

## Electronic Fluctuation and Cohesion in Metals

A. C. Maggs and N. W. Ashcroft

Laboratory of Atomic and Solid State Physics and Materials Science Center, Cornell University, Ithaca, New York 14853

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This Letter is concerned with effective interatomic potentials in metals specifically arising from electronic quantum fluctuations. The cohesive energy is shown to contain large terms arising from generalized dispersion forces. Further, the density-density response function of the *homogeneous* electron gas is shown to contain a part decaying monotonically as  $1/r^6$  in real space; this has consequences in the construction of generalized functional theories of interatomic potentials.

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The theory of interatomic potentials and cohesion in noble metals is normally treated in a self-consistent band picture, either numerically or by use of a tractable analytic approximation.<sup>1-3</sup> But it is also possible to take an entirely different viewpoint in treating the *d* electrons, namely to regard them as localized atomic orbitals in the spirit of the tight-binding approximation, while continuing to treat the *s-p* electrons with nearly-free-electron theory. The basic philosophy of the method is to incorporate the many-body nature of the interaction of the core states *from the very beginning*, rather than using correlation and exchange corrections to the single-particle band energy as is usual in most approaches. In this picture, our conclusion will be that many of the cohesive properties of noble metals are directly linked to fluctuation effects analogous to those important in the binding of *insulating* molecular crystals. Band-structure calculations are based on the construction of a static mean field; in contrast, we are able to isolate effects that are directly attributable to dynamical correlations.

As its first major point, this Letter proposes a new method of looking at the origin of metallic potentials in metals whose ions are highly polarizable. The calculations presented are based on diagrammatic perturbation theory of the electron gas; the terms that will be discussed are shown in sequence in Fig. (1). Some of these are familiar in the context of standard linear-response theory. However, perhaps the key point we wish to make is that many other of the effects treated here involve the *nonlinear response* of the homogeneous electron gas. This is because the dynamical effects we consider *first* appear at this order in perturbation theory. We shall therefore conclude that it is insufficient to use linear response in metals in which core polarization is important.

The second major point of this Letter is that we have identified large contributions to the potentials whose origin is in certain diagrams for the free, interacting electron gas which have been overlooked in the consideration of the *linear response* of homogeneous systems. These terms have implications for the functional methods used in numerical calculations, and they lead to the possibility

of recovering van der Waals forces in *nonlocal* functional theories of the electron gas.

To set the context of the treatment that follows recall that cohesion in a molecular crystal, such as argon, is dominated by dispersion forces that are dynamical in origin. The ions of a metal with polarizable cores can be described in a very similar manner. Even in noble metals, in spite of the hybridization between bands, the optical properties are reasonably well described by first separating the electrons into polarizable core states embedded in a quasifree-electron gas.<sup>4-6</sup> The modification of the optical properties resulting from the interaction between the two sets of electrons has an exact parallel in the theory of cohesion. Thus in silver the plasmon has an energy considerably below the free-electron predic-

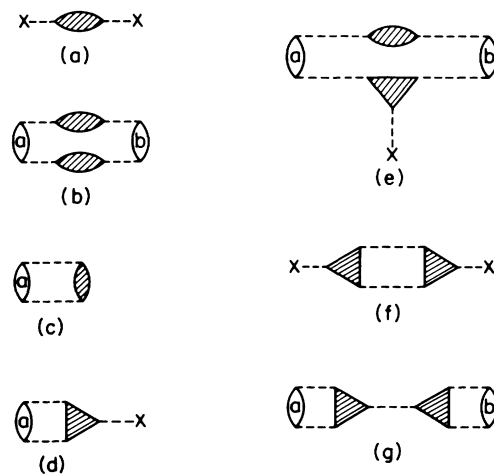


FIG. 1. (a) The usual screened Coulomb interaction between ions. (b) A term contributing to a dynamically screened van der Waals interaction. (c) The coupled dipole-plasmon mode. (d) The dipole-plasmon mode coupled to a local inhomogeneity. (e) Change in the van der Waals energy arising from inhomogeneity. (f) Fluctuation-derived interaction between two pseudoatoms. (g) A new electrostatic mechanism for the interaction of pseudoatoms.

tion, showing that there is a lowering of the collective zero-point energy of the electron system, given by Eq. (4). With these general observations as a guide, we may take as a model for the noble metals a system of core (i.e.,  $d$ ) electrons which are treated in a dipole approximation and an initially homogeneous interacting electron gas to model the valence ( $s$ - $p$ ) electrons. The corresponding Hamiltonian is then

$$H = \sum_i \frac{p_i^2}{2m} + \sum_l \int V_l(\mathbf{r}) \hat{n}_e(\mathbf{r}) d^3r + \int \int \hat{n}_e(\mathbf{r}) \frac{1}{|\mathbf{r}-\mathbf{r}'|} \hat{n}_e(\mathbf{r}') d^3r d^3r' \\ + \sum_l \int \int [\mathbf{d}_l(\mathbf{r}) \cdot \nabla_r] \frac{1}{|\mathbf{r}-\mathbf{r}'|} \hat{n}_e(\mathbf{r}') d^3r d^3r' + \sum_{l \neq k} \int \int [\mathbf{d}_l(\mathbf{r}) \cdot \nabla_r] [\mathbf{d}_k(\mathbf{r}') \cdot \nabla_{r'}] \frac{1}{|\mathbf{r}-\mathbf{r}'|} d^3r d^3r', \quad (1)$$

where  $V_l$  is the ionic pseudopotential and  $\mathbf{d}_l$  the dipole operator for the  $l$ th core;  $\hat{n}_e$  is the valence-charge-density operator. To study the properties of the Hamiltonian (1) we use standard time-ordered perturbation theory in the Goldstone formulation.<sup>7,8</sup> The results are most conveniently summarized in diagrams with use of the conventional rules. We shall give all results in atomic units. The simplest diagram leading to a contribution to the effective potentials is Fig. 1(a)<sup>9</sup>; it is the well-known screened Coulomb interaction between pseudoatoms by which we mean the ion together with the surrounding, induced free-electron cloud. Figure 1(b), on the other hand, corresponds to van der Waals interactions between the core electrons which are here screened by the intervening electron gas. The contribution to the energy of a pair of atoms separated by  $\mathbf{r}$  is

$$E_b(\mathbf{r}) = \int_0^\infty \frac{d\omega}{2\pi} \int \frac{d^3q}{(2\pi)^3} \int \frac{d^3q'}{(2\pi)^3} \alpha^2(i\omega) (\mathbf{q} \cdot \mathbf{q}')^2 \frac{4\pi}{q^2} \frac{4\pi}{q'^2} \frac{1}{\epsilon(\mathbf{q}, i\omega)} \frac{1}{\epsilon(\mathbf{q}', i\omega)} e^{i(\mathbf{q}+\mathbf{q}') \cdot \mathbf{r}}. \quad (2)$$

Note that the core density-density response function for diagram 1(b) is given by

$$\alpha(\omega) \mathbf{q} \cdot \mathbf{q}', \quad (3)$$

where  $\alpha(\omega)$  is the frequency-dependent core polarizability. In (2),  $\epsilon(\mathbf{q}, \omega)$  is the dielectric function for the homogeneous electron gas. With  $\alpha(\omega)$  extracted from optical measurements, Eq. (2) is easily evaluated and contributes typically 40 meV to the interaction energy of a nearest-neighbor pair in a noble metal.

The contribution summarized by (2) has been considered by a number of authors.<sup>7,8</sup> It is large because the internal Coulomb lines in the loop of Fig. 1(b) are integrated over frequency; thus we are led to consider the screening of *dynamical effects* in an electron gas. Most importantly, at finite frequencies, the perfect screening sum rule  $\lim_{q \rightarrow 0} \epsilon^{-1}(\mathbf{q}, 0) = 0$  no longer holds. In fact, to a good approximation the internal lines can be replaced with the simplified expression  $4\pi\omega^2/q^2(\omega^2 + \omega_p^2)$ , with  $\omega_p$  the plasma frequency of the electron gas. The simplest model is then to assume that the core fluctuations are dominated by a single excited state with energy  $\Delta$ , for which  $\alpha(\omega) = \alpha(0)\Delta^2/(\Delta^2 - \omega^2)$ . The integrals over  $\omega$  are then straightforward, and we find an approximate formula for the screened van der Waals interactions in a polarizable metal,

$$E_b(\mathbf{r}) = \frac{3\Delta}{4} \frac{\alpha^2(0)}{r^6} \left( \frac{\Delta}{\Delta + \omega_p} \right)^3.$$

The usual van der Waals result for an insulator follows on substitution of  $\omega_p = 0$ . The approximation of a single characteristic excitation of energy  $\Delta$  is certainly not adequate for a noble metal since excitations to a continuum in the range 5–50 eV are important, but the result demonstrates an essential qualitative point, namely that

dispersion forces keep their usual asymptotic form even in the presence of dynamic screening by an electron gas.

Fluctuation or zero-point contributions give a large contribution to the total cohesive energy of a noble metal. In the language appropriate to metallic systems, this is a one-body potential; it can be regarded as a coupling of the zero-point motions of the dipole oscillators with the plasma oscillations of the free-electron gas. In the same way that the instantaneous polarization field of a dipole can polarize a second dipole, thereby lowering the total energy of the atoms, so also it is possible for a dipolar fluctuation to polarize the surrounding electron gas and lower the joint energy. Diagrammatically this is shown in Fig. 1(c); analytically we find that the mechanism contributes

$$E_c = 4\pi \int_0^\infty \frac{d\omega}{2\pi} \int \frac{d^3q}{(2\pi)^3} \chi(\mathbf{q}, i\omega) \alpha(i\omega) \frac{4\pi}{q^2} \quad (4)$$

to the energy. Here  $\chi$  is the density-density response function of the homogeneous electron gas. Numerical calculations show that typically 3 eV of the total cohesive energy of a noble metal is contributed by this mechanism, though the exact answer obtained is *strongly* dependent on the large- $q$  behavior of the electron response function, and any assumed form factor for the coupling of the free-electron gas and dipoles. This energy is correlation energy and in the band approach is included in the construction of the self-consistent one-particle potential. The picture, just described, of coupled dipole-plasmon modes gives a simple intuitive explanation of this effect.

We now consider Fig. 1(d) which expresses the coupling of the dipolar fluctuations of the core electrons to the local change in the plasmon properties associated

with an inhomogeneity. The process involves the nonlinear, frequency-dependent response of the electron gas. Note that we have neglected variations of the atomic polarizability with density, which should be of less importance than the change in properties of the free-electron gas, but variations in  $\alpha(\omega)$  can be included in principle. Figure 1(d) is then given analytically by

$$E_d(\mathbf{r}) = \int_0^\infty \frac{d\omega}{2\pi} \int \frac{d^3q}{(2\pi)^3} \int \frac{d^3q'}{(2\pi)^3} \mathbf{q} \cdot \mathbf{q}' \alpha(i\omega) \Gamma^{(3)}(\mathbf{q}, i\omega; \mathbf{q}', -i\omega; -\mathbf{q} - \mathbf{q}', 0) \frac{4\pi}{q^2} \frac{4\pi}{q'^2} V_{\text{ion}}(\mathbf{q} + \mathbf{q}') e^{i(\mathbf{q} + \mathbf{q}') \cdot \mathbf{r}}, \quad (5)$$

where  $\Gamma^{(3)}$  is the three-point function of the electron gas and  $V_{\text{ion}}(\mathbf{q})$  the Fourier transform of the ionic pseudopotential. We can write  $\Gamma^{(3)}$  in terms of the irreducible three-point function,  $\Lambda^{(3)}$ . The convention that we used for  $\Lambda^{(3)}$  is such that

$$\Lambda^{(3)}(\mathbf{q}, \omega; -\mathbf{q}, -\omega; 0, 0) = d\chi^0(\mathbf{q}, \omega)/d\mu,$$

where  $\mu$  is the chemical potential. For the present illustrative purposes,  $\Lambda^{(3)}$  is adequately given by its random-phase-approximation value, and is written down with well-known diagrammatic methods. We see that the internal Coulomb lines of the diagram are again incompletely screened so that the asymptotic behavior of this contribution to the pair potential is  $1/r^6$ , the familiar van der Waals form. Numerically we find that this term contributes 20 meV to the pair potential of a noble metal at nearest-neighbor spacings.

The dynamic three-point function of the electron gas has an important *dual* role: First, in Eq. (5) it is directly related to the polarizability of the screening cloud induced by the ionic charge, that is, it contains the pseudoatom polarization operator. This arises because in the

limit of small  $q$  and  $q'$  with  $\omega$  finite  $\Lambda^{(3)}$  contains a term proportional to  $\mathbf{q} \cdot \mathbf{q}'/\omega^2$  which should be compared directly with the core density-density response function, Eq. (3). In many ways the screening electrons induced in the vicinity of the ion core behave *exactly* like the bound charges but with the characteristic excitation energy,  $\Delta$ , set equal to zero. The other role of  $\Lambda^{(3)}$  is to change the properties of the *collective* modes such as the plasmon in regions of inhomogeneity. Both functions are displayed in Fig. 1(e) which contains contributions to both the two- and three-body potentials; in a region of changed local density and lower symmetry the different scalings of the pair and three-center potentials with separation, and the angular dependence of the three-center potentials, mean that we expect this diagram to be qualitatively important for the structure of defects and grain boundaries. Because of the behavior of  $\Lambda^3$ , the three-center interactions asymptotically have the Axilrod-Teller form.

We can go further and also consider the interaction of the fluctuations of two pseudoatoms. This is the content of Fig. 1(f). Analytically it gives

$$E_f(\mathbf{r}) = \int_0^\infty \frac{d\omega}{2\pi} \int \frac{d^3q}{(2\pi)^3} \int \frac{d^3q'}{(2\pi)^3} V_{\text{ion}}^2(\mathbf{q}) \frac{4\pi}{q^2} \frac{4\pi}{(q + q')^2} [\Lambda^{(3)}(\mathbf{q} + \mathbf{q}', i\omega; \mathbf{q}', -i\omega; -\mathbf{q}, 0)]^2 e^{i\mathbf{r} \cdot \mathbf{q}} \times \frac{1}{\epsilon^2(\mathbf{q}, 0)} \frac{1}{\epsilon(\mathbf{q} + \mathbf{q}', i\omega)} \frac{1}{\epsilon(\mathbf{q}', i\omega)}. \quad (6)$$

We note that this term is also present in the exact density-density correlation function of the homogeneous electron gas and so is in principle included in Fig. 1(a); most theories of the response of the homogeneous electron gas do *not* consider such a term and so we have explicitly excerpted it for further consideration. If we extract the long-range part of the figure by using an asymptotic expansion in real space, we find a contribution to the effective pair potential of

$$E_f(r) = 3z^2/16\omega_p^3 r^6,$$

with  $z$  the number of valence electrons per atom. It has been pointed out<sup>10</sup> that the large- $|\mathbf{q}'|$  part of this expression is divergent and must be taken with other related but short-range diagrams to obtain the full real-space behavior. Another interpretation of this diagram is that it is the sum of the correlation ring diagrams of a free, *inhomogeneous* electron gas with the wave functions corrected to second order in the external potential. We again note that the diagram contains the important feature of an internal dynamic loop and hence incom-

pletely screened interactions. This is why the term is large even though the diagram is formally of high order.

Finally we consider the possible implications of this viewpoint for fully numerical studies of interatomic potentials. Higher-order corrections to the polarization of the homogeneous electron gas, such as are implied by Eq. (6), are often expressed in terms of the local-field correction which contains information on terms beyond the usual random-phase-approximation response function. From the considerations above, it can be shown that part of the local-field corrections have a *monotone* power-law decay in real space, and this has a direct bearing on in functional theories of the inhomogeneous electron gas based on the response functions of homogeneous systems and in addition for effective electron-electron interactions.<sup>11</sup> In a nonlocal, weighted-density approach it should be possible to recover at least part of the full van der Waals interaction normally attributed to closed-shell atoms; the local-field correction is directly related to the weighting function used in such theories.<sup>12</sup> In systems

with open shells, such as transition metals, we would expect these nonlocal terms to give a large contribution to the interatomic potentials.

As a final mechanism for consideration in polarizable metals we consider Fig. 1(g), which has the following physical interpretation: The coupling between the core electrons and the valence electrons is strongly attractive, and valence electrons are drawn in around the ion. The charge excesses now based at each ion then interact via the usual static, screened Coulomb interaction. Through this figure we again see the tendency of the dipole-electron-gas coupling to increase the density of the system.

To summarize, we have shown that instead of the usual static response mechanisms found to be important in theories of potentials in simple metals, it is possible to view the potentials in noble metals as dominated by generalized dispersion forces which are dynamic in origin. To account fully for the coupling of the electrostatics and the dynamics of the system it is natural to introduce the dynamic nonlinear response functions of the electron gas. These comments apply equally to any simple metal which has a highly polarizable core, but whose core electrons may be well separated from the  $s$ - $p$  band.

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