) related by

\[
\mathbf{r}_i(\tau) = \mathbf{R}_i(\tau) + \mathbf{u}_i(\tau). \tag{3.14}
\]

The variables \( \{ \mathbf{R}_i(\tau) \} \) represent the coordinates of the centres of mass of the polarons, to which we assign the mass \( M_p \), i.e. the polaron mass described above. They are assumed to be classical variables (non-degenerate). The path integration on these variables is reduced to the saddle point classical trajectory, and the partition function is obtained by averaging over these variables.
On the contrary, the variables \( u_i(\tau) \) are highly oscillating (quantum) variables and represent the coordinates of the electrons inside their polaronic walls. The path-integral formulation is necessary to describe the behavior of these quantum variables. The next step is to proceed to a quadratic expansion of the different terms with respect to \( \{ u_i(\tau) \} \), which are small in amplitude in comparison with \( \{ R_i \} \).

Following this procedure, we obtain

\[
S(|r_i(\tau))| \approx S_{cl}(|R_i|) + S_q(|u_i(\tau)|)
\]  

with, respectively,

\[
S_{cl}(|R_i|) = \beta \sum_i \frac{M_p}{2} R_i^2 - \frac{e^2 n^2 \beta}{2 \epsilon_s} \int \int \frac{d^3r d^3r'}{|r - r'|} \]

\[
+ \frac{e^2 n \beta}{\epsilon_s} \sum_i \int \frac{d^3r \tau}{|r - R_i|} - \frac{e^2 \beta}{2 \epsilon_s} \sum_{i \neq j} \frac{1}{|R_i - R_j|},
\]

\[
S_q(|u_i|) = \frac{1}{2} \sum_i \left[ \int_0^\beta m \ddot{u}_i(\tau) d\tau + \frac{\omega_{LO} e^2}{2 \epsilon} \int_0^\beta \int_0^\beta d\sigma d\tau G_{\beta,\omega_{LO}}(\tau - \sigma) \right]
\]

\[
- \frac{e^2}{2 \epsilon_{\infty}} \sum_{i \neq j} \int_0^\beta \int_0^\beta u_i^\dagger(\tau) \cdot T_{ij} \cdot u_j(\tau) \tilde{G}_{\beta,\omega_{LO}}(|\tau - \sigma|) d\tau d\sigma.
\]  

The new propagator \( \tilde{G} \) is now defined as

\[
\tilde{G}_{\beta,\omega_{LO}}(x) = \delta(x) - \frac{\omega_{LO} e^2}{2 \epsilon} G_{\beta,\omega_{LO}}(x)
\]

and includes instantaneous dipole–dipole interactions (\( \delta \) function) and the retarded ones mediated by the phonons. We have also introduced the dipolar tensor \( T_{ij} \equiv T_{ij}(R_i - R_j) \), whose matrix coefficients are

\[
T_{ij}^{\alpha\gamma} = \frac{\delta_{\alpha\gamma} R_{ij}^2 - 3 R_{ij}^\alpha R_{ij}^\gamma}{R_{ij}^2}.
\]

Note that by performing the quadratic expansion of the action, the sum of all crossed terms with \( u_i \) and \( R_j \) systematically vanish on average owing to the spherical symmetry of the gas state. Finally, equations (3.15)–(3.19) constitute our model for evaluating the effects of the dispersion forces in an interacting non-degenerate polaron gas.

4. Free energy of the system

The free energy per particle of the system at finite densities can now be derived from (3.16) and (3.17) and can be decomposed into a classical part and a quantum one:

\[
f(n, T) = f_{cl}(n, T) + f_q(n, T).
\]

Each part is calculated in the next two sub-sections. The total free energy will depend on the variational parameters \( \omega_0 \) and \( \omega_1 \) introduced in the preceding section (single polaron) and may be calculated by minimization of the total free energy per particle:

\[
\frac{\partial f(n, T)}{\partial \omega_0} \bigg|_{n,T} = 0 \quad \text{and} \quad \frac{\partial f(n, T)}{\partial \omega_1} \bigg|_{n,T} = 0.
\]
Let us note that when the free energy is obtained as a function of the density $n$ and the temperature $T$, all the thermodynamical properties of the system may be derived [4, 5].

4.1. Classical part of the energy

The partition function $Z_{cl}$ for the classical degrees of freedom $\{R_i\}$ is easily obtained, because it corresponds to the ocp of classical point charged particles with mass $M_p$ in a jellium ($f_{cl}(n, T) \equiv f_{ocp}(n, T)$). The free energy per particle is [38]

$$f_{cl}(n, T) = \frac{1}{\beta} \left[ \ln(n \Lambda^3) - 1 \right] + f_{ex}(n, T).$$

(4.3)

The first term is the usual ideal term of a gas, whereas the second term is the excess free energy due to the interactions, and $\Lambda = [2\pi \beta \hbar^2/M_p]^{1/2}$ is the de Broglie wavelength for polarons.

Literature data give us analytical expressions for the excess term, as a function of a unique plasma dimensionless parameter $\Gamma$, available in the range $1 < \Gamma < 160$ [38, 40]:

$$f_{ex}(n, T) \approx \frac{1}{\beta} \left[ -0.90\Gamma + 3.62\Gamma^{-1/4} - 0.81 \ln(\Gamma) - 2.58 \right].$$

(4.4)

4.2. Quantum part of the energy

The quantum energy contains two terms: the polaron formation energy $f_{pol}$ already discussed in section 3.1 and the quantum energy due to the vdW interactions:

$$f_q(n, T) = f_{pol} + f_{vdW}(n, T).$$

(4.5)

The last term may be written as the difference between the energy of the interacting oscillating dipoles and their non-interacting energy:

$$f_{vdW}(n, T) = \frac{1}{\beta} \int_0^\infty \left[ D(\omega, n) - 3\delta(\omega - \omega_0) \right] \ln \left( \frac{2 \sinh \left( \frac{\beta \omega}{2} \right) \right) d\omega,$n,

(4.6)

where $D(\omega, n)$ is the density of states of the collective modes at $\omega$ and a given polaron density $n$.

To obtain the requested density of states, we use the results of the theory of polarizable fluids [30]–[34]. Adopting this theory to our case, we consider the dipolar contribution to the effective action of the non-interacting polarons:

$$S_d = \frac{1}{2} \sum_{ij} \left[ \int_0^\beta \dot{u}_i^2(\tau) d\tau + \frac{(\omega_0^2 - \omega_1^2)\omega_1}{4} \int_0^\beta \int_0^\beta d\tau d\sigma G_F(\tau - \sigma)|u_i(\tau) - u_i(\sigma)|^2 \right]$$

$$+ \sum_{i \neq j} \int_0^\beta \int_0^\beta \dot{u}_i^+(\tau) \cdot T_{ij} \cdot \dot{u}_j(\sigma) \frac{\tilde{G}(\tau - \sigma)}{2\beta\epsilon_\infty} d\tau d\sigma.$$

(4.7)

After the Fourier transform of the quantum variable,

$$u_i(\omega) \sim \int u_i(\tau) \exp[i\omega \tau] d\tau,$$

(4.8)

we obtain the variational action for the dipoles:

$$S_d = \frac{1}{2} \sum_{ij} \int u_i(\omega) \left[ \frac{I_{ij}}{\alpha_F(\omega)} + \frac{T_{ij}}{\epsilon_h(\omega)} \right] \cdot u_j(\omega) d\omega,$$

(4.9)
where \(\epsilon_h(\omega)\) is given by (2.5), and where we defined the bare polarizability \(\alpha_F(\omega)\) of the Feynman particle as
\[
\alpha_F(\omega) = \frac{\omega^2 - \omega_1^2}{\omega^2[\omega_0^2 - \omega^2]} \frac{\epsilon^2}{\hbar m}.
\]

The effective polarizability of the medium \(\alpha(\omega)\) is defined as
\[
\alpha(\omega) = \langle [I_{ij}/\alpha_F(\omega) + T_{ij}(\{R_k\})/\epsilon_h(\omega)]^{-1} \rangle, \tag{4.11}
\]
where the brackets denote the average over the distribution of the classical variables \(\{R_k\}\). The density of state of the collective (dipolar) modes is then related to the imaginary part of the polarizability by [30, 31]
\[
D(\omega, n) = \frac{6\omega_0 \alpha_i(\omega)}{\pi}. \tag{4.12}
\]

In the framework of the theory of polarizable fluids, this problem has been intensively studied [30]–[34]. We use the results of it and refer the reader to these references for details. Essentially, the effective polarizability may be calculated through an implicit equation under the form of Dyson’s one:
\[
\alpha(\omega) - 1 = \alpha_F(\omega) - 1 - U(\alpha(\omega)/\epsilon_h(\omega))/\epsilon_h(\omega). \tag{4.13}
\]

One of the simplest methods to approximate the function \(U(\alpha)\) is the Padé approximation as was done in [30]. At low density, a simple expression is obtained:
\[
U(\alpha/\epsilon_h(\omega)) \approx \frac{8\pi n\alpha(\omega)}{3\sigma^3 \epsilon_h(\omega)}. \tag{4.14}
\]

In (4.14) \(\sigma\) represents the size (diameter) of the particles below which they become impenetrable, i.e. the hard-core part of the short-range interaction. Since we neglect the exchange between polarons, we may approximate \(\sigma \approx 2R_p\). The polaron radius \(R_p\) is itself related to the variational parameter \(\omega_0\) (see section 3.1). Eventually, the substitution of (4.14) into (4.13) gives the density of states (4.12), which allows us to estimate the vdW energy (4.6).

We have thus obtained the total free energy (4.1) at a given density \(n\) and temperature \(T\) as a function of the variational parameters \(\omega_0\) and \(\omega_1\). Using minimization (4.3), we may calculate the variational free energy. The model includes all the effects of the long-range Coulomb forces, especially the collective properties of an interacting non-degenerate polaron gas at low enough density (see the Introduction). Complete numerical calculations in a wide range of parameters require a lot of details and will be provided elsewhere. In the present paper, we now restrain ourselves to the low temperature and the strong electron–phonon coupling regime. This procedure allows us to obtain semi-analytical results that catch the main effect of the vdW forces, i.e. an NMT at finite densities.

Finally, one point needs to be discussed. In our model, we explicitly neglect all retarded effects in the direct dipole–dipole interaction between the polarons. However, in a rigorous consideration the electric field induced by oscillating dipoles is expressed as
\[
E \sim \frac{A}{r^3} + \frac{B}{\lambda r^2} + \frac{C}{\lambda^2 r}, \tag{4.15}
\]
where \(r\) is the distance between dipoles, \(A\), \(B\) and \(C\) are constants depending on the parameters of the dipole–dipole interactions, and \(\lambda\) is the wavelength of the oscillation \(\lambda \sim 2\pi c/\omega_0\). In our
case, $\omega_0 \sim 0.1$–0.5 eV so that $\lambda \sim 5$–10 $\mu$m (i.e. $10^4$ Å). The first term in (4.15) is the quasi-
static near field in the sense that it oscillates without retardation, whereas the two others are the
mesoscopic field (second term) and far field (third term) provided the retarded effects. Since
the mean distance between the dipoles is much lower than $\lambda$, the two retarded terms may be
safely neglected. This is what we are doing in the present paper because the mean distance
(about a few tenths of Å) is much less than $\lambda \approx 10^4$ Å. That leads to the $1/r^6$ asymptotics
in the vdw contribution. Taking into account the retarded effects would indeed change the $1/r^6$
to $1/r^7$ forces and would correspond to the Casimir forces, but may certainly be neglected in the
range of the polaron densities under consideration, i.e. $10^{18}$–$10^{21}$ cm$^{-3}$. However, such Casimir
interactions could become pertinent at densities lower than about $10^{16}$ cm$^{-3}$.

5. NMT due to vdw interactions in the strong electron–phonon limit

Equation (4.13) for the effective polarizability is quadratic and may be easily solved by
using (4.14):

$$\sum_{n=0}^{\infty} \left( \frac{\alpha(\omega)}{\epsilon_0(\omega)} \right)^2 - \left( \frac{\epsilon_0(\omega)}{\alpha_0(\omega)} \right) \left( \frac{\alpha(\omega)}{\epsilon_0(\omega)} \right) + 1 = 0. \tag{5.1}$$

We now consider the strong electron–phonon coupling, i.e. $\Omega \gg 1$, and low temperature, i.e.
$\omega_0 \gg k_B T$. In that case, it is well known that $\omega_1 \approx \omega_{LO}$ and $\omega_0 \gg \omega_{LO}$. The polaron energy
becomes in this limit $f_{pol} \approx -3\omega_0/4$. In the region of interest, we may also approximate $\epsilon_0(\omega) \approx \epsilon_{\infty}$ and $\alpha_0 \approx 1/(\omega_0^2 - \omega^2)$. Considering (5.1), we see that the imaginary part of $\alpha(\omega)$ is not zero
if the determinant of the equation is negative. That yields the interval of eigenfrequencies

$$\omega_-(n) < \omega < \omega_+(n) \tag{5.2}\$$

with

$$\omega_{\pm}(n) = \omega_0 \sqrt{1 \pm (n/n_0)^{1/2}} \tag{5.3}$$

and

$$n_0 = \frac{3R_p^3\omega_0^4\overline{\epsilon}_0^2\hbar^2m^2}{4\pi e^4}. \tag{5.4}$$

The imaginary part and the real part of the effective polarizability, respectively, $\alpha_0(\omega)$ and $\alpha_0(\omega)$,
are then given by

$$\alpha_0(\omega < \omega_-) = \frac{2n_0[(\omega_0^2 - \omega^2) - (\omega_0^2 - \omega_0^2)^{1/2}(\omega_-^2 - \omega_0^2)^{1/2}]}{n\omega_0^4} \frac{e^2}{\hbar m},$$

$$\alpha_0(\omega > \omega_+) = \frac{2n_0[(\omega_0^2 - \omega^2) + (\omega_0^2 - \omega_0^2)^{1/2}(\omega_0^2 - \omega_0^2)^{1/2}]}{n\omega_0^4} \frac{e^2}{\hbar m},$$

$$\alpha_0(\omega_- < \omega < \omega_+) = \frac{2n_0(\omega_0^2 - \omega^2)^{1/2}(\omega_0^2 - \omega_0^2)^{1/2}}{n\omega_0^4} \frac{e^2}{\hbar m}. \tag{5.5}$$

The use of these formulae allows us to evaluate not only the vdw free energy, but also
the stability of the system and its dielectric properties. The renormalized density of states
is sketched in figure 1(a), whereas figure 1(b) shows the effective polarizability $\alpha(\omega)$ versus
frequency. For these and all other calculations, we use $\epsilon_\infty = 4$, $\epsilon_s = 30$, $m/m_e = 1$ and
Figure 1. Dimensionless density of states $3D(\omega, n)\omega_0$ (a) and real part $\alpha_r(\omega)/\alpha_0(0)$ (in atomic units) (b) of the effective polarizability of the strongly coupled polaron gas versus dimensionless frequency $\omega/\omega_0$ at various polaron densities $n$: dotted lines correspond to $0.1n_0$, dashed to $0.5n_0$ and solid to $n_0$. Arrows depict $\omega_{LO}$ and $\omega_{TO}$, respectively.

$\omega_{LO}/\omega_0 = 0.1$. As seen, at low densities the density of states is confined around $\omega_0$ because the dispersion forces are weak. However, as the density increases $\omega_-$ decreases and $\omega_+$ increases, spreading out the dispersion on a wider region.

To solve equation (5.1) and obtain the simple analytic formulae (5.2)–(5.5), we have neglected the absorption by the phonons and by the electrons in their polaronic potential. In other words, $\epsilon_h(\omega)$ and $\alpha_F(\omega)$ have been taken real. Taking into account dissipative effects by introducing two phenomenological parameters and writing $\epsilon_h(\omega + i\Gamma_h)$ and $\alpha_F(\omega + i\Gamma_F)$ in (5.1), would have slightly changed quantitatively the results provided that $\Gamma_h \ll \omega$ and $\Gamma_F \ll \omega$ in the range of frequencies that we consider. In fact, our approximation is correct as a first approximation because the phonon linewidth is generally much lower than its frequency $\omega_{LO}$, and the linewidth for the polaron excitation at $\omega_0$ is of the order of $\omega_{LO}$ in the strong electron–phonon limit (see, for example, [39]). We do not calculate the total absorption of the
system in this paper. However, in the case of such calculations, it would be necessary to include these dissipative effects.

5.1. Estimates of the free energy

The vdW energy may be evaluated using (4.6). At low temperature, we have

\[ f_{\text{vdW}}(n, T) = \frac{\hbar}{2} \int_0^\infty \omega D(\omega, n) \, d\omega - \frac{3\hbar}{2} \omega_0. \]  

(5.6)

Replacing \( D(\omega, n) \) by its value from (4.12) and (5.5) yields

\[ f_{\text{vdW}}(n, T) = \frac{6\hbar n_0}{\pi \omega_0} \int_{\omega_-(n)}^{\omega_+(n)} \omega^2 \sqrt{(\omega^2 - \omega_-^2(n))(\omega_-^2(n) - \omega^2)} \, d\omega - \frac{3\hbar \omega_0}{2}. \]  

(5.7)

We now perform the change of variables: \( \omega^2 = \omega_0^2(1 + \sqrt{n/n_0} \cos(y)) \). That results in

\[ f_{\text{vdW}}(n, T) = \frac{3\hbar \omega_0}{\pi} \int_0^\pi \left( 1 + \sqrt{\frac{n}{n_0}} \cos(y) \right)^{1/2} \sin^2(y) \, dy - \frac{3\hbar \omega_0}{2}. \]  

(5.8)

At low densities, i.e. \( n \ll n_0 \), the integrand may be expanded in terms of the small parameter \( \sqrt{n/n_0} \). We obtain an estimate of the vdW energy in this limit:

\[ f_{\text{vdW}}(n, T) \approx -\frac{3\hbar \omega_0}{\pi} \left[ \frac{\pi}{64} \left( \frac{n}{n_0} \right) + \frac{5\pi}{2048} \left( \frac{n}{n_0} \right)^2 + O \left( \frac{n^3}{n_0^3} \right) \right]. \]  

(5.9)

We find a negative contribution of the vdW interactions, which corresponds to an attraction as it should. Moreover, the first linear term indicates a total free energy \( F \sim nf_{\text{vdW}} \sim n^2 \sim R_s^{-6} \), which is also correct in the dilute regime. The comparison with \( f_{\text{pol}} \) (the polaronic part of the energy at strong electron–phonon coupling) indicates that vdW remains small since \( f_{\text{vdW}}/f_{\text{pol}} \approx (1/16)n/n_0 \ll 1 \) (see figure 2). However, it may also be seen that when the density increases and becomes comparable to \( n_0 \), the situation completely changes and the vdW contribution becomes much more important for determining the collective properties of the polaron gas.

5.2. Mechanical instability

First, we emphasize that the density of states should have a finite width. However, when the lowest band edge \( \omega_-(n) \) reaches \( \omega_{h,0} \), there is a mechanical instability of the system, because below \( \omega_{h,0} \) the values of \( \epsilon_b(\omega) \) and \( \alpha_F(\omega) \) become negative. That means there is no more restoring force for a collective mode below \( \omega_{h,0} \). Therefore, the criterion of instability is expressed as

\[ \omega_-(n_c) = \omega_{h,0}. \]  

(5.10)

which gives the critical density

\[ n_c = n_0 \left( 1 - \frac{\omega_{h,0}^2}{\omega_0^2} \right)^2. \]  

(5.11)
Figure 2. The $f_{vdW}/f_{pol}$ ratio versus dimensionless polaron density $n/n_0$ (solid line). The dashed line corresponds to the asymptotical linear dependence.

Beyond this density, due to the dynamical effects some polarons necessarily dissociate. We should note that criterion (5.10) is nothing but the continuation of the instability criterion already proposed for the PWC [21]. We may replace $R_p$ by its value as a function of $\omega_0$ so that

$$n_c \approx \frac{3^{5/2} \epsilon_\infty^2 a_0^{-3}}{(2)^{3/2}4\pi} \omega_0^{5/2} \left( \frac{\hbar a_0}{m_e^4} \right)^{5/2} \left( 1 - \frac{\omega_{LO}^2}{\omega_0^2} \right)^2 = \frac{243 \epsilon_\infty^2 a_0^2}{64\pi R_p^5} \left( 1 - \frac{\omega_{LO}^2}{\omega_0^2} \right)^2. \quad (5.12)$$

In the strong coupling limit, i.e. when $\Omega \to \infty, \omega_{LO}/\omega_0 \ll 1$ and using (3.13) for $R_p$, the critical density can be expressed only in terms of the static, the high-frequency dielectric constants of the host medium and the effective mass of the electron:

$$n_c = \frac{\epsilon_\infty^2}{2(3^{3/2})\pi^{1/2} \tilde{\epsilon}^5} \left( \frac{m_e}{m_e} \right) a_0^{-3}. \quad (5.13)$$

The high-frequency dielectric constant $\epsilon_\infty$ generally varies between 2 and 5, whereas $\epsilon_\infty \gg \epsilon_\infty$ in highly polar materials, so that the critical density is to be of the order of $10^{19}$–$10^{21}$ cm$^{-3}$, which corresponds to many practical cases of doped dielectrics (in particular oxides). Therefore, the considered instability is quite realistic for highly polar dielectrics in which strong Fröhlich electron–phonon coupling may occur.

5.3. Polarization (dielectric) catastrophe and the NMT

Since some polarons should dissociate in the vicinity of $n_c$, quasi-free electrons may also exist in this region and that leads to the onset of metallization. A simple way to confirm that point is to calculate the static dielectric constant of the system. Using the Maxwell–Garnett relation (2.5)

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with the effective polarizability $\alpha(\omega)$ calculated above, the dielectric constant of the system becomes

$$\epsilon(\omega) = \epsilon_s \frac{3\epsilon_\infty + 8\pi n\alpha(\omega)}{3\epsilon_\infty - 4\pi n\alpha(\omega)}.$$  \hfill (5.14)

It may be seen that the static dielectric constant rises strongly as the density increases and becomes infinite ($\epsilon \to \infty$) at some critical density $n_\infty$ defined by

$$\alpha_r(0)n_\infty = \frac{3\epsilon_\infty}{4\pi}.$$  \hfill (5.15)

This critical density clearly determines the onset of metallization. The static polarizability and the static dielectric constant are represented in figure 3 as a function of the density, while figure 4 also depicts the real and the imaginary parts of the dielectric constant as a function of $\omega$.
at various densities. In general, it is possible to extend the calculations to the case $k \neq 0$ by the nonlocal electrostatics approach [41]; however, it is clear that the dielectric function $\epsilon(\omega, k \neq 0)$ should also be negative at certain wave vectors [42]. When the density approaches $n_\infty$, the static dielectric constant increases by more than an order of magnitude due to dispersion interactions. In contrast, the GH model gives only a slight increase in this range of density (figure 3). The divergence of the static dielectric constant provides indirect evidence of the NMT in the vicinity of $n_\infty$. It is interesting to compare both the critical densities $n_c$ and $n_\infty$. Using (5.5) and (5.15), we estimate the ratio $n_\infty/n_c \approx n_\infty/n_0$ in the strong-coupling case as

$$\frac{n_\infty}{n_0} \approx 1 - \left[ 1 - \frac{\pi}{3} \frac{\epsilon_\infty}{\epsilon} \right]^2.$$

(5.16)

It can be easily seen that for highly polar dielectrics, i.e. $\epsilon_\infty \ll \epsilon_s$, the difference between the two critical densities does not exceed a few per cent. Both of these effects, i.e. the mechanical
instability and the dielectric catastrophe, are thus the two faces of the same phenomenon, namely an NMT resulting from dispersion interactions between polarons and associated with the dissociation of some polarons beyond this density.

6. Discussion and conclusion

In this paper, we have evaluated the effects of dispersion forces on dielectric and thermodynamic properties of a many-polaron system in the strong electron–phonon coupling limit. Starting from the coupling between the electrons and the longitudinal polarization of the medium, we have derived the free energy of the system at low densities. The large difference in time scales between the quantum and the classical degrees of freedom allows us to separate the relevant contributions and obtain semi-analytical estimates for these contributions. Classical terms were evaluated with the use of the theory of ocp, whereas the quantum contributions by the Feynman polaron model together with the theory of quantum polarizable liquids. Considering the diluted limit \( n R_p^3 \ll 1 \), we have obtained an explicit expression for the dispersion contribution. The analysis of this contribution indicates that the dispersion effect is collective and strongly nonlinear at large enough densities of polarons. The main consequence of these vdW forces is a quantum phase transition occurring at densities about \( n_\infty \approx n_c \) leading to an NMT. The latter is realized as a polarization catastrophe and a mechanical instability of the system.

We have considered the diluted case corresponding to the limit \( n R_p^3 \rightarrow 0 \). The evaluations of the critical densities confirm this suggestion, since in the vicinity of \( n_c \) the parameter \( n R_p^3 \approx 0.05 \). However, a careful estimation of the influence of this parameter requires a more sophisticated model for the dispersion effects close to \( n_c \). For example, an advanced model for the density dependence of \( U(\alpha, n) \) may be used. Various models of polarized liquids [30] or disordered lattice, such as the effective medium approximation [43] or the coherent potential approximation (see, for example, [35]), could improve our simple evaluations.

Although we have ignored the bipolaron formation in our system, the attraction due to vdW forces between polarons indicates the possibility of associations such as multi-electron polaronic clusters. Of course, to model such aggregates we should account for both long-range and short-range correlations between polarons. However, the latter are completely ignored in our current model, although the short-range correlations participate for the stability of such multi-polaron clusters in ionic systems [44] and polar dielectrics [45]. Nevertheless, our analysis indicates that any criterion for the stability of such multielectron states should be sufficiently modified by the account of dispersion forces. A proper treatment of both types of correlation (short-range and dispersion contributions) could be based on the explicit separation between them in the correlation potential [46] or by the construction of a ‘seamless’ functional [47], as was done for electronic systems. Additional efforts are required to explicitly separate these interactions in the case of polarons. It should be emphasized that the extension of our model requires a correct treatment of the exchange between electrons in the vicinity of the critical density. In this region of densities, the exchange effects should play a significant role, in particular they cannot be ignored when quasi-free electrons coexist with polarons. This effect is beyond the scope of the present paper and will be exposed in our forthcoming work.

It has been believed for a long time that a polarization catastrophe driving an NMT following the original Goldhammer–Herzfeld idea [6, 7] was not realistic in doped dielectrics (see, for example, the discussion in [48]). The original Goldhammer–Herzfeld theory indeed did not treat all the effects of dispersion forces. However, the critical density decreases
sufficiently due to their contribution, and the polarization catastrophe may occur in a low enough density regime where short-range correlations play a minor role. Our studies thus indicate that dispersion forces may completely change the scenario of the metal–insulator transition as viewed by Mott. In contrast to the usual Mott mechanism focused on the screening of the long-range Coulomb potential by a stable electron gas, our scenario assumes the dominant role of the dispersion attractions between localized electrons in polaronic states. Our model is also different from the Anderson localization, since localization is due to the polaronic effect in our case, and not to disorder. In any case, the present studies confirm and extend the results of our previous works concerning the PWC [20, 21], and the metal–ammonia solutions [4, 5]. Returning to the question of the influence of weak forces on the global phase behaviour, which has been recently debated [49, 50], we may respond now in the terminology of ‘mouse and mammoth’ (see the discussion by Anderson in [49]). Our study is just an example when such a mouse (the vdW interactions) controls the global behaviour of the whole system. Being less than 5% of $f_{pol}$ (the polaron energy), the vdW energy could provide a polaron dissociation resulting in a quantum phase transition for the whole system.

Finally, we may discuss to what extent our theory can be applied to realistic materials. The present three-dimensional model essentially wants to highlight a new phenomenon: the NMT due to vdW forces between polarons at strong-electron phonon coupling and low enough densities. For applications to cuprates, for example, as we believe that it may possibly be relevant for explaining the finite doping density at which superconductivity appears in these materials (about 6% of doping), the model needs to be rigorously extended to a quasi-two-dimensional case. This case has already been discussed in [20, 21], but it requires much more detail (as we will propose in a further publication) to be convincing. Moreover, the same kinds of effects of the dispersion forces have been shown to be essential for metal–ammonia solutions [4, 5]. This is due to the fact that solvated electrons in ammonia behave more or less as strong coupling polarons in polar solids. An analogy between cuprates and metal–ammonia solutions has also already been proposed in [42, 51].

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