PHYSICAL REVIEW B VOLUME 17, NUMBER 2 15 JANUARY 1978

Van der Waals forces in metals

J. Mahanty and Roger Taylor*

Department of Theoretical Physics, Research School of Physical Sciences, The Australian National University, Canberra, A.C.T., 2600, Australia

(Received 13 July 1977)

An analysis is made of the dispersion (Van der Waals) interaction between the ions in a metal. The role of the dielectric function $\epsilon(k,\omega)$ of the electron gas in screening polarization fluctuations of the ions is studied, and it is established that in Van der Waals interaction there will be terms which are analogs of the Thomas-Fermi screening term and the Friedel oscillation term occurring in the static interaction between ions. It is shown that reasonable estimates of the Van der Waals energy can be made by ignoring the spatial dispersion aspect of $\epsilon(k,\omega)$, using a local approximation based on the bulk-plasmon term only.

I. INTRODUCTION

Broadly speaking, the cohesive energy of a metal can be divided into two parts, i.e., that which is derived from the nearly free conduction electrons, and that which is derived from the interaction of the ions imbedded in the former. The latter constitutes only a small fraction of the cohesive energy, but it has important physical implications. Such properties as crystal structure, lattice vibrations, and, in general, dynamic response of the metal would depend on the ion-ion interaction. Because of the very effective screening due to the conduction electrons, the Coulomb interaction between the ions is more or less snuffed out—only the residual long-range Friedel oscillations remain in the static part of the ion-ion interaction. The nature and physical effects of the static Coulomb interaction between the ions in a metal have been investigated extensively.[1-3] There is, however, another type of ion-ion interaction, the dispersion or Van der Waals interaction, which has been neglected to a large extent in the study of metals. It has recently been suggested that Van der Waals forces make a significant contribution to the cohesive energy of some metals.[4] In that case, we would expect contributions from these forces to other properties of these metals, such as vacancy and void formation energies and phonon-dispersion curves. They would also contribute to the surface energy of metals in a manner entirely analogous to the contribution of the dispersion interaction between the constituent molecules to the surface energy of nonconducting dielectrics.[5,6] This contribution would supplement the estimates made of such properties based only on the properties of the electrons in a jellium model of a metal, as has been done for the surface energy.[7] The importance of ionic polarizability, which determines the strength of the Van der Waals force, has been emphasized in a different context by Kukkonen.[8] The normal jellium approach to Rb and Cs gives a negative or near negative electron gas compressibility at the electron gas densities in these metals. However, Kukkonen has shown that if a jellium with a polarizable background (such as would arise with polarizable ions) is used, the system is stabilized enabling calculations to be performed in the normal manner.

The purpose of this paper is to investigate the Van der Waals pair potential between two ions immersed in an electron gas. The analysis here is more analytical than are the calculations of Rehr *et al.*[4] We find that there are two distinct contributions to this pair potential. One arises from the normal inability of a plasma to screen completely the potential due to dipole fluctuations on the imbedded ions. This gives rise to the well-known R^{-6} law. The other contribution has two parts; one is the analog of the Thomas-Fermi screening term and the other is the analog of the Friedel oscillations, both of which occur in the static Coulomb interaction of the ions.

II. THEORY

The theory of the Van der Waals interaction potential is well known.[4,6] For completeness we shall briefly indicate here the formalism we shall follow in this paper, starting with two molecules.

Taking the two interacting molecules at $\vec{r}_1$ and $\vec{r}_2$, and with their polarizabilities given by $\alpha_1(\omega)$ and $\alpha_2(\omega)$, if we start with an initial polarization $\vec{p}_2(\omega)$ on the second molecule, the electric field due to that at r_1 is

$$\vec{\epsilon}(\vec{r}_1)=\overleftrightarrow{G}(\vec{r}_1,\vec{r}_2;\omega)\cdot\vec{p}_2(\omega), \tag{1}$$

where $\overleftrightarrow{G}(\vec{r}_1,\vec{r}_2;\omega)$ is the dyadic Green's function giving the field at $\vec{r}_1$ due to a unit dipole source at $\vec{r}_2$ oscillating with a frequency ω. The resulting induced polarization of the first molecule is

$$\vec{p}_1(\omega)=\alpha_1(\omega)\overleftrightarrow{G}(\vec{r}_1,\vec{r}_2;\omega)\cdot\vec{p}_2(\omega). \tag{2}$$

Proceeding similarly we also obtain the equation connecting the polarization $\vec{p}_1$ with that induced on the second molecule

$$\vec{p}_2(\omega)=\alpha_2(\omega)\overleftrightarrow{G}(\vec{r}_2,\vec{r}_1;\omega)\cdot\vec{p}_1(\omega)\,. \tag{3}$$

Equations (2) and (3) have to be solved self-consistently, and the solvability condition is

$$D(\omega)\equiv\begin{vmatrix}\overleftrightarrow{I} & -\alpha_1(\omega)\overleftrightarrow{G}(\vec{r}_1,\vec{r}_2;\omega)\\ -\alpha_2(\omega)\overleftrightarrow{G}(\vec{r}_2,\vec{r}_1;\omega) & \overleftrightarrow{I}\end{vmatrix}=0\,. \tag{4}$$

The zeroes of $D(\omega)$ give the frequencies of the electromagnetic-field modes as perturbed by the presence of the two molecules, and the poles give the free-field frequencies. The dispersion interaction, being the difference in the energies of the field in the two situations, can be written as a contour integral

$$\begin{aligned}V(\vec{r}_{12})&=\frac{1}{2\pi i}\int d\omega\left(\frac{\hbar\omega}{2}\right)\frac{d}{d\omega}\ln[D(\omega)]\\ &=-\frac{\hbar}{4\pi i}\int d\omega\,\ln[D(\omega)]\,.\end{aligned} \tag{5}$$

The contour here encloses the positive real axis in the ω plane. If we take the contour along the imaginary axis, and expand the logarithm to leading order, we get

$$\begin{aligned}V(\vec{r}_{12})=-\frac{\hbar}{4\pi}\int_{-\infty}^{\infty}&d\xi\,\alpha_1(i\xi)\alpha_2(i\xi)\\ &\times\mathrm{Tr}[\overleftrightarrow{G}(\vec{r}_1,\vec{r}_2;i\xi)\overleftrightarrow{G}(\vec{r}_2,\vec{r}_1;i\xi)]\,.\end{aligned} \tag{6}$$

Equation (6) is the basis of our treatment.

It may be noted that when Eq. (6) is applied to ions in a metal, the medium determines the dyadic Green's function $\overleftrightarrow{G}(\vec{r}_1,\vec{r}_2;\omega)$. This is given, in terms of the electric potential $\phi(\vec{r}_1,\vec{r}_2;\omega)$ at $\vec{r}_1$ due to a unit monopole source at $\vec{r}_2$ oscillating with a frequency ω, by the relation

$$\overleftrightarrow{G}(\vec{r}_1,\vec{r}_2;\omega)=-(\nabla_1\nabla_2)\phi(\vec{r}_1,\vec{r}_2;\omega)\,. \tag{7}$$

To apply this to the case of ions in a homogeneous electron gas, we need

$$\begin{aligned}\phi(\vec{r}_1,\vec{r}_2;\omega)&\equiv\phi(\vec{r}_1-\vec{r}_2;\omega)\\ &=\frac{4\pi}{(2\pi)^3}\int\frac{d^3k\,e^{i\vec{k}\cdot(\vec{r}_1-\vec{r}_2)}}{k^2\epsilon(\vec{k},\omega)}\,,\end{aligned} \tag{8}$$

where $\epsilon(\vec{k},\omega)$ is the dielectric function of the electron gas. In terms of ϕ, Eq. (6) becomes (with $\vec{R}=\vec{r}_1-\vec{r}_2$)

$$\begin{aligned}V(R)=-\frac{\hbar}{2\pi}\int_0^{\infty}&d\xi\,\alpha_1(i\xi)\alpha_2(i\xi)\\ &\times\left[\left(\frac{\partial^2\phi}{\partial R^2}\right)^2+\frac{2}{R^2}\left(\frac{\partial\phi}{\partial R}\right)^2\right]\,.\end{aligned} \tag{9}$$

In obtaining Eq. (9), spatial isotropy is assumed, as is also the fact that $\alpha_1(\omega)$, $\alpha_2(\omega)$, and $\epsilon(\vec{k},\omega)$ are even functions of $\omega=i\xi$.

III. ANALYSIS OF SCREENING

The properties of $\phi(R;\omega=0)$ in a metal are well known, but those of $\phi(R,\omega)$ are not. Rehr *et al.*[4] have given numerical values for imaginary frequencies for use in Eq. (9) using the random-phase-approximation (RPA) form of $\epsilon(k,\omega)$. We shall briefly indicate here some of the analytic features of the problem using the RPA form of $\epsilon(k,\omega)$, and also indicate the modifications that would occur when improvements are made over the RPA form.

Writing Eq. (8) for the isotropic case and imaginary frequencies in the form

$$\phi(R,i\xi)=\left(\frac{2}{\pi R}\right)\int_0^{\infty}\frac{dk\,\sin(kR)}{k\epsilon(k,i\xi)}\,, \tag{10}$$

we note that for large R there will be two types of contributions. The first part, $\phi_1(R,i\xi)$, arises from the pole of $[1/\epsilon(k,\omega)]$ in the small-k region; and the second part, $\phi_2(R,i\xi)$, arises from the branch points of $\epsilon(k,i\xi)$. In the Appendix the contribution from the branch points will be evaluated. The pole term can be estimated with reasonable accuracy using the hydrodynamic approximation for

$$\epsilon(k,\omega)=1-\omega_p^2/(\omega^2-\beta^2k^2)\,. \tag{11}$$

Here ω_p is the bulk-plasmon frequency, and the RPA estimate of β is $\beta^2=\frac{3}{5}v_F^2$, v_F being the Fermi velocity. The relation between this form and the full RPA form has been discussed by Lindhard.[9] Although the hydrodynamic form is an oversimplification and does not correctly represent the analytic behavior of the RPA $\epsilon(k,\omega)$ in the large-k region, it is adequate for our purpose since it has the correct limiting behavior for $k\to0$, $\omega\neq0$ and for $\omega\to0$, $k\neq0$; we shall be concerned with this small-k and -ω region. Use of Eq. (11) in (10) gives us

$$\begin{aligned}\phi_1(R,i\xi)=\left(\frac{\xi^2}{\omega_p^2+\xi^2}\right)\frac{1}{R}&+\left(1+\frac{\xi^2}{\omega_p^2+\xi^2}\right)\\ &\times\frac{\exp[-(R/\beta)(\omega_p^2+\xi^2)^{1/2}]}{R}\,.\end{aligned} \tag{12}$$

The first term is the Coulomb potential in a dielectric medium with the spatially nondispersive dielectric function

$$\epsilon(\omega)=1-\omega_p^2/\omega^2\,, \tag{13}$$

and it indicates the incapacity of the electron gas to screen out an oscillating charge completely. The other part arises out of the spatial dispersion in $\epsilon(k,\omega)$, and in the static limit (i.e., $\xi=0$), goes over to the usual Thomas-Fermi screened Coulomb potential.

The contribution $\phi_2(R, i\xi)$ from the branch points as shown in the Appendix, is basically of the form of exponentially damped Friedel-type oscillations for $\xi \neq 0$. As a function of the frequency the exponent is rather complicated, being proportional to ξ for small ξ, and to $\sqrt{\xi}$ for large ξ. The second term in $\phi_1(R, i\xi)$, and $\phi_2(R, i\xi)$ is consistent with what one would expect after realizing that the potential inside the electron gas due to an oscillating source would arise out of the propagation of the field in it governed by the structure of $\epsilon(k, \omega)$; at least a part of it may be expected to be a retarded potential with a phase that depends linearly on the distance from the source.

In the retarded terms we need to concern ourselves only with the small-ξ behavior, since in Eq. (9) for the retarded terms at large R, the major contribution to the ξ integral would come from the small-ξ region. The appropriate small-ξ form of $\phi(R, i\xi)$ that we need is

$$\phi(R, i\xi) \approx \left(\frac{\xi^2}{\omega_p^2+\xi^2}\right)\frac{1}{R} + \left(1+\frac{\xi^2}{\omega_p^2+\xi^2}\right)\frac{\exp[-(R/\beta)(\omega_p^2+\xi^2)^{1/2}]}{R} + \left(B_1(\xi)\frac{\cos(2k_FR)}{(2k_FR)^2} + B_2(\xi)\frac{\sin(2k_FR)}{(2k_FR)^3}\right)\frac{e^{-\nu\xi R}}{R}\,. \tag{14}$$

The symbols have been explained in the Appendix.

Using this potential in Eq. (9), we get, for the leading terms of the Van der Waals interaction potential,

$$V(R) \approx -\frac{1}{R^6}\left(\frac{3\hbar}{\pi}\int_0^\infty \frac{d\xi\, \xi^4\alpha_1(i\xi)\alpha_2(i\xi)}{(\omega_p^2+\xi^2)^2}\right) - \frac{\hbar}{2\pi}\alpha_1(0)\alpha_2(0)\left(\frac{\sqrt{\pi}\omega_p{}^{5/2}}{2\beta^{3/2}}\frac{e^{-2\omega_pR/\beta}}{R^{5/2}} + \frac{B_1{}^2\cos^2(2k_FR)}{(2\nu)R^7} + \cdots\right)\,. \tag{15}$$

We thus note that besides a London-type $(1/R^6)$ interaction, the two ions inside a metal will also interact with an additional oscillatory-type potential. There will also be an exponentially damped term, which will damp out twice as fast as the Thomas-Fermi screening term in the static case.

If instead of the RPA form a more-realistic $\epsilon(k, \omega)$ is used, it is not difficult to show that the exponentially damped term in Eq. (14) will become less significant due to increased damping. In Eq. (15) the zero-frequency form of this occurs, and the increase of the Thomas-Fermi damping in the static case, when the RPA $\epsilon(k, 0)$ is improved by inclusion of correlation and exchange corrections is well known.[10] Furthermore, the part related to Friedel-type oscillations, which is due to the sharpness of the Fermi surface (at zero temperature), will persist when improved versions of $\epsilon(k, \omega)$ are used. For small ξ, it would be reasonable to expect that the oscillatory part of $\phi_2(R, i\xi)$, which we shall denote $\phi_2{}^{(\mathrm{os})}(R, i\xi)$, will be of the form

$$\phi_2^{(\mathrm{os})}(R, i\xi) \approx e^{-\nu\xi R}\phi_2^{(\mathrm{os})}(R, 0)\,. \tag{16}$$

This part will thus contribute to $V(R)$, to leading orders in $(1/R)$, terms which will arise from

$$V^{(\mathrm{os})}(R) \approx -\left(\frac{\hbar}{2\pi}\right)\left(\frac{\alpha_1(0)\alpha_2(0)}{2\nu R}\right) \times \left[\left(\frac{\partial^2\phi_2^{(\mathrm{os})}(R,0)}{\partial R^2}\right)^2 + \frac{2}{R^2}\left(\frac{\partial\phi_2(R,0)}{\partial R}\right)^2\right]. \tag{17}$$

Care has to be exercised in evaluating and retaining terms of the desired order in this, as in higher orders in $(1/R)$ the cross terms occuring when the full potential $\phi(R, i\xi)$ is used will start contributing.

IV. RESULTS AND DISCUSSION

We have attempted to evaluate the Van der Waals energy in noble metals using the approach outlined in Secs. II and III.

The numerical values of $\phi(R, i\xi)$, obtained by direct integration with the RPA $\epsilon(k, i\xi)$ and by use of Eq. (14), are in good agreement. As expected, the screening becomes effective only for $\xi < \omega_p$. Furthermore, the strengths of the analogs of the Thomas-Fermi screened-Coulomb term and the Friedel-oscillation term are much less than that of the R^{-6} term even at distances of the order of the nearest-neighbor spacing in noble metals. These results are consistent with the numerical estimate of $\phi(R, i\xi)$ made by Rehr *et al.*[4] Since the principal effect of the use of a more-sophisticated $\epsilon(k, i\xi)$ will be to render the analog of the screened-Coulomb term insignificant, the use of just R^{-6} is clearly a good approximation to the Van der Waals force in these systems. We therefore write

$$V(R) = -A/(R/a)^6\,, \tag{18}$$

where a is the face-centered-cubic lattice parameter. Using the information on ionic polarizabilities of the noble metals taken from Rehr *et al.*,[4] we list in Table I the values of A that we obtained plus the contribution of this potential to the formation energy of a vacancy. The corresponding exper-

TABLE I. Values of the coefficient A in Eq. (18) plus estimates of the dipole-dipole Van der Waals contribution to the formation energy of a vacancy (E_{fv}) in the noble metals. The experimental values are taken from Simmons and Balluffi (Ref. 11). All quantities are in eV.

	Cu	Ag	Au
A	0.002 82	0.005 86	0.008 61
E_{fv} (theory)	0.161	0.333	0.489
E_{fv} (expt.)	1.17 ± 0.11	1.09 ± 0.10	0.94 ± 0.09

imental values of Simmons and Balluffi[11] are also listed for comparison.

Although the contribution to E_{fv} from the Van der Waals force is only about 15% for Cu, it is about 30% for Ag and 50% for Au, the trend being that the more strongly polarizable the ion, the larger the Van der Waals contribution. Clearly this effect will be important in all materials, such as transition metals, with highly polarizable ions and therefore a R^{-6} term should be included in a pair-potential description of any such metals. This term does not seem to be included in any treatment of noble and transition metals of which we are aware, including sophisticated approaches such as those of Moriarty[12] and Dagens.[13]

We have also investigated the contribution of the Van der Waals force to the phonon frequencies of each of the noble metals. Because of the attractive nature of the force it softens the phonon modes and provides a negative contribution to the calculation of ω^2. In each case it turns out that this contribution is about 10% of the experimental value. Thus it is possible for a theory with one or two adjustable parameters to give a good description of the lattice dynamics and totally misrepresent contributions to the interionic potential which may be important from the point of view of defect properties.

ACKNOWLEDGMENTS

One of the authors (R.T.) is indebted to the authorities of the Australian National University and to Professor K. J. Le Couteur for financially supporting his visit, which made this collaboration possible.

APPENDIX

In this Appendix we examine the asymptotic form of $\phi(R, i\xi)$. The RPA expression for $\epsilon(k, i\xi)$ is

$$\epsilon(k, i\xi) = 1 + (\lambda/z^2) f(z, i\xi)\,, \tag{A1}$$

with

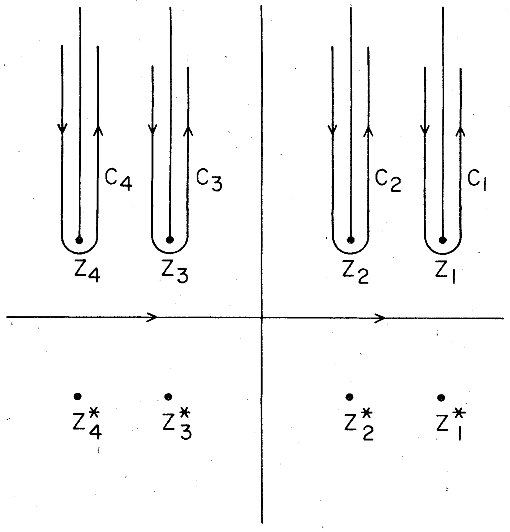

FIG. 1. Contours used in doing the integration in the Appendix, to obtain the contribution to the potential from the branch points.

$$f(z, i\xi) = \frac{1}{2} + \left(\frac{1}{8z^3}\right)[z^2 - (z^2 - i\alpha)^2] \ln\left(\frac{z^2 + z - i\alpha}{z^2 - z - i\alpha}\right) + \left(\frac{1}{8z^3}\right)[z^2 - (z^2 + i\alpha)^2] \ln\left(\frac{z^2 + z + i\alpha}{z^2 - z + i\alpha}\right). \tag{A2}$$

Here,

$$\lambda = (\pi a_0 k_F)^{-1}; \quad \alpha = \xi(\tfrac{1}{3}\lambda)^{1/2}; \quad z = (k/2k_F)\,. \tag{A3}$$

From Eq. (10), we get

$$\phi(R; i\xi) = \left(\frac{1}{i\pi R}\right) \int_{-\infty}^{\infty} dz\, e^{izx} \left(\frac{z}{z^2 + \lambda f(z, i\xi)}\right), \tag{A4}$$

where $x = 2k_F R$.

We need the contribution to the integral in (A4) from the branch points at the zeroes of the arguments of the logarithms. The contours to be used for obtaining the contribution $\phi_2(R; i\xi)$ to $\phi(R; i\xi)$ from the branch points, are illustrated in Fig. 1. The method is an adaption of that used earlier[3] for $\xi = 0$. The contour along the real axis can be replaced by the sum of the illustrated four contours C_1–C_4 around the branch lines, which are chosen parallel to the imaginary axis, for convenience. The relevant branch points in the upper half-plane, in terms of $\theta = \frac{1}{2}\tan^{-1}\alpha$ are

$$\begin{aligned} z_1 &= \tfrac{1}{2}[1 + (1 + \alpha^2)^{1/4} e^{i\theta}]\,, \\ z_2 &= -\tfrac{1}{2}[1 - (1 + \alpha^2)^{1/4} e^{i\theta}]\,, \\ z_3 &= \tfrac{1}{2}[1 - (1 + \alpha^2)^{1/4} e^{-i\theta}]\,, \\ z_4 &= -\tfrac{1}{2}[1 + (1 + \alpha^2)^{1/4} e^{-i\theta}]\,. \end{aligned} \tag{A5}$$

In any of the contours, going from one side to the other of the branch line, the discontinuity in the integrand arises from the phase of the relevant logarithm. Thus, in terms of

$$F(z;i\xi)=z/[z^2+\lambda f(z,i\xi)]\,, \tag{A6}$$

in the neighborhood of the branch points, we get

$$F(z_1+\delta)-F(z_1-\delta)=\left(\frac{\pi\lambda i}{8z_1^2}\right)\frac{(z^2-i\alpha)^2-z^2}{[z_1^2+\lambda f(z_1)]^2}\,,$$

$$F(z_2+\delta)-F(z_2-\delta)=\left(\frac{\pi\lambda i}{8z_2^2}\right)\frac{(z^2-i\alpha)^2-z^2}{[z_2^2+\lambda f(z_2)]^2}\,.$$

$F(z_3)$ and $F(z_4)$ lead to equations similar to those for $F(z_1)$ and $F(z_2)$, respectively, with a change in the sign of $(i\alpha)$. The contribution from the contour C_1, for instance, is

$$\left(\frac{1}{2i}\right)\left(\frac{-\lambda\pi i}{8z_1^2}\right)\frac{(z_1-z_2)(z_1-z_3^*)(z_1-z_4^*)}{[z_1^2+\lambda f(z_1)]^2}\int_{z_1}^{z_1+i\infty}(z-z_1)e^{izx}\,dz=\left(\frac{\lambda\pi}{16z_1^2}\right)\frac{(z_1-z_2)(z_1-z_3^*)(z_1-z_4^*)}{[z_1^2+\lambda f(z_1)]^2}\left(\frac{e^{iz_1x}}{x^2}\right). \tag{A7}$$

Obtaining the other contributions similarly, adding and simplifying them, we get the result

$$\phi_2(R;i\xi)\approx\frac{\lambda}{4(2k_F)^2R^3}(1+\alpha^2)^{1/4}e^{-(x/2)(1+\alpha^2)^{1/4}}\sin\theta$$
$$\times\left[\left(\frac{U_{(+)}^5}{W_{(+)}^2}\right)\cos(\beta_{(+)}x+\theta+5S_{(+)}-2V_{(+)})+\left(\frac{U_{(-)}^5}{W_{(-)}^2}\right)\cos(\beta_{(-)}x+\theta+5S_{(-)}-2V_{(-)})\right]. \tag{A8}$$

Here,

$$\beta_{(\pm)}=\tfrac{1}{2}[(1+\alpha^2)^{1/4}\cos\theta\pm1],\quad U_{(\pm)}=\tfrac{1}{2}[1+(1+\alpha^2)^{1/2}\pm2(1+\alpha^2)^{1/4}\cos\theta]^{1/2},$$

$$S_{(\pm)}=\tan^{-1}\left[\frac{(1+\alpha^2)^{1/4}\sin\theta}{(1+\alpha^2)^{1/4}\cos\theta\pm1}\right],$$

$$W_{(\pm)}=\left\{\left[U_{(\pm)}^5\cos5S_{(\pm)}+\frac{\lambda U_{(\pm)}^3}{2}\cos3S_{(\pm)}\pm\left(\frac{\lambda\alpha}{16}\right)Q_{(\pm)}Q_{1(\pm)}\sin(T_{(\pm)}+T_{1(\pm)})\right]^2\right.$$
$$\left.+\left[U_{(\pm)}^5\sin5S_{(\pm)}+\frac{\lambda U_{(\pm)}^3}{2}\sin3S_{(\pm)}\mp\left(\frac{\lambda\alpha}{16}\right)Q_{(\pm)}Q_{1(\pm)}\cos(T_{(\pm)}+T_{1(\pm)})\right]^2\right\}^{1/2}$$
$$\equiv[(\mathrm{Re}W_{(\pm)})^2+(\mathrm{Im}W_{(\pm)})^2]^{1/2}, \tag{A9}$$

$$V_{(\pm)}=\tan^{-1}(\mathrm{Im}W_{(\pm)}/\mathrm{Re}W_{(\pm)}),$$

with

$$Q_{(\pm)}=[1+\tfrac{1}{4}\alpha^2+(1+\alpha^2)^{1/2}\pm2(1+\alpha^2)^{1/4}\cos\theta\pm\alpha(1+\alpha^2)^{1/4}\sin\theta]^{1/2},$$

$$T_{(\pm)}=\tan^{-1}\left(\frac{(\frac{1}{2}\alpha)-(1+\alpha^2)^{1/4}\sin\theta}{1-(1+\alpha^2)^{1/4}\cos\theta}\right),\quad Q_{1(\pm)}=\left\{\left[\ln\left(\frac{2Q_{(\pm)}}{\alpha}\right)\right]^2+\left(T_{(\pm)}-\frac{\pi}{2}\right)^2\right\}^{1/2},$$

$$T_{1(\pm)}=\tan^{-1}[T_{(\pm)}-\tfrac{1}{2}\pi/\ln(2Q_{(\pm)}/\alpha)].$$

The extremely complicated algebraic form of the quantities occurring in Eq. (A8) reflects the complicated dispersion relation of the propagating waves connected with the branch points of $\epsilon(k,\omega)$, emanating from an oscillating charge source in the medium, even in the RPA.

For $\xi\to0$, i.e., in the static limit $\alpha\to0$, and Eq. (A8) reduces to

$$\phi_2(R;0)\approx\left[\frac{\lambda}{(2+\lambda)^2}\right]\frac{\cos(2k_FR)}{(2k_F)^2R^3}\,, \tag{A10}$$

which is the leading term in the Friedel-oscillation formula.

For small but finite frequency, Eq. (A8) reduces to

$$\phi_2(R;i\xi)\approx\left(\frac{B_2(\xi)}{R}\right)\frac{\cos(2k_FR)}{(2k_FR)^2}e^{-\nu\xi R}\,, \tag{A11}$$

where $\nu=2k_F(\frac{1}{3}\lambda)^{1/2}$. The structure of $B_2(\xi)$ is obtained trivially from Eq. (A8). Equation (A11) gives the leading term in an infinite series. At zero frequency it is usually necessary to consider also the next term which is of the form $[\sin(2k_FR)]/R^4$. At finite frequency the analysis of this term is extremely tedious and we have not attempted it. However, it is reasonable to suppose that it will be damped precisely in the same way as in Eq. (A11). We thus arrive at the following asymptotic form for $\phi_2(R;i\xi)$:

$$\phi_2(R;i\xi)\approx\left(B_2(\xi)\frac{\cos(2k_FR)}{(2k_FR)^2}+B_3(\xi)\frac{\sin(2k_FR)}{(2k_FR)^3}\right)\frac{e^{-\nu\xi R}}{R}. \qquad (\mathrm{A}12)$$

For large frequencies this approximation is clearly poor, but as discussed in Sec. III we do not need that for large R; and furthermore, the $\phi_1(R;i\xi)$ will dominate in that circumstance. We have tested Eq. (A12) by comparing with a numerical evaluation of $\phi(R;i\xi)$ from Eq. (10) and have found that it does indeed give a good fit for values of R greater than or equal to the near neighbor distance in a typical noble metal.

---

*Permanent address: Div. of Physics, National Research Council of Canada, Ottawa, Canada K1A 0R6.

[1] J. M. Ziman, *Principles of the Theory of Solids* (Cambridge U.P., Cambridge, England, 1972), Chap. 5.

[2] D. Pines, *The Many-Body Problem* (Benjamin, New York, 1961).

[3] A. L. Fetter and J. D. Walecka, *Quantum Theory of Many-Particle Systems* (McGraw-Hill, New York, 1971).

[4] J. J. Rehr, E. Zaremba, and W. Kohn, Phys. Rev. B 12, 2062 (1975).

[5] F. M. Fowkes, J. Colloid Interface Sci. 28, 493 (1968).

[6] J. Mahanty and B. W. Ninham, *Dispersion Forces* (Academic, London, 1976).

[7] J. Schmit and A. A. Lucas, Solid State Commun. 11, 415 (1972); 11, 419 (1972).

[8] C. A. Kukkonen, Ph. D. thesis (Cornell University, Ithaca, N.Y., 1975) (unpublished) (University Microfilms O. No. 75-18136).

[9] J. Lindhard, Dan. Mat. Fys. Medd. 28, No. 8 (1954).

[10] D. J. W. Geldart and Roger Taylor, Can. J. Phys. 48, 176 (1970).

[11] R. O. Simmons and R. W. Balluffi, Phys. Rev. 119, 600 (1960); 125, 862 (1962); 129, 1533 (1963).

[12] J. A. Moriarity, Phys. Rev. B 10, 3075 (1974).

[13] L. Dagens, J. Phys. F 7, 1167 (1977).