

Long-range polarization interaction in simple liquid metals

M. Blazej and N. H. March

Theoretical Chemistry Department, University of Oxford, 5, South Parks Road, Oxford OX1 3UB, England

(Received 30 December 1992)

In earlier work [F. Perrot and N. H. March, *Phys. Rev. A* **41**, 4521 (1990); **42**, 4884 (1990)], the electron theory of pair potentials in simple s - p liquid metals, such as Na and K near freezing, was set out. The potential thus derived for Na is in good agreement in its major features with that obtained by inverting diffraction measurements of the liquid structure factor $S(k)$. The present study addresses polarization effects in the interatomic interaction in such s - p metals, a simple physical model being introduced. By a lower-bound argument, this is shown to lead to an attractive contribution to the effective pair potential which decays as R^{-4} at large interionic separation R . Since it is recognized that some difficulties still remain in justifying the simple model employed in a dense system, it is important to test experimentally whether such a long-range interaction is actually present in liquid Na or K near freezing; it is proposed that highly accurate small-angle neutron scattering could resolve this question precisely. Though less decisive for detection of the long-range polarization effect, the possible relevance to (i) long-wavelength phonon properties in hot (and cold) crystalline Na metal and (ii) the interaction between charged defects in metals (e.g., a divacancy) is also noted.

PACS number(s): 61.25.Mv, 61.20.-p

I. INTRODUCTION

In previous studies by Perrot and March [1,2; referred to below as PM], the density-functional theory of pair potentials in simple metals such as Na and K near freezing was set out, and brought into contact with results from liquid-structure inversion. As shown in PM for liquid Na just above its freezing point, all the salient features of the “diffraction” pair potential as extracted from the liquid structure x-ray measurements of Greenfield, Wellendorf, and Wiser [3] by Reatto [4] are reflected in the “density functional” potential.

However, some quantitative differences remain between these two pair potentials. This has prompted us, especially because the diffraction potential at large interionic separation lies below the zero potential axis, whereas the electron-theory potential lies above this axis out to 6.5 Å, to enquire whether there may be another physical contribution to “correct” the electron-theory potential. We have been led thereby to consider the possibility of a long-range polarization interaction between a pair of screened ions embedded in a metallic medium.

The issue of polarization effects in the interatomic interaction in metals has already attracted some interest in recent years, notable work being that of Maggs and Ashcroft [5]. These workers had in mind rather specifically metals with d electrons (e.g., silver), whereas in the present study we focus exclusively on a model that should have relevance to “nearly-free-electron” metals such as Na and K above. However, we must stress at the outset that all our present results are based on a static computation of (a lower bound to) the polarization interaction between two ions and their screening electron clouds, on the basis of which (model) the centers of the blobs of electrons are found to be displaced from the positions of the ions.

It needs to be said, at the outset, that it remains to give a full theoretical justification of this approach in a dense system, and in particular to use the polarization interaction calculated here as a pairwise additive potential. It is a problem for the future to build a bridge between the present static calculation and a fluctuation description. Nevertheless, we believe the consequences of our admittedly oversimplified static computation are of sufficient interest to prompt experimental studies of the long-range polarization interaction that arises in the present work.

Returning to the original motivation of our static calculation, early work by Gurney and Magee [6] on the free-space H_2 molecule allowed the $1s$ hydrogen orbitals to “float” away from the protons. The distance along the H_2 molecular axis by which these orbitals move was then treated as a variational parameter. Such a treatment immediately gave a substantial improvement in the ground-state energy as a function of internuclear separation.

Since the earlier work of PM was built directly on the superposition density of single ions, it seemed clear that the simplest approach was to allow such spherical blobs of screening charge to float off the ionic centers, without, however, any deformation of the single-ion spherical blobs. This is the picture adopted in the present work. Remarkably, it then turns out that the new potential energy curve can be largely characterized by the original pair potential of PM, plus the (assumed vector) displacements of the two blobs of screening charge from the ionic centers. Since, at large interionic separations, such displacements must become small, the “correction” to the standard pair potential $\phi(R)$ of PM can be expressed in terms of this potential and its low-order derivatives, plus the vector displacements.

Sections II and III are concerned with reporting a calculation based on this simple floating blobs model of the polarization interaction. Thus Sec. II sets out the correc-

tion to $\phi(R)$, say $\Delta\phi(R)$, the essential asymptotic result being expressed in Eq. (2.16) below. The vector displacements, however, are input information into this equation.

Then, in Sec. III, we determine the lower bound of this correction $\Delta\phi(R)$ to the pair potential. This leads, in what seems a rather natural way, to a polarization interaction (3.7), which falls off as the inverse fourth power of the interionic pair separation. Section IV is concerned with the possible experimental implications that such an inverse power law would have. Section V constitutes a summary, with some proposals for further work.

II. POLARIZATION-EFFECTS-CORRECTED PAIR INTERACTION

The model of "valence blobs of charge floating off the nuclei" offers an approach to take into account long-range correlation effects. This is already evident from the free-space study of London dispersion forces in homonuclear diatomic molecules by Egorov and March [7].

Within the framework of the derivation of pair interactions from density functional theory, this would correspond to a change in the functional $G[n]$, where n is the electron density, which describes kinetic plus exchange and correlation effects, when two ions are present. In the case of a single ion, $G[n]$ is that of the uniform electron gas $G_0[n]$, with the corresponding response function related to the functional second derivative. For two ions, we assume that the second derivative, and thus the response function, are changed due to polarization effects. The displaced density then becomes

$$\Delta n(\mathbf{r} + \mathbf{R}/2 - \delta\mathbf{R}_1) + \Delta n(\mathbf{r} - \mathbf{R}/2 - \delta\mathbf{R}_2).$$

For any system containing one or two ions screened in a bath of conduction electrons, the change in total energy, with respect to that of the originally uniform electron background (i.e., without the ions embedded) can be written, as commonly done in second-order perturbation theory:

$$\Delta E = \int v_{\text{ext}} \bar{n} d\mathbf{r} + \frac{1}{2} \int v_{\text{ext}} \delta n d\mathbf{r} + (\text{change in ion-ion interaction}). \quad (2.1)$$

In this equation, \bar{n} denotes the density of the unperturbed homogeneous electron gas, v_{ext} the perturbing external potential, while δn is the total displaced electron density due to embedding the ions in the background of conduction electrons.

It will be assumed that the system with a pair of ions embedded in the electron gas, and the system with but a single ion, both satisfy Eq. (2.1). Thus the change in the pair interaction results from the change in the second term of ΔE , associated with floating the electron clouds, all the other quantities (v_{ext} and R , the interionic separation) being fixed.

We note here that Eq. (2.1) is applicable to weak perturbations, i.e., with v_{ext} taken as a pseudopotential. In what follows, it will be used with the true Coulomb potential of the nuclei. It is easy to verify that this does not change the form of the results at large R , except for the values of the constants.

A. Change in pair interaction due to floating of electronic clouds off the ionic centers

With the ions at positions separated by the vector \mathbf{R} , let us now allow the (assumed spherical) blob of screening charge to float off ion 1 by an amount determined by the vector $\delta\mathbf{R}_1$. Similarly, the electron valence cloud round ion 2 floats off by amount $\delta\mathbf{R}_2$.

The change $\Delta\phi(R)$ in the pair potential $\phi(R)$ is then calculable, with Δn denoting the density displaced by one ion acting alone. With the notation that a circle (\circ) means integration through the whole of space, $\Delta\phi(R)$ can be written, with Z denoting the valence ($Z=1$ for Na and K, 2 for Be),

$$\Delta\phi(R) = -\frac{1}{2}Z \left[\frac{1}{|\mathbf{r} + \delta\mathbf{R}_2|} + \frac{1}{|\mathbf{r} + \mathbf{R} + \delta\mathbf{R}_2|} + \frac{1}{|\mathbf{r} - \mathbf{R} + \delta\mathbf{R}_1|} + \frac{1}{|\mathbf{r} + \delta\mathbf{R}_1|} - \frac{1}{|\mathbf{r}|} - \frac{1}{|\mathbf{r} + \mathbf{R}|} - \frac{1}{|\mathbf{r} - \mathbf{R}|} - \frac{1}{|\mathbf{r}|} \right] \circ \Delta n(r). \quad (2.2)$$

Recalling next that the "standard" pair interaction is

$$\phi(R) = \frac{Z^2}{R} - \frac{Z}{|\mathbf{r} - \mathbf{R}|} \circ \Delta n(r), \quad (2.3)$$

one can transform the expression (2.2) to read

$$2\Delta\phi(R) = \phi(|\mathbf{R} + \delta\mathbf{R}_2|) + \phi(|\mathbf{R} - \delta\mathbf{R}_1|) - 2\phi(R) - \frac{Z^2}{|\mathbf{R} + \delta\mathbf{R}_2|} - \frac{Z^2}{|\mathbf{R} - \delta\mathbf{R}_1|} + \frac{2Z^2}{R} + N(\delta\mathbf{R}_1) + N(\delta\mathbf{R}_2). \quad (2.4)$$

In Eq. (2.4), $N(\delta\mathbf{R})$ denotes the quantity

$$N(\delta\mathbf{R}) = -Z \left[\frac{1}{|\mathbf{r} + \delta\mathbf{R}|} - \frac{1}{\mathbf{r}} \right] \circ \Delta n(r). \quad (2.5)$$

B. Approximate treatment for small floating distances

In what follows, we shall now develop the above results in a form which will lead to the asymptotic behavior of $\Delta\phi(R)$: the change in the standard $\phi(R)$ due to the long-range polarization interaction. From Eq. (2.5), one can first write

$$N(\delta\mathbf{R}) = \frac{-Z}{\delta R} \int_0^{\delta R} \Delta n(x) 4\pi x^2 dx + Z \int_0^{\delta R} \Delta n(x) 4\pi x dx. \quad (2.6)$$

Assuming that $\Delta n(r)$ is almost constant and equal to $\Delta n(0)$ in the range $0 \rightarrow \delta R$, one readily obtains

$$N(\delta\mathbf{R}) = \frac{2\pi}{3} Z \Delta n(0) (\delta R)^2 \quad (2.7)$$

(see also the Appendix, where the cruder Thomas-Fermi

approximation is employed).

This is the point at which to return to Eq. (2.4) for $\Delta\phi(R)$. One can expand this equation in terms of $s = \delta R/R$ and θ , the angle between $\delta\mathbf{R}$ and \mathbf{R} for the first term on the right-hand side of Eq. (2.4). One can then develop such an expansion by noting that

$$\begin{aligned} \phi(|\mathbf{R} + \delta\mathbf{R}|) &= \phi(R) + \phi'_R [|\mathbf{R} + \delta\mathbf{R}| - R] \\ &+ \frac{\phi''_R}{2} [|\mathbf{R} + \delta\mathbf{R}| - R]^2 + \dots \end{aligned} \quad (2.8)$$

In terms of s and θ introduced above:

$$|\mathbf{R} + \delta\mathbf{R}| - R = R[s \cos\theta + \frac{1}{2}s^2(1 - \cos^2\theta) + O(s^3)] \quad (2.9)$$

and

$$(|\mathbf{R} + \delta\mathbf{R}| - R)^2 = R^2[s^2 \cos^2\theta + O(s^3)]. \quad (2.10)$$

We must stress here the considerable advantage that has been gained in replacing Δn in Eq. (2.2) by ϕ to reach Eq. (2.4). Since, as discussed in PM, at large R , ϕ decreases as $R^{-3} \cos(2k_f R + \alpha)$, all its derivatives fall off with distance as R^{-3} , and in particular ϕ' is negligible compared to Z^2/R^2 . Specifically, Eq. (2.4) becomes

$$\begin{aligned} 2\Delta\phi(R) &= R \left[\phi'_R + \frac{Z^2}{R^2} \right] [-s_1 \cos\theta_1 + \frac{1}{2}s_1^2(1 - \cos^2\theta_1)] \\ &+ \frac{R^2}{2} \left[\phi''_R - \frac{2Z^2}{R^3} \right] s_1^2 \cos^2\theta_1 + Ms_1^2 + O(s_1^3) \\ &+ (\text{similar expression in } s_2, -\cos\theta_2). \end{aligned} \quad (2.11)$$

Here, the quantity M follows from Eq. (2.7) as

$$M = \frac{2\pi}{3} Z \Delta n(0) R^2 \equiv mR^2. \quad (2.12)$$

It is now useful to define three quantities A , B , and C and to note, as we do this, their asymptotic forms as $R \rightarrow \infty$. The definitions adopted are

$$A = R \left[\phi'_R + \frac{Z^2}{R^2} \right]_{R \rightarrow \infty} \sim \frac{Z^2}{R}, \quad (2.13)$$

$$B = \frac{R^2}{2} \left[\phi''_R - \frac{2Z^2}{R^3} \right]_{R \rightarrow \infty} - \frac{A}{2} \sim -\frac{3Z^2}{2R}, \quad (2.14)$$

and

$$C = M + \frac{A}{2} \sim mR^2. \quad (2.15)$$

Returning to Eq. (2.11), one then finds

$$\begin{aligned} 2\Delta\phi(R) &= -As_1 \cos\theta_1 + Bs_1^2 \cos^2\theta_1 + Cs_1^2 \\ &+ (\text{similar terms with } s_1 \rightarrow s_2, \theta_1 \rightarrow \pi - \theta_2). \end{aligned} \quad (2.16)$$

Equation (2.16) is then the basic consequence of the "floating-valence-blobs" model to represent the long-range polarization interaction in simple liquid metals such as Na and K near freezing.

Of course, the above expression (2.16) is valid within that model, for given displacements of the screening charges from the ionic centers 1 and 2, described by the variables (s_i, θ_i) , $i = 1$ and 2. But to complete the calculation, one must determine these variations by a first-principles method.

III. LOWER BOUND TO THE CHANGE $\Delta\phi(R)$ IN THE PAIR INTERACTION

The major step still to be taken is to turn the form (2.16), which follows very generally for $\Delta\phi(R)$, the correction to the standard pair interaction $\phi(R)$ at large R , into an explicit asymptotic result for $\Delta\phi(R)$. We shall tackle this by determining the maximum correction that this floating-blobs model can make to the original pair potential $\phi(R)$. In order to find this lower bound to $\Delta\phi$, we must minimize Eq. (2.16) with respect to (s_i, θ_i) , $i = 1$ and 2. One is then led to the equations

$$As_1 \sin\theta_1 - 2Bs_1^2 \sin\theta_1 \cos\theta_1 = 0 \quad (3.1)$$

and

$$-A \cos\theta_1 + 2Bs_1 \cos^2\theta_1 + 2Cs_1 = 0. \quad (3.2)$$

To satisfy Eq. (3.1), one must take the solution $\sin\theta_1 = 0$. The other solution $s_1 \cos\theta_1 = A/2B$ is not physically acceptable because, at large R , using Eq. (2.13) and (2.14), $A/B \rightarrow \frac{2}{3}$ and thus is not small. With $\sin\theta_1 = 0$, one has

$$\cos\theta_1 \equiv \epsilon_1 = \pm 1 \quad (3.3)$$

and inserting this into Eq. (3.2) yields

$$-A\epsilon_1 + 2(B+C)s_1 = 0. \quad (3.4)$$

Inserting the asymptotic forms of A , B , and C from Eqs. (2.13)–(2.15), one finds

$$s_1 \equiv \frac{\delta R_1}{R} = \frac{\epsilon_1 Z^2}{2m} \frac{1}{R^3} \quad (3.5)$$

or

$$\delta R_1 \equiv \frac{\epsilon_1 Z^2}{2m} \frac{1}{R^2} \quad \text{for } \epsilon_1 = 1. \quad (3.6)$$

The plus sign in Eq. (3.3) follows because the magnitude δR_1 must be positive.

The expression in $(s_2, -\cos\theta_2)$ is exactly symmetric, so that one finds $\epsilon_2 = -1$. Hence, returning to Eq. (2.16) and inserting these results, together with the asymptotic forms for large R of A , B , and C , one is led to the final form of the lower bound:

$$\Delta\phi(R) = \frac{-A^2}{4(B+C)} \rightarrow \frac{-Z^4}{4m} \frac{1}{R^4}. \quad (3.7)$$

The displacements of the floating blobs of valence screening from the ionic centers are in opposite directions along the axis joining the ionic centers. The distance between the centers of the electronic charge is less than R .

It must be stressed that the inverse-fourth-power dependence on the interionic separation R given for the

change in the standard pair potential $\phi(R)$ in Eq. (3.7) does not behave like the London dispersion force. It is specifically a polarization interaction in a simple metallic medium such as liquid Na or K near freezing.

IV. POSSIBLE EXPERIMENTAL IMPLICATIONS OF INVERSE-FOURTH-POWER POLARIZATION INTERACTION

The first comment to make in relation to Eq. (3.7) is that it is qualitatively in accord with the differences between the diffraction potential for Na obtained by Reatto [4] and the density functional standard pair potential calculated by Perrot and March [1]. The lowering of the standard electron theory potential predicted in Eq. (3.7) qualitatively brings the two potentials together at large R . However, the asymptotic form (3.7) could not be expected to work inside some 4.5 Å, as the electron theory and diffraction potentials cross one another at just less than 4 Å.

The second point relating to Eq. (3.7) is that, guided by pseudopotential representations of $\phi(R)$, which yield most directly its Fourier transform $\tilde{\phi}(k)$, the leading asymptotic form

$$\phi(R) \propto \frac{\cos(2k_f R + \alpha)}{R^3} \quad (4.1)$$

leads to singularities at $k = 2k_f$ in $\tilde{\phi}(k)$. However, the correction $\Delta\phi(R)$ in Eq. (3.7) leads to $\Delta\tilde{\phi}(k)$ having a term proportional to k as $k \rightarrow 0$, i.e., the total Fourier transform now has two singular points: $k = 0$ and $k = 2k_f$, in contrast to the standard $\phi(R)$ in Eq. (4.1) for a sharp Fermi surface of diameter $2k_f$.

Such behavior in the Fourier transform of the effective potential is accessible to diffraction experiments on simple liquid metals through the Ornstein-Zernike direct correlation function $c(r)$. If $g(r)$ denotes the pair function, then the total correlation function $h(r) = g(r) - 1$ is related to $c(r)$ via the convolution equation

$$h(r) = c(r) + n_a \int c(r') h(r - r') dr', \quad (4.2)$$

where n_a is the atomic-number density. With the usual liquid structure factor $S(k)$ related to the Fourier transform $\tilde{h}(k)$ through

$$\tilde{h}(k) = S(k) - 1, \quad (4.3)$$

Eq. (4.2) can be solved for $\tilde{c}(k)$, the Fourier transform of $c(r)$, as

$$\tilde{c}(k) = \frac{S(k) - 1}{S(k)}. \quad (4.4)$$

Since $S(k = 0)$ is known from the fluctuation theory result

$$S(0) = n_a k_B T K_T, \quad (4.5)$$

where K_T is the isothermal compressibility, it follows from Eqs. (4.5) and (4.4) that $\tilde{c}(k = 0)$ is determined by thermodynamic measurements. Then it is widely accepted by workers in classical liquid-structure theory that, at sufficiently large r ,

$$c(r) \sim \frac{-\phi(r)}{k_B T}. \quad (4.6)$$

Hence one is led, since there is an inverse-fourth-power "tail" according to the bound (3.7) on the corrected pair potential, to the small-angle form of $\tilde{c}(k)$:

$$\tilde{c}(k) = \tilde{c}(k = 0) + c_1 k + c_2 k^2 + \dots \quad (4.7)$$

Equation (4.7), a consequence of the R^{-4} form in Eq. (3.7) for liquid metals, is crucially different from the small-angle scattering from the insulating liquid argon, where $c_1 = 0$ and the London dispersion force referred to in Sec. I introduces a term $c_3 k^3$ into Eq. (4.7). This term is verified to be present from the neutron diffraction measurements on liquid argon near the triple point by Yarnell *et al.* [8]. The magnitude of c_3 can be obtained in terms of the London dispersion coefficient C_6 , and theory and experiment agree well for argon.

While there are indications [9] from the x-ray experiments of Greenfield, Wellendorf, and Wisner [3] that there is a k term in the expansion of $\tilde{c}(k)$ at small k as in Eq. (4.7), very careful small-angle scattering experiments will be required before contact can be made with the magnitude of the R^{-4} term given in Eq. (3.7). It does, however, depend explicitly on Z^4 , so that a comparison of a trivalent liquid metal such as Al with monovalent Na might be useful experimentally.

V. SUMMARY AND PROPOSALS FOR FURTHER WORK

The lower bound (3.7) to the polarization interaction between screened ions in simple liquid metals such as Na and K falls off according to the floating-blobs model like the inverse fourth power of the interionic separation. Though the calculation of the coefficient of this R^{-4} interaction energy is from a lower-bound result, it does suggest a strong dependence on valence Z .

Already, such a term does tend to lessen the (already modest) discrepancy at large R between diffraction and electron theory standard pair potentials for liquid Na. However, it is pointed out that a direct test of the presence of an R^{-4} interaction at large R is possible by studying the small-angle scattering of neutrons from liquid Na or K, and Dr. M. W. Johnson of the Rutherford Laboratory, U.K., is currently assessing the feasibility of such an experiment. The aim would be to measure the liquid-structure factor $S(k)$ down to very small k , and then to construct the Ornstein-Zernike function $\tilde{c}(k)$ from Eq. (4.4). The question to be answered then is whether the small-angle scattering can be explained by the expansion (4.7) with $c_1 \neq 0$. The magnitude of c_1 is directly connected with the magnitude of the R^{-4} polarization interaction in Eq. (3.7) through the asymptotic relation (4.5), which is valid in classical liquids provided one is far from the critical point.

Harker [10] has raised the question as to whether such a polarization interaction might also be accessible to experiment via phonon dispersion relations in a Na or K metallic crystal. In this context, it is highly relevant that recent studies of the phonon-dispersion relations in hot

crystals, i.e., near the melting point, have expressed these dispersion relations in terms of the direct correlation function $c(r)$ in the liquid at melting [11,12]. The result may be written

$$\omega_q^2 = \frac{n_a}{m} \sum_{\mathbf{K}} \left\{ \left[\frac{\mathbf{q} \cdot \mathbf{q} + \mathbf{K}}{q} \right]^2 \bar{\phi}(\mathbf{q} + \mathbf{K}) - \left[\frac{\mathbf{q} - \mathbf{K}}{q} \right]^2 \bar{\phi}^2(\mathbf{K}) \right\}, \quad (5.1)$$

where the \mathbf{K} 's denote reciprocal lattice vectors, provided (i) the low-temperature result quoted in Eq. (5.1) has a Debye-Waller factor incorporated following Ferconi and Tosi [11] and (ii) the Fourier transform $\bar{\phi}(k)$ of the pair interaction is replaced by

$$-\bar{\phi}(k) \rightarrow (k_B T c(k))_{T=T_m}, \quad (5.2)$$

where T_m is the melting temperature. We emphasize below the hot crystal because of the link (5.2) to the direct correlation function in the liquid metal at freezing. Of course, the phonons in the cold crystal will also reflect any polarization interaction in the long-wavelength limit. Since, with polarization interaction as in Eq. (3.7), $\bar{c}(k)$ has the small k expansion (4.7), we must expect from Eq. (5.1) that, at least in principle, $c_1 \neq 0$ will be reflected in the phonon dispersion ω_q in Eq. (5.1) when the replacement (5.2) is made. However, until a decisive theoretical prediction (or liquid diffraction measurement) of c_1 in Eq. (4.7), or equivalently of the coefficient of R^{-4} in Eq. (3.7), can be made, which may well require transcending the floating-blobs model employed throughout this paper (see Sec. I) no quantitative assessment will be possible of the effect of polarization interaction on the phonons.

In a different area, the work in Refs. [13] and [14] cited in the Appendix prompts us to add that the long-range polarization effect predicted in the present investigation may also have relevance to the interaction between charged defects in simple metals (e.g., a divacancy).

ACKNOWLEDGMENTS

We are deeply indebted to Dr. F. Perrot for his invaluable help and advice at every stage of this investigation. One of us (M.B.) has been supported by the ICI Soros Fund during his stay in Oxford. N.H.M. wishes to thank Dr. A. Harker and his colleagues in the Theoretical Stud-

ies Department, AEA Industrial Tech. Harwell, for much support and numerous valuable discussions.

APPENDIX: THOMAS-FERMI ENERGY FUNCTIONAL AND LINEARIZED DISPLACED CHARGE

To investigate the dependence of the results of the main text on the form of the energy functional, we have extended the treatment of March and co-workers [13,14] within the Thomas-Fermi approximation. These workers expanded the Thomas-Fermi kinetic energy to second order in the displaced charge, when measured from the unperturbed homogeneous electron gas, as in the main text. Within this framework, we have also used the floating-blobs model to repeat the calculation of the correction to the pair interaction, which in the Thomas-Fermi linearized approximation is $\phi(R) = [(Ze)^2/R] \exp(-qR)$, with q the inverse Thomas-Fermi screening length [see Eq. (A1) below]. We have studied the energy as a function of the amount of floating δR from the ionic centers, and have performed numerical calculations which show that there is no minimum for $\Delta\phi$, except at $\delta R = 0$. These calculations have also been repeated using the next-highest-order approximation in the displaced charge in the kinetic energy, with the same conclusion.

Looked at in a manner entirely paralleling the approach in the main text, one can use alternatively the linearized Thomas-Fermi approximation for the displaced charge, namely,

$$\Delta n = \frac{K}{r} \exp(-qr), \quad (A1)$$

$$q^2 = \frac{4k_f}{\pi a_0} \quad \text{where } a_0 = \frac{\hbar^2}{me^2}.$$

Then the contribution (2.5) of the text can be readily evaluated and the central point is that, because of the semiclassical form (A1), the quantity $N(\delta R)$ now has a term linear in δR and a quadratic term with a negative coefficient. The conclusion is again the same as in the calculation outlined immediately above; there is no minimum in $\Delta\phi$ except at $\delta R = 0$. So one concludes that the polarization interaction in the text only follows provided a refined density-functional theory is used which transcends the semiclassical approximations inherent in the Thomas-Fermi theory.

- [1] F. Perrot and N. H. March, Phys. Rev. A **41**, 4521 (1990).
- [2] F. Perrot and N. H. March, Phys. Rev. A **42**, 4884 (1990).
- [3] A. J. Greenfield, J. Wellendorf, and N. Wiser, Phys. Rev. A **4**, 1607 (1971).
- [4] L. Reatto, Philos. Mag. A **58**, 37 (1988).
- [5] A. C. Maggs and N. W. Ashcroft, Phys. Rev. Lett. **59**, 113 (1987).
- [6] E. F. Gurney and J. L. Magee, J. Chem. Phys. **18**, 142 (1950).
- [7] S. A. Egorov and N. H. March, Phys. Lett. A **157**, 57 (1991).
- [8] J. L. Yarnell, M. J. Katz, R. G. Wenzel, and S. H. Koenig,

- Phys. Rev. A **7**, 2130 (1973).
- [9] C. C. Matthai and N. H. March, Phys. Chem. Liq. **11**, 207 (1982).
- [10] A. H. Harker (private communication).
- [11] M. Ferconi and M. P. Tosi, Europhys. Lett. **14**, 797 (1991).
- [12] N. H. March and B. V. Paranjape, Phys. Chem. Liq. **24**, 223 (1992).
- [13] L. C. R. Alfred and N. H. March, Philos. Mag. **2**, 985 (1957).
- [14] G. K. Corless and N. H. March, Philos. Mag. **6**, 1285 (1961).