Correlation energy and van der Waals interaction of coupled metal films

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We derive a general expression for the density response function of two films separated by distance d in terms of the response function of the isolated films. Using the random-phase approximation and a semiclassical infinite-barrier model, we then calculate the total correlation energy of the system and hence the van der Waals interaction of the coupled films. Both of these quantities can be written in terms of the zero-point energy of the normal modes. Explicit calculations of the van der Waals interaction indicate that the dominant contribution is from the surface plasmon modes. The connection between the surface correlation energy and the work done against the van der Waals force is discussed. In the infinite-barrier model these quantities differ by a cleavage energy whose dominant contribution comes from the particle-hole modes and which forms half the surface correlation energy.

I. INTRODUCTION

The main aim of this paper is to present a theory of the attractive interaction between two metal films separated by a distance d which does not depend on the assumption of a local frequency-dependent dielectric function (as in the Lifschitz approach).[1] In general, the treatment of nonlocal response in an inhomogeneous system is extremely difficult, and we are reduced, for calculational purposes, to a simple model which regards the film surfaces as infinite plane barriers from which the electrons reflect specularly like classical particles. While this may seem a rather crude model, it is the only one for which a closed-form solution for the density response function can be obtained, even in the random-phase approximation (RPA). For this reason its conclusions have a special significance, and from them we can draw qualitative information concerning the important processes which enter into, for example, the surface correlation energy and the van der Waals interaction. Specific to these two cases is our conclusion that while particle-hole excitations dominate the former quantity, surface-plasmon excitations dominate the latter.

The system we consider is depicted in Fig. 1. The metal films are represented by two jellium slabs each consisting of a gas of electrons and a positive background which cuts off sharply at two parallel planes separated by distance L. In a realistic model the electron density might be as in Fig. 1(a), while in the infinite-barrier model [Fig. 1(b)] it, too, cuts off sharply at the surfaces. The distance between the closest edges of the positive backgrounds of the two films is denoted by d and the coordinate z is taken to be the normal to all the four surfaces, each of which has surface area $A \gg L^2$. If the distance d is large enough so that the electron tunneling from one film to the other is effectively zero, we may regard the films as isolated but coupled by the electromagnetic fluctuations which occur in each film. The interaction energy between the films is then of the van der Waals type.[1] In the infinite-barrier model there is no electron tunneling and the van der Waals region extends down to $d=0$.

Whatever the density profile, the relevant part of the exchange and correlation energy is given by[2]

$$E_{\rm xc}(d) = -\frac{\hbar}{2}\int d\vec{r}\int d\vec{r}\,' v(\vec{r}-\vec{r}\,')\int_0^1 d\lambda \int_c \frac{d\omega}{(2\pi i)} \times \chi_d^\lambda(\vec{r},\vec{r}\,',\omega)\,. \tag{1.1}$$

Here $v(\vec{r})$ is the Coulomb interaction and χ_d^λ is the density response function of the total system at separation d, with coupling constant λe^2. The contour encloses the positive real ω-axis in a clockwise sense and clearly picks up contributions from the poles of χ_d^λ which occur at the normal-mode frequencies of the coupled films. If χ_d^λ satisfies the RPA integral equation

$$\chi_d^\lambda(\vec{r},\vec{r}\,',\omega) = \chi_d^0(\vec{r},\vec{r}\,',\omega) + \lambda\int d\vec{r}_1\int d\vec{r}_2\,\chi_d^0(\vec{r},\vec{r}_1,\omega) \times v(\vec{r}_1-\vec{r}_2)\chi_d^\lambda(\vec{r}_2,\vec{r}\,',\omega)\,, \tag{1.2}$$

it can readily be shown, using an eigenfunction method similar to that first employed by Feibelman,[3] that the total exchange and correlation energy can be written[4]

$$E_{\rm xc}(d) = \frac{\hbar}{2}\sum_i [\omega^d(i) - \omega_0^d(i)]\,. \tag{1.3}$$

Here $\omega^d(i)$ are the normal-mode frequencies at separation d and $\omega_0^d(i)$ the corresponding quantities for $\lambda=0$, i.e., poles of χ_d^0. The result (1.3) holds in the RPA for any system, whether homogeneous or inhomogeneous.

The van der Waals interaction energy is defined by

$$E_{\rm VW}(d) \equiv E_{\rm XC}(d) - E_{\rm XC}(d \to \infty) \tag{1.4}$$

and so is given by

$$E_{\rm VW}(d) = \frac{\hbar}{2}\sum_i [\omega_+^d(i) + \omega_-^d(i) - 2\omega_F(i)] \ . \tag{1.5}$$

We have noted explicitly that the modes can be classed as symmetric (ω_+^d) or antisymmetric (ω_-^d) about the plane $z=0$, and have denoted by $\omega_F(i)$ the normal modes of a single isolated film of thickness L. Equation (1.5) is a natural generalization of the ansatz of Van Kampen, Nijboer, and Schram,[5] who showed that a similar formula (but including only dispersionless surface plasmons) led to the Lifschitz result for $E_{\rm VW}(d)$.

While (1.5) is a formal solution for the van der Waals interaction, it is not very useful unless one knows the form of the normal-mode sum and can compute the normal-mode frequencies. For a realistic model of the surface this is prohibitively difficult and we will use the infinite-barrier model which has been extensively studied in recent years (see, for example, Refs. 6–9). In Sec. II, we derive a closed expression for the density response of the coupled films using the RPA and discuss the normal modes of the system. In Sec. III, we then derive and evaluate a simple expression for $E_{\rm VW}(d)$ and demonstrate explicitly that it can be written in the form (1.5). We find that even at small values of d, where one expects short-wavelength modes to be important, the van der Waals energy is dominated by the surface plasmons. This conclusion is noteworthy since it implies that a good estimate of the van der Waals energy for any model of the surface accrues merely from a knowledge of the surface-plasmon dispersion relations for coupled and uncoupled surfaces.

In recent years several attempts[10–13] have been made to estimate the surface correlation energy via simple normal-mode formulas. In Sec. IV, we show that these formulas, which involve only plasmons, in fact estimate not the surface correlation energy but the work done against the van der Waals force. These quantities are shown to differ by a cleavage energy $E_{\rm CL}$, which supplies about one-half of the surface correlation energy and so is as important as the work done against the van der Waals force. Furthermore, we show that the surface-plasmon contribution to $E_{\rm CL}$ is large and negative, more than canceling the surface-plasmon contribution to $E_{\rm VW}(d=0)$. The surface energy is therefore dominated by particle-hole modes and not plasmons.

For the most part, this paper is a natural development of two earlier[14,15] papers on the surface energy and the reader is referred to these for more detailed discussion of certain points. We might also remark that our ground-state results are easily extended to cover finite temperatures. For example, (1.3) gives the free energy due to interactions if we replace the zero-point energy $\hbar\omega_i/2$ by

$$k_B T \ln(2\sinh\hbar\omega_i/2k_BT) \ . \tag{1.6}$$

Other expressions in this paper involving the zero-point energies of normal modes can be similarly generalized to give the interaction free energy of coupled films.

II. DENSITY RESPONSE FUNCTION FOR COUPLED FILMS

Consider two films S_L and S_R each of thickness L and cross-sectional area A, separated by distance d (see Fig. 1). If a small external field $\delta U_{\rm ext}(k_\parallel, z, \omega)$ is applied to the system, the resulting density fluctuation in S_L is given by

$$\delta n_L(k_\parallel, z, \omega) = \int_{-L-d/2}^{-d/2} dz'\, \chi_{L,L}(k_\parallel, z, z', \omega) \times \delta U_{\rm ext}^L(k_\parallel, z', \omega) + \int_{d/2}^{L+d/2} dz' \times \chi_{L,R}(k_\parallel, z, z', \omega)\delta U_{\rm ext}^R(k_\parallel, z', \omega) . \tag{2.1}$$

Here $\chi_{L,L}$ and $\chi_{L,R}$ determine the response in S_L to the external field in S_L and S_R, respectively. For brevity, we drop the parametric dependence of all quantities on the frequency (ω) and the wave-vector parallel to the surface ($k_\parallel$). For $d > \delta$, the sole source of the coupling between the films is the electric field set up by the charge fluctuations. Thus we may write in place of (2.1)

$$\delta n_L(z) = \int_{-L-d/2}^{-d/2} dz'\, \chi_L(z, z') \left(\delta U_{\rm ext}^L(z') + \frac{2\pi e^2}{k_\parallel} \int_{d/2}^{L+d/2} dz''\, e^{-k_\parallel |z'-z''|} \delta n_R(z'') \right), \tag{2.2}$$

where $\chi_L(z, z')$ is the density response function of a single isolated film. In order to avoid the continual appearance of $d/2$, we translate all coordinates in S_L (S_R) by $d/2$ ($-d/2$) so that (2.2) and its equivalent for $\delta n_R(z)$ take the form

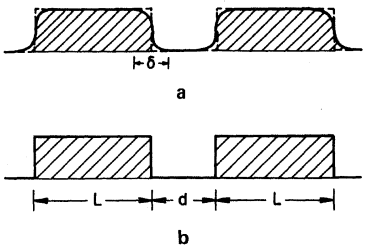

FIG. 1. Electron charge-density profile of two films, each of thickness L. A realistic model is shown in (a) while the semiclassical infinite-barrier model is shown in (b).

$$\delta n_{L,R}(z)=\int_{-L,0}^{0,L} dz'\,\chi_{L,R}(z,z')\left(\delta U_{\rm ext}^{L,R}(z')+\frac{2\pi e^2}{k_\parallel}\,e^{-k_\parallel d}\sigma_{R,L}\,e^{-k_\parallel|z'|}\right), \quad (2.3)$$

where

$$\sigma_{R,L}\equiv\int_{0,-L}^{L,0} dz\,e^{-k_\parallel|z|}\delta n_{R,L}(z)\,. \quad (2.4)$$

Equations (2.3) and (2.4) can now readily be transformed into simultaneous algebraic equations for $\sigma_{R,L}$ whose solution is

$$\sigma_{R,L}=(1/Y^d)(I_{L,R}+e^{-k_\parallel d}\Gamma_{L,R}I_{R,L})\,, \quad (2.5)$$

where

$$Y^d\equiv(1-e^{-2k_\parallel d}\Gamma_L\Gamma_R) \quad (2.6)$$

and

$$I_{R,L}\equiv\int_{0,-L}^{L,0} dz\int_{0,-L}^{L,0} dz'\,\chi_{R,L}(z,z')\,e^{-k_\parallel|z|}\delta U_{\rm ext}^{R,L}(z'), \quad (2.7)$$

$$\Gamma_{R,L}\equiv\frac{2\pi e^2}{k_\parallel}\int_{0,-L}^{L,0} dz\int_{0,-L}^{L,0} dz'\,\chi_{R,L}(z,z')\,e^{-k_\parallel|z|}e^{-k_\parallel|z'|}\,. \quad (2.8)$$

Using (2.5) in (2.3) and comparing with (2.1) we obtain the exact results

$$\chi_{L,L}(z,z')=\chi_L(z,z')+\frac{2\pi e^2}{k_\parallel Y^d}\Gamma_L\,e^{-2k_\parallel d}\int_{-L}^{0} dz_1\int_{-L}^{0} dz_2\times\chi_L(z,z_1)\,e^{k_\parallel(z_1+z_2)}\chi_L(z_2,z')\,,$$
$$\chi_{L,R}(z,z')=\frac{2\pi e^2}{k_\parallel Y^d}\,e^{-k_\parallel d}\int_{-L}^{0} dz_1\int_{0}^{L} dz_2\,\chi_L(z,z_1)\times e^{k_\parallel(z_1-z_2)}\chi_R(z_2,z')\,. \quad (2.9)$$

Note that the zeros of $Y^d(k_\parallel,\omega)$ correspond to poles of the response function and are therefore the normal-mode frequencies of the coupled films.

In order to proceed we require an approximation for the density response function of an isolated film. This can be determined analytically only for an infinite-barrier model and on the assumption of classical specular scattering at the boundaries. This model has been extensively discussed in the literature and we remark only that, in spite of its simplicity, it exhibits the full spectrum of density fluctuations associated with a bounded electron gas. Indeed, it is the only analytically soluble model which does so. Within this model, the double cosine Fourier transform[16] of $\chi_{L,R}(z,z')$ is given by[8,9]

$$\chi_{L,R}(k_z,k_z')=\frac{L}{2a_k}\delta_{kk'}\chi_B^{L,R}(k,\omega)-\frac{k_\parallel e^2}{4\pi}v(k)v(k')\frac{\chi_B^{L,R}(k,\omega)\chi_B^{L,R}(k',\omega)}{D_{L,R}^{S,A}(k_\parallel,\omega)}\,, \quad (2.10)$$

where

$$k\equiv(k_\parallel^2+k_z^2)^{1/2}\,,$$
$$v(k)\equiv 4\pi/k^2\,, \quad (2.11)$$
$$D_{L,R}^{S,A}(k_\parallel,\omega)\equiv\frac{1}{2}+\frac{2}{L}\sum_{k_z}a_k\frac{k_\parallel}{k^2}\,\frac{1}{\epsilon_B^{L,R}(k,\omega)}\,.$$

The cosine transform variable is $k_z=n\pi/L$ with $n=0,1,2,\ldots$, and the notation $a_k=1-\frac{1}{2}\delta_{n0}$ takes into account the proper weighting of the $k_z=0$ Fourier component. The functions $\chi_B^{L,R}(k,\omega)$, $\epsilon_B^{L,R}(k,\omega)$ are the density response and dielectric functions for a homogeneous system of the same composition as $S_{L,R}$. In (2.11) the notation S (A) implies summation only over even (odd) multiples of π/L and in (2.10) the function D^S (D^A) is to be used if k_z, k_z' are both even (odd). If k_z and k_z' have different symmetry, then $\chi_{L,R}(k_z,k_z')=0$.

Applying the double cosine transform to (2.9) and using (2.10), we obtain as our final result

$$\chi_{L,L}(k_z,k_z')=\chi_L(k_z,k_z')+\frac{e^2}{8\pi}\,\frac{k_\parallel e^{-2k_\parallel d}}{Y^d}\,\frac{\Gamma_L}{D_L^k D_L^{k'}}\times v(k)v(k')\chi_B^L(k,\omega)\chi_B^L(k',\omega)\,,$$
$$\chi_{L,R}(k_z,k_z')=\frac{e^2}{8\pi}\,\frac{k_\parallel e^{-k_\parallel d}}{Y^d}\,\frac{1}{D_L^k D_R^{k'}}v(k)v(k')\times\chi_B^L(k,\omega)\chi_B^R(k',\omega)\,, \quad (2.12)$$

which, together with

$$\Gamma_{L,R}(k_\parallel,\omega)=1-\frac{1}{2D_{L,R}^S(k_\parallel,\omega)}-\frac{1}{2D_{L,R}^A(k_\parallel,\omega)}\,, \quad (2.13)$$

determines completely the density response of the coupled films in our infinite-barrier model. In (2.12) the notation $D_{L,R}^k(k_\parallel,\omega)$ implies taking $D_{L,R}^S$ ($D_{L,R}^A$) if k_z is even (odd).

We conclude this section with some brief comments concerning the normal modes of the system. In the limit $d\to\infty$, all coupling between the films vanishes and the normal modes correspond to poles of $\chi_{L,R}(k_z,k_z')$, which occur[8,9] only at the zeros of $D_{L,R}^{S,A}(k_\parallel,\omega)$. For any finite d, however, one can show that $\chi_{L,L}$ and $\chi_{L,R}$ are not singular at the zeros of $D_{L,R}^{S,A}$ but at the zeros of

$$Y^d(k_\parallel,\omega)=1-e^{-2k_\parallel d}\Gamma_L(k_\parallel,\omega)\Gamma_R(k_\parallel,\omega)\,. \quad (2.14)$$

The equation $Y^d(k_\parallel,\omega)=0$ therefore determines all the normal modes of the coupled films. An interesting special case is the limit $d\to 0$, $L\to\infty$, where (2.14) reduces to $1=D_R+D_L$ or

$$\int_{-\infty}^{\infty}\frac{dk_z}{2\pi}\,\frac{k_\parallel}{k_z^2+k_\parallel^2}\left(\frac{1}{\epsilon_B^L(k,\omega)}+\frac{1}{\epsilon_B^R(k,\omega)}\right)=0\,. \quad (2.15)$$

If $\epsilon_B^R=1$ (single metal-vacuum interface), (2.15) reduces to the dispersion relation of surface plasmons first obtained by Ritchie and Marusak[17] and Wagner.[18] If both films are of the same material

(2.14) can be factorized and one obtains uncoupled dispersion relations for the modes symmetric (ω_+) and antisymmetric (ω_-) about $z=0$,

$$Y^d_\pm(k_\parallel,\omega_\pm)=1\mp e^{-k_\parallel d}\Gamma(k_\parallel,\omega_\pm)=0 \tag{2.16}$$

or

$$\frac{1}{D^S(k_\parallel,\omega_\pm)}+\frac{1}{D^A(k_\parallel,\omega_\pm)}=2(1\mp e^{k_\parallel d})\ . \tag{2.17}$$

Notice that in the limit $d\to 0$, the symmetric modes satisfy

$$D^S(k_\parallel,\omega_+)+D^A(k_\parallel,\omega_+)=0\ . \tag{2.18}$$

This equation may be rewritten

$$D^S_{2L}(k_\parallel,\omega_+)=\frac{1}{2}+\frac{2}{2L}\sum_{k_z=n\pi/2L} a_k\frac{k_\parallel}{k^2}\frac{1}{\epsilon_B(k,\omega_+)}=0, \tag{2.19}$$

with $n=0,2,4,\ldots$, which is the dispersion relation of the symmetric modes of an isolated film of thickness $2L$. In our model, therefore, the symmetric modes of the coupled systems become degenerate with those of a film of thickness $2L$ as $d\to 0$. This is not so for the antisymmetric modes of the coupled system, as we discuss in Sec. IV.

III. VAN DER WAALS INTERACTION ENERGY

We now assume that S_L and S_R are identical in composition and use the result (1.1) to obtain for the total exchange and correlation energy of the two films at separation d:

$$E_{XC}(d)=-\frac{\hbar}{2}\sum_{\vec{k}_\parallel}\int_c\frac{d\omega}{2\pi i}\int_0^1 d\lambda\, E^\lambda_{XC}(d)\ , \tag{3.1}$$

where

$$E^\lambda_{XC}(d)=\frac{4e^2}{L}\sum_{k_z} a_k v(k)\chi^\lambda_{L,L}(k_z,k_z)$$
$$-\frac{k_\parallel e^2}{2\pi}\left(\frac{2}{L}\right)^2\sum_{k_z,k_z'}{}' a_k a_{k'} v(k)v(k')\chi^\lambda_{L,L}(k_z,k_z')$$
$$+\frac{k_\parallel e^2}{4\pi}e^{-k_\parallel d}\left(\frac{2}{L}\right)^2\sum_{k_z,k_z'} a_k a_{k'} v(k)v(k')$$
$$\times\chi^\lambda_{L,R}(k_z,k_z')\ . \tag{3.2}$$

Here the prime on the double sum indicates that k_z, k_z' must be either both even or both odd multiples of π/L. We now use the result (2.12) of our model calculation to evaluate $E_{RC}(d)$ explicitly. For $d\to\infty$ the coupling vanishes and $\chi_{L,L}$ is given by (2.10). Using this in (3.2), we find

$$E_{XC}(\infty)=\hbar\sum_{\vec{k}_\parallel}\int_c\frac{d\omega}{2\pi i}\left(\sum_{k_z}\ln\epsilon_B(k,\omega)\right.$$
$$\left.+\ln D_S(k_\parallel,\omega)+\ln D_A(k_\parallel,\omega)\right). \tag{3.3}$$

This is just twice the total exchange and correlation energy of a film of width L [see Eq. (3) of Griffin, Kranz, and Harris[15] (GKH)]. As was first shown by Peuckert,[8] in the limit of large L, (3.3) can be written

$$E_{XC}(\infty)=2E_B+4E_S+\cdots, \tag{3.4}$$

where

$$E_B=\frac{\hbar V}{2}\int\frac{d\vec{k}}{(2\pi)^3}\int_c\frac{d\omega}{2\pi i}\ln\epsilon_B(k,\omega) \tag{3.5}$$

is the volume energy of one film and

$$E_S=\frac{\hbar A}{2}\int\frac{d\vec{k}_\parallel}{(2\pi)^2}\int_c\frac{d\omega}{2\pi i}\left[\ln D(k_\parallel,\omega)+\tfrac{1}{4}\ln\epsilon_B(k_\parallel,\omega)\right] \tag{3.6}$$

is the surface energy per surface. Other terms in the series (3.4) are of relative order $1/L$.

We now consider d finite and note the definition of the van der Waals energy

$$E_{VW}(d)=E_{XC}(d)-E_{XC}(\infty)\ . \tag{3.7}$$

Using (2.12) in (3.2) one can show, after a little algebra, that

$$[E^\lambda_{XC}(d)-E^\lambda_{XC}(\infty)]=-\frac{\partial}{\partial\lambda}\ln[1-e^{-2k_\parallel d}\Gamma^2_\lambda(k_\parallel,\omega)]$$

and hence

$$E_{VW}(d)=\frac{\hbar}{2}\sum_{\vec{k}_\parallel}\int_c\frac{d\omega}{2\pi i}\left[\ln Y^d_+(k_\parallel,\omega)+\ln Y^d_-(k_\parallel,\omega)\right]. \tag{3.8}$$

The van der Waals energy is thus completely determined by functions $Y^d_\pm(k_\parallel,\omega)$, whose zeros, as we have discussed, occur at the normal-mode frequencies of the coupled systems. Following an integration by parts we have

$$E_{VW}(d)=-\frac{\hbar}{2}\sum_{\vec{k}_\parallel}\int_c\frac{d\omega}{2\pi i}\,\omega\left(\frac{1}{Y^d_+}\frac{\partial}{\partial\omega}Y^d_+ +\frac{1}{Y^d_-}\frac{\partial}{\partial\omega}Y^d_-\right), \tag{3.9}$$

so that, as in GKH, the contour integral may be performed once we locate the zeros and poles of $Y^d_\pm(k_\parallel,\omega)$ on the positive real axis.

Our classification of these singularities is identical to that employed by GKH. Each pole of $Y^d_\pm$, along with its associated zero, can be traced back to a specific pole of the bulk dielectric function $\epsilon_B(k_\parallel,k_z,\omega)$. For each value of $k=(k_\parallel^2+k_z^2)^{1/2}$, $\epsilon_B(k,\omega)$ has a fixed number of poles (which we label q_n) occurring at the particle-hole frequencies $\omega_0(k_\parallel,k_z,q_n)$. Each pole has its associated zero, $\omega_B(k_\parallel,k_z,q_n)$, occurring at the normal-mode frequencies of a homogeneous electron gas.[19] Directly from its definition (2.11), one can see that D^S (D^A) has poles at the frequencies $\omega_B(k_\parallel,k_z,q_n)$ for k_z even (odd). Each pole has its associated zero (of *lower* frequency) $\omega_F(k_\parallel,k_z,q_n)$ at the normal-mode frequencies of a film of thickness L.

We are now in a position to discuss the analytic structure of $Y^d_\pm$. From (2.13) and (2.14) we note that $Y^d_\pm(k_\parallel,\omega)$ has poles at the zeros of $D^{S,A}(k_\parallel,\omega)$,

namely, $\omega = \omega_F(k_\parallel, k_z, q_n)$, and zeros whenever (2.17) is fulfilled, namely, at the normal-mode frequencies $\omega_\pm^d(k_\parallel, k_z, q_n)$ of the coupled films. The solutions of (2.17) corresponding to the single-plasmon zero q_M in ϵ_B are shown graphically in Fig. 2. Each of the zeros of ϵ_B gives rise to a similar structure and it is clear that in the limit $L \to \infty$, $Y_\pm^d(k_\parallel, \omega)$ like $D(k_\parallel, \omega)$ has a branch cut extending along the positive real axis. Quite generally, for a given $(k_\parallel, k_z, q_n)$, one has

$$\omega_-^d < \omega_F < \omega_+^d < \omega_B \ . \tag{3.10}$$

Performing the contour integral in (3.9) gives

$$E_{\rm VW}(d) = \frac{\hbar}{2} \sum_{k_\parallel} \sum_{k_z} \sum_{q_n} [\omega_+^d(k_\parallel, k_z, q_n) + \omega_-^d(k_\parallel, k_z, q_n) - 2\omega_F(k_\parallel, k_z, q_n)], \tag{3.11}$$

and we have reduced the van der Waals interaction to the difference in zero-point energy of the normal modes at separation d and at separation ∞.[20] As remarked in the Introduction, (3.11) is not restricted to the infinite-barrier model but depends only on the RPA. While our derivation of (3.8) was for the classical infinite-barrier model, this equation is, in fact, valid for any model of the surface, the appropriate functions $Y_\pm^d(k_\parallel, \omega)$ being given by (2.16) and (2.8).

Equation (3.11) may be separated into surface plasmon, mixed plasmon, and particle-hole contributions as follows. The total plasmon contribution originates from the single term q_M in the q_n summation. It can be separated off from the remainder since over a wide range of $k_\parallel$, k_z (i.e., for $k < k_c$, the critical wave vector), the plasmon zero of ϵ_B is split off from the particle-hole zeros. Inspection of Fig. 2 shows that for $k_z \geq 2\pi/L$, whatever the value of d,

$$\omega_\pm^d(k_\parallel, k_z, q_M) - \omega_F(k_\parallel, k_z, q_M) \sim 1/L \ . \tag{3.12}$$

These modes correspond to density fluctuations which extend throughout both films. They have frequencies close to the frequency of plasmons in a homogeneous system and give rise to the mixed-mode contribution to the van der Waals energy,

$$E_{\rm VW}^{\rm MM}(d) = \frac{\hbar}{2} \sum_{k_\parallel} \sum_{k_z \geq 2\pi/L} [\omega_+^d(k_\parallel, k_z, q_M) + \omega_-^d(k_\parallel, k_z, q_M) - 2\omega_F(k_\parallel, k_z, q_M)] \ , \quad k < k_c \ . \tag{3.13}$$

The remaining plasmon modes (those labeled by $k_z = 0, \pi/L$) can be shown to correspond to charge fluctuations localized near the surfaces. They form the symmetric and antisymmetric surface plasmons for the coupled films and have frequencies $\omega_\pm^d(k_\parallel)$ which depend strongly on d. In the limit of large L, they give rise to the surface-plasmon contribution to the van der Waals energy

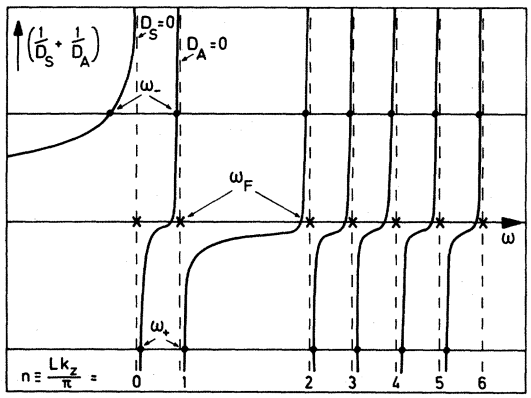

FIG. 2. Graphical solution (schematic) for the dispersion relations of the plasmon modes of two coupled films, as given by (2.17). The normal modes of an isolated film are denoted by ω_F and correspond to singularities of the left-hand side of (2.17). The modes are labeled by $k_z = n\pi/L$ and their spacing is of order $1/L$ for $n \geq 2$.

$$E_{\rm VW}^{\rm SP}(d) = \frac{\hbar A}{2} \int_0^{k_c} \frac{k_\parallel dk_\parallel}{2\pi} [\omega_+^d(k_\parallel) + \omega_-^d(k_\parallel) - 2\omega_{\rm SP}(k_\parallel)], \tag{3.14}$$

where $\omega_{\rm SP}(k_\parallel) = \omega_+^\infty(k_\parallel) = \omega_-^\infty(k_\parallel)$ is the surface-plasmon frequency at wave vector $k_\parallel$ for a half space. Equation (3.14) is the ansatz of Van Kampen, Nijboer, and Schram,[5] who showed that for large d (where only small values of $k_\parallel$ contribute to the integral) it is equivalent to the Lifschitz formula.[1] The remaining contribution to the van der Waals energy arises from all terms in (3.11) with $q_n \neq q_M$. The modes involved originate from particle-hole zeros of ϵ_B and we therefore refer to this contribution as the particle-hole contribution.

A direct numerical integration of (3.8) is straightforward using the equivalent form[14]

$$\epsilon_{\rm VW}(d) \equiv \frac{(\frac{4}{3}\pi r_s^3)^{2/3}}{2A} E_{\rm VW}(d) = \frac{6.068}{r_s^2} \int_0^\infty d\Omega \int_0^\infty S\, dS \ln[1 - e^{-2S\bar{d}} \Gamma^2(S, i\Omega)], \tag{3.15}$$

where $\Omega \equiv \omega/\epsilon_F$, $S \equiv k_\parallel/k_F$, $\bar{d} \equiv dk_F$. The result is given by the full curve shown in Fig. 3. For comparison we plot the Lifschitz formula,[1] which follows from (3.15) on the assumption that the bulk dielectric function is independent of $k_\parallel$, in which case one has

$$\Gamma(k_\parallel, \omega) \to \frac{1 - \epsilon_B(\omega)}{1 + \epsilon_B(\omega)} \ . \tag{3.16}$$

Since the region $k_\parallel \lesssim 1/d$ dominates the $k_\parallel$ sum, the Lifschitz approximation is clearly asymptotically correct. As d becomes smaller, this local approximation begins to break down because modes of shorter and shorter wavelength are becoming

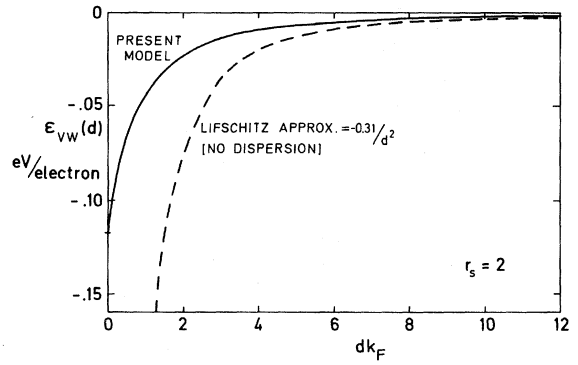

FIG. 3. Van der Waals interaction between two metal surfaces as a function of the separation d (in units of k_F^{-1}). Dotted line is Lifschitz approximation (no dispersion). Full line is infinite-barrier model, calculated from (3.15). For a more realistic model the interaction at small d ($d k_F \lesssim 4$) is modified due to the mixing of the electronic charge of the two films.

important. The divergence of the Lifschitz formula as $d \to 0$ is a result of the neglect of the electron-gas dispersion at larger values of $k_\parallel$.

We might remark on why the corrections to the Lifschitz result are so large even for relatively large values of d (see Fig. 3). In the local approximation, the surface plasmons have no dispersion, and correspond to δ-function charge sheets localized at the surface planes. This is true no matter what the wave vector. On the other hand, the inclusion of dispersion in infinite-barrier models leads to essentially exponential charge fluctuations which have a center of mass located at some point z_0 inside the metal films. Thus in the infinite-barrier model the surface charge-density fluctuations interact as though the films were a distance $(d+2z_0)$ apart, leading to a relative correction factor[21] of order $-4z_0/d$. However, a realistic model will lead to much smaller values of z_0 than the infinite-barrier model (possibly even with a changed sign). For this reason, one should view (3.15) as a lower bound for the magnitude of the van der Waals interaction energy.

In order to estimate the relative importance of plasmons and particle-hole excitations we have evaluated the surface-plasmon contribution (3.14) at $d=0$, where the relevant dispersion relations are readily obtainable from (2.17). The result is $E_{VW}^{SP}(d=0) = 0.105$ eV/electron versus $E_{VW}(d=0) = 0.117$ eV/electron using (3.15). This shows that the surface-plasmon excitations dominate the van der Waals energy for small as well as large d and that the mixed plasmon and particle-hole modes give rise to a relatively small correction. This result, which is presumably true for all models of the surface, indicates that a good estimate of the van der Waals energy can be obtained merely by inserting the dispersion relations of the collective surface-plasmon modes in (3.14). For this reason, the "hydrodynamic" model employed by Heinrichs[22] (see also Davies and Ninham[23]), when supplemented by an appropriate cutoff wave vector, gives a semiquantitative estimate of (3.8) for all d, in spite of its complete neglect of the particle-hole modes.[24]

IV. CONNECTION BETWEEN VAN DER WAALS AND SURFACE ENERGY

In Sec. III we showed that in the limit of $d \to \infty$, and for L large, the total exchange and correlation energy of the system is given by (3.4). Combining this result with the definition of the van der Waals energy (3.7), we have

$$E_{XC}(d=0) = 2E_B + 4E_S + E_{VW}(d=0), \tag{4.1}$$

namely, that the total exchange and correlation energy of the coupled films at zero separation equals that at infinite separation *plus* the work done against the van der Waals force in drawing the two films apart. This is *not* the exchange and correlation energy of a single film of thickness $2L$, which would be

$$E_{XC}^{2L} = 2E_B + 2E_S\ . \tag{4.2}$$

The difference between (4.1) and (4.2) will be referred to as a cleavage energy

$$E_{CL} \equiv E_{XC}(d=0) - E_{XC}^{2L} = 2E_S + E_{VW}(d=0). \tag{4.3}$$

Rewriting (4.3) in the form

$$2E_S = E_{CL} - E_{VW}(d=0), \tag{4.4}$$

one sees that the surface energy is the sum of the cleavage energy (namely, the energy required to isolate one-half of a film from the other) *plus* the work done against the van der Waals force in separating the isolated films to infinite separation. In the infinite-barrier model, these two contributions to the surface energy are quite distinct.[25]

In order to understand the physical origin of the cleavage energy, we return to a normal-mode analysis and note first that the total exchange and correlation energy of an isolated film of thickness $2L$ may be written[15]

$$E_{XC}^{2L} = \frac{\hbar}{2} \sum_{\vec{k}_\parallel, q_n} \sum_{k_z = n\pi/2L} \left[\omega_F^{2L}(k_\parallel, k_z, q_n) - \omega_0(k_\parallel, k_z, q_n) \right], \tag{4.5}$$

where ω_F^{2L} are the normal-mode frequencies of a film of thickness $2L$. Second, the total exchange and correlation energy of coupled films each of thickness L is

$$E_{XC}(d) = \frac{\hbar}{2} \sum_{\vec{k}_\parallel, q_n} \sum_{k_z = n\pi/L} \left[\omega_+^d(k_\parallel, k_z, q_n) \right.$$

$$+\omega_{-}^{d}(k_{\parallel}, k_z, q_n) - 2\omega_0(k_{\parallel}, k_z, q_n)]. \quad (4.6)$$

Finally, we observed at the end of Sec. II that at zero separation the symmetric modes of the coupled systems are degenerate with those of a film of length $2L$, that is,

$$\omega_{+}^{0}(k_{\parallel}, n\pi/L, q_n) = \omega_F^{2L}(k_{\parallel}, 2n\pi/2L, q_n), \quad (4.7)$$

where n is any positive integer. Thus from (4.3), (4.5), and (4.6), we have

$$E_{CL} = \frac{\hbar}{2}\sum_{\vec{k}_{\parallel}, q_n}\Bigg(\sum_{n\ \text{even}}[\omega_{-}^{0}(k_{\parallel}, n\pi/2L, q_n) - \omega_0(k_{\parallel}, n\pi/2L, q_n)] - \sum_{n\ \text{odd}}[\omega_F^{2L}(k_{\parallel}, n\pi/2L, q_n) - \omega_0(k_{\parallel}, n\pi/2L, q_n)]\Bigg). \quad (4.8)$$

One sees that the cleavage energy is the total change in the zero-point energy of the antisymmetric modes of a film on introducing a plane barrier at the film center ($z=0$). That only antisymmetric modes are involved is due to the specular scattering boundary condition which we have assumed. For a symmetric mode, the electric field driving the electrons is symmetric with respect to reflection and the electron trajectories in the two halves of the film are mirror images of each other. The introduction of a plane barrier at the film center does not change these trajectories as long as the scattering is specular. For an antisymmetric mode, however, the electron trajectories are not mirror images of each other and the introduction of an impenetrable barrier disturbs the system and alters the mode frequencies.

The normal-mode formula (4.8) can, as usual, be separated into surface-plasmon, mixed-plasmon, and particle-hole parts. In the limit of large L, the surface-plasmon contribution is

$$E_{CL}^{SP} = \frac{\hbar A}{2}\int_0^{k_c}\frac{k_{\parallel}\,dk_{\parallel}}{2\pi}\{[\omega_{-}^{0}(k_{\parallel}) - \omega_{\max}(k_{\parallel})] - \tfrac{1}{2}[\omega_P(k_{\parallel}) - \omega_{\max}(k_{\parallel})]\}, \quad (4.9)$$

where ω_p is the bulk-plasmon frequency and $\omega_{\max}$ is the maximum bulk-particle-hole frequency.[15] This quantity can be easily calculated and is large and negative. Although $E_{VW}(0)$ and E_{CL} have large surface-plasmon contributions, these tend to cancel each other when inserted in (4.4) and one finds the surface-plasmon contribution to E_S to be[26]

$$E_S^{SP} = \frac{\hbar A}{2}\int_0^{k_c}\frac{k_{\parallel}\,dk_{\parallel}}{2\pi}\{2[\omega_{SP}(k_{\parallel}) - \omega_{\max}(k_{\parallel})] - \tfrac{3}{2}[\omega_P(k_{\parallel}) - \omega_{\max}(k_{\parallel})]\}, \quad (4.10)$$

TABLE I. Cleavage energy E_{CL}, van der Waals energy $E_{VW}(0)$, and surface correlation energy E_S as a function of r_S. The values for E_S are taken from Ref. 14. Units are eV/(surface electron).

r_s	E_{CL}	$-E_{VW}(0)$	E_S
2	0.108	0.118	0.227
4	0.067	0.068	0.136
6	0.050	0.048	0.098

which is identical to Eq. (20) of GKH. Equation (4.10) gives a negative contribution to the surface correlation energy which is much smaller in magnitude than the surface-plasmon contribution to E_{CL} and $E_{VW}(0)$. In fact, the surface correlation energy is dominated by the particle-hole modes and the plasmon contribution can almost be neglected.[15]

Some recent estimates of the plasmon contribution to the surface energy[11,12] are actually estimates of $-E_{VW}(0)$. As (4.4) demonstrates, this is *not* the surface energy. The reason why these authors appear to give a sensible estimate of E_S is illustrated in Table I, where E_{CL} and $-E_{VW}(d=0)$ are explicitly tabulated. One sees that for all r_s, E_{CL} and $-E_{VW}(d=0)$ each contribute about one-half of the surface energy. Thus, incorrectly assuming the work done against the van der Waals force to be the surface energy only leads to an error of a factor of about 2. In our opinion, however, the decomposition of E_S into cleavage and van der Waals parts is unnatural in that neither has a well-defined meaning outside the semiclassical infinite-barrier model.

V. SUMMARY AND CONCLUDING REMARKS

We have presented a theory of the van der Waals interaction between two metallic films using a model which includes the complete spectrum of the normal modes. In particular, we have shown that $E_{VW}(d)$ is given by a natural generalization of the ansatz of Van Kampen, Nijboer, and Schram[5] even when a complete nonlocal RPA description of the dynamics of the bounded electron gas is used instead of a local approximation.[20] We find that when the correct dispersion relations are employed the surface-plasmon contribution dominates the van der Waals energy. For a given value of d, $E_{VW}(d)$ is sensitive to the dispersion relation for $k_{\parallel} \lesssim 1/d$, and it is easily seen that a proper account of the dispersion is necessary when d becomes comparable with λ_{TF} (Thomas-Fermi wavelength). The only previous discussions[22,23] of the effect of dispersion on the van der Waals interaction are based on a plasmon-pole approximation. The main limitation of our calculations is that they are based on

the semiclassical infinite-barrier model.

In Sec. IV we made a detailed study of the relationship between the van der Waals energy and the surface correlation energy. It was demonstrated that the latter is not equal to the work done against the van der Waals force in increasing d from 0 to ∞, but that there is an extra contribution (E_{CL}) which can be thought of as a cleavage energy. Explicit numerical calculations show that the contribution of E_{CL} to the surface energy is roughly equal in magnitude to the work done against the van der Waals force. The cleavage energy arises because the antisymmetric modes of a film of thickness $2L$ are different from those of two adjacent films of thickness L. Thus the act of erecting a plane potential barrier impenetrable to electrons costs a certain amount of energy and this must be added to the work done against the mutual attraction in order to arrive at the surface energy. The surface-plasmon contribution to E_{CL} was found to be negative and slightly greater in magnitude than the surface-plasmon contribution to $E_{VW}(0)$. This explains why surface plasmons, though they dominate the van der Waals energy, make a relatively small (and negative) contribution to the surface correlation energy. In our semiclassical RPA model (see Refs. 8 and 15), E_S is dominated by the zero-point energy of the particle-hole modes.

In Sec. IV, we remarked on some of the deficiencies of the infinite-barrier model we employed for the surfaces and emphasized that our numerical results for the van der Waals attraction form a lower bound. The most important physical deficiency of the infinite-barrier model is that the electronic charge is not allowed to relax outside the background. The consequent piling up of negative charge at the infinite barriers is responsible for the strong linear dispersion of surface plasmons predicted by the model, as well as for the relatively large asymptotic corrections to the image potential[27] and the van der Waals energy. In a more general model, one would expect much smaller corrections. As we have noted in the Introduction, the normal-mode formula (3.11) is valid for any RPA model. This fact, coupled with our conclusion that only the surface-plasmon modes are important, enables one to estimate $E_{VW}(d)$ for any model and for any separation from a knowledge of the dispersion relation of the surface plasmons. For example, the recent calculations of Feibelman,[28] who used a self-consistently determined surface potential barrier, imply a negative long-wavelength dispersion. Using this result in (3.14) would lead to negative leading-order corrections to the asymptotic Lifschitz force (i.e., increased attraction). At smaller values of d, plasmons of larger wave vectors begin to play a role and there is some evidence that in this region the dispersion relation is less sensitive to the details of the surface.[29] This suggests that as d becomes smaller, $E_{VW}(d)$ tends to approach our infinite-barrier-model results (see Fig. 2). Of course, in a more general model it makes no sense to speak of a van der Waals interaction if the distance d is so small that the electron densities overlap.

Experimentally there seems little hope that direct measurements can be made of the van der Waals attraction between two metal surfaces with a separation small enough to make corrections to the Lifschitz theory significant. On the other hand, similar effects might be usefully studied through physisorption of inert-gas atoms on metal substrates.[30] For example, the equilibrium position of a He atom physisorbed on a simple metal is about 5 Å from the surface. At such distances, however, it is misleading to include the effect of electron gas dispersion without using a more realistic model of the metal surface.[31]

As it was introduced in Sec. IV, the cleavage energy is a feature of the infinite-barrier model. A contribution to the surface correlation energy of this type is always involved, however, when an electron gas is separated into two parts, though in general both symmetric and antisymmetric modes will have shifted frequencies. For a more general model, where there are also kinetic, electrostatic, and exchange contributions to the cleavage energy, the separation of the surface correlation energy into cleavage and van der Waals parts is probably not useful.

In concluding, we note that Harris and Jones[14] have argued that the surface correlation energy should be relatively insensitive to the surface details. While this might be true if plasmons formed the dominant contributions, it is not so clear in the light of the conclusion of the present paper (and of GKH) that only the particle-hole modes are important. We feel that further progress concerning this question must await a better treatment of the particle-hole modes in a bounded system. One interesting calculation in this regard would be the evaluation of the total surface correlation energy to second order in the Coulomb potential for a realistic model of the surface. Pines and Nozières[2] have developed a theory of the bulk correlation energy by treating the short-wavelength contributions to second order. A similar approach might be fruitful in dealing with the surface correlation energy.

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[19]Following GKH, the pole and zero of largest frequency are labeled by q_M. For $k < k_c$, $\omega_B(k_\parallel, k_z, q_M)$ is the bulk-plasmon frequency $\omega_P(k)$ and is well separated from the other zeros. The associated pole, $\omega_0(k_\parallel, k_z, q_M) = (k^2 + 2kk_F)/2m$, is denoted $\omega_{\max}(k)$.

[20]*Note added in proof.* Our RPA equations [(2.1)–(2.3)] are completely equivalent to those of A. A. Lusknikov and V. V. Malov [Phys. Lett. A 49, 317 (1974)]. However, the correct expression (3.11) was not obtained for $E_{VW}(d)$ in this reference.

[21]Corrections of this kind have been obtained analytically by Heinrichs (Ref. 22), who used an infinite-barrier model together with a plasmon-pole (or hydrodynamic) approximation for the bulk dielectric function.

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