

## van der Waals forces in the noble metals\*

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The van der Waals (or polarization) force between ions in the noble metals is calculated within a simplified model in which the ions are regarded as nonoverlapping and immersed in a uniform electron gas. The conduction-electron screening of the ion-ion interactions is straightforwardly taken into account. Using effective ionic polarizabilities derived from the measured optical constants, we find that the contribution of the polarization forces to the cohesive energy per atom is 0.21, 0.42, and 0.63 eV for Cu, Ag, and Au, respectively. By comparison, the total cohesive energies in these metals are 3.50, 2.96, and 3.78 eV, respectively.

### I. INTRODUCTION

It has long been recognized that the attractive van der Waals forces between ions in a metal contribute to the total cohesive energy.<sup>1</sup> However, the magnitude and relative importance of this contribution has remained an unresolved question. For the noble metals, the estimates have ranged from being of negligible importance<sup>2</sup> to contributing roughly a third<sup>3</sup> of the total cohesive energy, which is typically 3 to 4 eV.<sup>4</sup> This large variation reflects discrepancies in the estimates of the ionic polarizabilities and differences in the calculation of the conduction-electron screening of the polarization forces.

In an attempt to resolve this issue, we have estimated the magnitude of these polarization forces by a perturbation-theory calculation in a simplified model in which the ions are regarded as nonoverlapping and imbedded in a uniform electron gas. While the use of this model is of course much too crude<sup>5</sup> to determine other contributions to the cohesive energy, it should be appropriate for the calculation of the polarization forces between the ions.

We obtain an expression for the dipole-dipole contribution to the polarization force which is analogous to the usual expression<sup>5</sup> for the van der Waals interaction between atoms or molecules. This interaction depends explicitly on the frequency-dependent polarizability of the ions  $\alpha_{\text{ion}}(\omega)$  which is determined phenomenologically from the observed optical constants.<sup>6</sup> Local-field effects, which we find to be important in these calculations, are taken into account using an appropriate modification of the Lorentz-Lorenz formula.<sup>7</sup>

The presence of the electron gas gives rise to a dynamically screened interaction between the ions. This screening is given in terms of the dielectric function of the electron gas  $\epsilon(q, \omega)$  which, in our calculations, is approximated by the random-phase approximation (RPA) expres-

sion evaluated for the value of  $r_s$  corresponding to the "free-electron" densities in the noble metals.

Our calculations give for the dipole-dipole contribution to the cohesive energy 0.18, 0.35, and 0.52 eV, for Cu, Ag, and Au, respectively; higher-order polarization forces are estimated to increase these figures by roughly 20%.

A description of the model and a summary of the theoretical results are given in Sec. II. These results are applied to the noble metals in Sec. III. Details of the theoretical development are contained in an Appendix.

### II. SCREENED VAN DER WAALS INTERACTION

Let us consider the interaction between two ions,  $a$  and  $b$ , a distance  $R$  apart, immersed in a uniform electron gas of density  $n = 4\pi/3r_s^3$ . We assume that  $R$  is large enough that the ionic charge distributions are nonoverlapping and spherically symmetric. The Hamiltonian of the system consists of two parts,<sup>8</sup>

$$\mathcal{H} = \mathcal{H}_0 + \mathcal{H}_1. \quad (1)$$

The unperturbed part,  $\mathcal{H}_0$ , includes three terms: the Hamiltonian for a noninteracting electron gas and two effective one-electron Hamiltonians<sup>9</sup> which respectively describe each of the ions in the metal,

$$\mathcal{H}_0 = \mathcal{H}_e + \mathcal{H}_a + \mathcal{H}_b. \quad (2)$$

The perturbation  $\mathcal{H}_1$  consists of the Coulomb interaction between the charge distributions of the ions and the electron gas,

$$\begin{aligned} \mathcal{H}_1 &= \mathcal{H}_{ab} + \mathcal{H}_{ae} + \mathcal{H}_{be} + \mathcal{H}_{ee} \\ &= \int \frac{d\vec{q}}{(2\pi)^3} v(q) (\rho_a^a \rho_{-\vec{q}}^b + \rho_a^a \rho_{-\vec{q}}^e \\ &\quad + \rho_a^b \rho_{-\vec{q}}^e + \rho_a^e \rho_{-\vec{q}}^e). \end{aligned} \quad (3)$$

Here  $\rho_{\vec{q}}^j$  ( $j = a, b, e$ ) are the appropriate density fluctuation operators, and  $v(q) \equiv 4\pi/q^2$  is the Coulomb interaction (we use atomic units,  $e = \hbar = m = 1$ ).

We now calculate the net interaction between the ions in perturbation theory, treating the interactions between the ions and the electron gas and between the ions themselves to lowest nonvanishing order, while keeping the electron-electron interactions to all orders. The details of this perturbation expansion are given in the Appendix; here we merely summarize the results.

First, the electron-electron interactions, when summed, give rise to a frequency-dependent screened interaction of the form

$$V(q, \omega) = v(q)/\epsilon(q, \omega), \quad (4)$$

where  $\epsilon(q, \omega)$  is the electron-gas dielectric function. In terms of this effective potential, the polarization interaction between the ions is given by the expression

$$U(R) = - \int_0^\infty \frac{d\omega}{2\pi} \int \frac{d\vec{q}}{(2\pi)^3} \frac{d\vec{q}'}{(2\pi)^3} \mathcal{D}^a(\vec{q}, \vec{q}', i\omega) \times V(\vec{q}', i\omega) \mathcal{D}^b(\vec{q}', \vec{q}, i\omega) V(\vec{q}, i\omega), \quad (5)$$

where we have chosen to evaluate the frequency integral over the positive imaginary frequency axis  $\omega = i\omega$ , and  $\mathcal{D}^j(\vec{q}, \vec{q}', i\omega)$  is the continuation to complex frequencies of the Fourier transform of the density-density correlation function

$$\mathcal{D}^j(\vec{q}, \vec{q}', t) = -i \langle 0 | T \rho_{\vec{q}}^j(t) \rho_{\vec{q}'}^j(0) | 0 \rangle, \quad j = a, b. \quad (6)$$

In this expression, the state  $|0\rangle$  indicates the ground state of the ion with Hamiltonian  $\mathcal{H}_j$ . With the assumption of spherically symmetric ions, we find that  $\mathcal{D}^j(\vec{q}, \vec{q}', i\omega)$  to leading order in  $\vec{q}$  and  $\vec{q}'$  is proportional to the ionic polarizability  $\alpha^j(i\omega)$

$$\mathcal{D}^j(\vec{q}, \vec{q}', i\omega) \cong -\vec{q} \cdot \vec{q}' e^{i(\vec{q}-\vec{q}') \cdot \vec{R}_j} \alpha^j(i\omega), \quad (7)$$

where

$$\alpha^j(i\omega) \equiv \frac{2}{3} \sum_n^j \frac{E_{n0} |\langle 0 | \vec{r} | n \rangle|^2}{E_{n0}^2 + \omega^2}, \quad (8)$$

and  $E_{n0}$  is the excitation energy of state  $|n\rangle$ . On using the approximation (7) in Eq. (5), we can write the dipole-dipole contribution to the polarization forces between the ions as follows:

$$U_{\text{dip-dip}}(R) = - \int_0^\infty \frac{d\omega}{2\pi} \alpha^a(i\omega) \alpha^b(i\omega) \times \left[ \left( \frac{\partial^2 V(R, i\omega)}{\partial R^2} \right) + \frac{2}{R^2} \left( \frac{\partial V(R, i\omega)}{\partial R} \right)^2 \right]. \quad (9)$$

Here,  $V(R, i\omega)$  is the screened Coulomb interaction at the separation  $R$  and complex frequency  $i\omega$ ,

$$V(R, i\omega) = \int \frac{d\vec{q}}{(2\pi)^3} \frac{4\pi}{q^2} \frac{e^{i\vec{q} \cdot \vec{R}}}{\epsilon(q, i\omega)} = \frac{2}{\pi} \int_0^\infty dq \frac{\sin qR}{qR} \frac{1}{\epsilon(q, i\omega)}. \quad (10)$$

Note that in the limit that  $\epsilon \rightarrow 1$ , i.e., for a very dilute electron gas or for frequencies much larger than the plasma frequency, the bracketed quantity in Eq. (9) is equal to  $6/R^6$ , in which case the expression for  $U_{\text{dip-dip}}(R)$  reduces to the usual expression<sup>5</sup> for the van der Waals interaction between atoms or molecules. The screening at the lower frequencies is important, however, and reduces the magnitude of the ion-ion interaction considerably.

### III. RESULTS AND DISCUSSION

The essential ingredients which are required in the evaluation of the dipole-dipole contribution to the van der Waals interaction (9) between the ion cores are: (i) the screened Coulomb interaction in Eq. (10), and (ii) the frequency dependent polarizabilities of the ions. The screened Coulomb interaction, together with its first and second derivatives with respect to  $R$ , was evaluated numerically using the RPA dielectric function. This potential is reproduced in Fig. 1 for representative values of the frequency  $\omega$ . As one would expect, the screening is most effective for frequencies less than the plasma frequency.

The oscillator strengths defining the effective

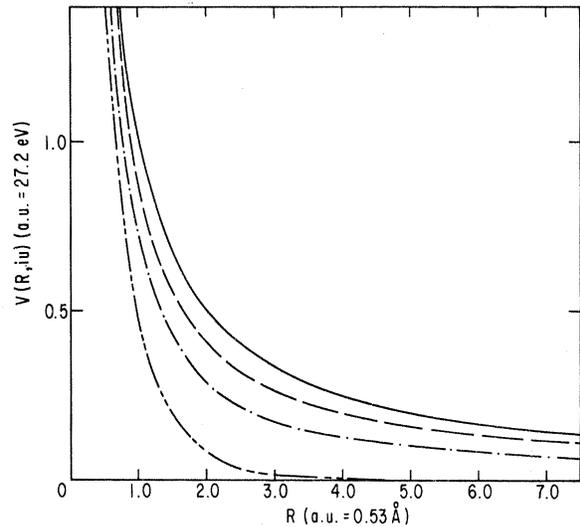


FIG. 1. Screened potential  $V(R, i\omega)$  in Au ( $u=0$ , long-dash-short-dash line;  $u=\omega_p$ , dot-dash line;  $u=2\omega_p$ , dash line;  $u=\infty$ , solid line). Here  $\omega_p^2 = 3/r_s^3$  with  $r_s = 3.01$ .

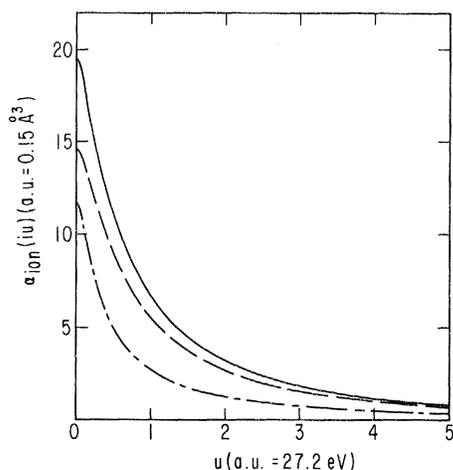


FIG. 2. Plot of the ionic polarizabilities in the noble metals as a function of the complex frequency  $\omega = iu$ . (Au, solid line; Ag, long-dash line; Cu, long-dash-short-dash line).

ionic polarizabilities used in the calculations were extracted from the optical data for the noble metals given in Ref. 5. Within the model being considered, the long-wavelength limit of the dielectric function of the metal can be expressed in terms of these ionic polarizabilities. Accounting for the local field at the position of the ions approximately by the Lorentz-Lorenz relation, one finds that the ionic polarizability is given by

$$\alpha_{\text{ion}}(iu) = \alpha(iu) / [1 + \frac{4}{3}\pi n \alpha(iu)], \quad (11)$$

where  $n$  is the number of ions per unit volume, and  $\alpha(iu)$  is obtained from the imaginary part of the observed dielectric function

$$\alpha(iu) = \frac{2}{\pi \omega_p^2} \int_0^\infty d\omega \frac{\omega \epsilon_2'(\omega)}{\omega^2 + u^2}. \quad (12)$$

Here  $\omega_p = (4\pi n)^{1/2}$ . The prime on  $\epsilon_2(\omega)$  signifies that the "free-electron" part of the dielectric function is subtracted. Since the core electrons in the noble metals are relatively well localized, Eqs. (11) and (12) should provide a good approxi-

mation to the effective ionic polarizability.

The subtraction of the "free-electron" contribution was performed by extrapolating the low-frequency part of  $\epsilon_2(\omega)$  past the onset of the  $d$ -electron transitions using a simple Drude formula. While this procedure is crude, the error incurred is negligible; the associated error in the oscillator strength is a small fraction of an electron, and furthermore, the ion-ion interaction at these low frequencies is highly screened.

The ionic polarizabilities obtained in this manner are plotted in Fig. 2. On going from Cu to Ag to Au, the increasing magnitude of the polarizability reflects the increasingly larger low-frequency oscillator strengths. A significant part of the low-frequency oscillator strengths is attributable to  $d$ -electron transitions; excitations of the lower core states make a rather small contribution to the static polarizabilities.

The total dipole-dipole interaction per atom is obtained by summing one half of the interaction (9) over all ion pairs. This sum is rapidly convergent; the results for the three nearest neighbors (nn) and the total dipole-dipole contribution ( $E_{\text{dip-dip}}$ ) are listed in Table I.

The importance of including the local-field correction is demonstrated by evaluating Eq. (9) with the uncorrected  $\alpha(iu)$  rather than the corrected  $\alpha_{\text{ion}}(iu)$  of Eq. (11). In this case, the calculated dipole-dipole interactions were typically twice as large as the results based on Eq. (11).

The conduction-electron screening of the ion-ion interactions was also found to be a significant effect. By setting  $\epsilon(q, iu) = 1$  in Eq. (10), the conduction-electron screening is neglected altogether; the resulting value for the integral in Eq. (9) is then about 2–3 times larger than the screened results listed in Table I. It should also be noted that at the relatively large ionic separations in the metals, only the small- $q$  behavior of the dielectric function is important in evaluating  $V(R, iu)$ . Thus the local approximation  $\epsilon(0, iu) = 1 + \omega_p^2/u^2$  gave values for the interaction which were typically only 10% smaller than those obtained with the full RPA dielectric function. This simple expression

TABLE I. Estimates of the van der Waals contribution to the cohesive energy of the noble metals.

|    | Contribution to cohesive energy from polarization forces (eV/atom) |        |        |                      |                                  | Experimental cohesive energy (Ref. 4) (eV/atom) |                           |
|----|--|--------|--------|----------------------|----------------------------------|---|---------------------------|
|    | Dipole-dipole energy   |        |        |                      | Higher-order polarization energy |   | Total polarization energy |
|    | 1st nn   | 2nd nn | 3rd nn | $E_{\text{dip-dip}}$ |                                  |   |                           |
| Cu | 0.151  | 0.009  | 0.010  | 0.179                | 0.036                            | 0.21  | 3.50                      |
| Ag | 0.289  | 0.018  | 0.021  | 0.347                | 0.069                            | 0.42  | 2.96                      |
| Au | 0.438  | 0.027  | 0.031  | 0.524                | 0.105                            | 0.63  | 3.78                      |

could therefore be used to obtain a good estimate of the effect of screening.

The total contribution to the cohesive energy from the polarization forces includes the dipole-quadrupole, quadrupole-quadrupole terms, etc., which arise on expanding  $\mathfrak{D}^i(\vec{q}, \vec{q}', i\omega)$  to higher orders in  $q$  and  $q'$ . These higher-order terms are also attractive, but are usually much smaller than the dipole-dipole term. The magnitude of these additional terms was estimated on the basis of the model calculation of Fontana<sup>10</sup> for the rare-gas atoms. At the equilibrium separation in the rare-gas solids, the higher-order terms are approximately 20% of the dominant dipole-dipole term. The importance of the ion-ion interactions in determining the elastic constants of the noble metals suggests that the ion cores in these metals are not far from a corresponding "equilibrium separation." We have therefore assumed that the higher-order terms make a contribution which is 20% of the dipole-dipole term, as indicated in Table I. (Screening of the higher-order terms is expected to be similar to that of the dipole-dipole term.) The magnitude of the repulsive three-body forces was also estimated using an appropriate generalization of the usual expression<sup>11</sup> to include conduction-electron screening. These forces can be thought of as representing the screening of the two-body van der Waals interaction by the surrounding ions. In this respect, they are analogous to the local-field corrections considered previously. Since their magnitude was found to be roughly 5% of the pair-wise interactions, their contribution to the cohesive energy was neglected.

Including the higher-order terms, the contribution of the polarization forces to the total cohesive energy is estimated to be 6%, 14%, and 17% in Cu, Ag, and Au, respectively.

#### APPENDIX

In this appendix we present some additional details in the derivation of Eq. (9). The analysis is based on a straightforward application of many-body perturbation theory<sup>12</sup> to the model introduced in Sec. II. The interaction energy between ions  $a$  and  $b$  is

$$U(R) = E(R) - E(\infty), \quad (\text{A1})$$

where  $E(R)$  is the ground-state energy of the system at separation  $R$ . Making use of the Feynman-Hellman theorem,  $E(R)$  is given by

$$\begin{aligned} E(R) &= E_0 + \int_0^1 d\lambda \langle \Psi_\lambda | \mathfrak{H}_1 | \Psi_\lambda \rangle \\ &= E_0 + \int_0^1 d\lambda \sum_{n=0}^{\infty} \frac{(-i)^n}{n!} \lambda^n \int_{-\infty}^{\infty} dt_1 \dots \end{aligned} \quad (\text{A2})$$

$$\times \int_{-\infty}^{\infty} dt_n \langle \Psi_0 | T \mathfrak{H}_1 \mathfrak{H}_1(t_1) \dots \mathfrak{H}_1(t_n) | \Psi_0 \rangle_c. \quad (\text{A3})$$

Here  $E_0$  is the energy of the noninteracting ground state  $\Psi_0$ ,  $T$  is the time-ordering operator, and the subscript  $c$  indicates that only connected graphs are to be summed. Of all possible connected graphs, only those containing *both* charge-density operators  $\rho^a$  and  $\rho^b$  contribute to  $U(R)$ , since the remaining ones are cancelled by  $E(\infty)$ . This restriction will be implicit in the following.

The  $n$ th-order contribution to (A3) is

$$\frac{(-i)^n}{(n+1)!} \int_{-\infty}^{\infty} dt_1 \dots dt_n \times \langle \Psi_0 | T \mathfrak{H}_1 \mathfrak{H}_1(t_1) \dots \mathfrak{H}_1(t_n) | \Psi_0 \rangle_c, \quad (\text{A4})$$

the  $\lambda$  integration having been done explicitly. When (3) is substituted for  $\mathfrak{H}_1$  in (A4), a large number of different terms is generated; a typical term will contain  $m_i$  factors of each component  $\mathfrak{H}_i$  with  $\sum_{i=1}^4 m_i = n+1$ . The permutation of the time arguments  $(t_1, \dots, t_n)$  among these factors gives  $n!$  equal contributions. There is, in general, an additional factor of  $(n+1)$  corresponding to the number of ways of positioning the external fixed point  $t=0$  on the graph. However, not all positions necessarily give distinct contributions, since identical contractions may arise. This possibility must be accounted for by multiplying the contribution of a given graph by an appropriate factor.

This counting problem is trivial when only the limited set of diagrams leading to (9) are retained. These diagrams correspond to keeping only the lowest-order interactions with ions  $a$  and  $b$  and only simple screening processes in the conduction-electron gas. A typical diagram is illustrated in Fig. 3(a); the shaded bubble represents an arbitrary polarization insertion and the appropriate factor to such a diagram is  $(n+1)!$ . Fig. 3(b) can

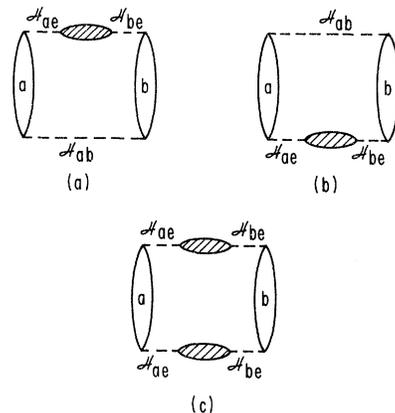


FIG. 3. Diagrams retained in the derivation of Eq. (9).

be included as a distinct contribution if the sum of Figs. 3(a) and 3(b) is divided by 2. Symmetric diagrams such as shown in Fig. 3(c) similarly have a weighting factor  $\frac{1}{2}(n+1)!$

Summing (A4) over all diagrams of the type in Fig. 3, we obtain

$$U(R) = \frac{i}{4\pi} \int_{-\infty}^{\infty} d\omega \int \frac{d\vec{q}}{(2\pi)^3} \int \frac{d\vec{q}'}{(2\pi)^3} \mathfrak{D}^a(\vec{q}, \vec{q}', \omega) \times V(\vec{q}', \omega) \mathfrak{D}^b(\vec{q}', \vec{q}, \omega) V(\vec{q}, \omega), \quad (\text{A5})$$

with

$$\mathfrak{D}^i(\vec{q}, \vec{q}', \omega) \equiv \int_{-\infty}^{\infty} dt e^{i\omega t} \mathfrak{D}^i(\vec{q}, \vec{q}', t), \quad (\text{A6})$$

$$\mathfrak{D}^i(\vec{q}, \vec{q}', t) = -i \langle 0 | T \rho_{\vec{q}}^i(t) \rho_{-\vec{q}'}^i(0) | 0 \rangle, \quad (\text{A7})$$

and

$$V(\vec{q}, \omega) = \frac{v(\vec{q})}{\epsilon(\vec{q}, \omega)}; \quad \epsilon(\vec{q}, \omega) = 1 - v(\vec{q})\Pi(\vec{q}, \omega). \quad (\text{A8})$$

Here  $\Pi(\vec{q}, \omega)$  is the proper polarization insertion which determines the dielectric function  $\epsilon(\vec{q}, \omega)$  of the electron gas. By choosing an integration contour along the imaginary frequency axis in Eq. (A5), we obtain Eq. (5) of Sec. II.

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