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Free energies across inhomogeneous dispersive media: III. Metals and retardation effects

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Abstract. A general expression, including retardation effects, is derived for the van der Waals free energy of interaction between two spatially dispersive semi-infinite half spaces using the infinite barrier model in which the currents are reflected specularly at the interface. The answer is given in terms of model independent longitudinal and transverse bulk dielectric permittivities which are functions of the wavenumber. Numerical estimates of the effects of spatial dispersion on the interaction energy are given using the hydrodynamic model for the permittivities. The choice for the hydrodynamic model is based on its analytical simplicity and its ability to yield an estimate of the minimum effect of spatial dispersion. It is demonstrated that, for two like metallic half spaces across vacuum, spatial dispersion can cause at least a 20% reduction in the effective Hamaker 'constant' at separations $\simeq 4k_F^{-1}$ where k_F is the Fermi wavenumber. Some inadequacies in the hydrodynamic model are pointed out.

1. Introduction

There is currently much interest in van der Waals forces between macroscopic bodies. The practical applications of such calculations are of great importance and relevant to many areas of science and technology. Modern theoretical studies stem from the early work of Lifshitz (1956) who studied the van der Waals interaction between two dielectric bodies across a vacuum. More recently, emphasis has been placed on the modifications of the Lifshitz expression due to spatial dispersion in the material media. In general this problem is very difficult. However a fairly simple model which regards the material surfaces as infinite barriers from which the charges are specularly reflected is amenable to analysis.

Recently we (Chan and Richmond 1975a, b (I), 1975c; see also Lushnikov and Malov 1974) have demonstrated how free energies for such a system may be derived without using a particular model for the dielectric permittivity as has been implicit in some earlier works (Davies and Ninham 1972, Richmond *et al* 1972, Chang *et al* 1971, Heinrichs 1975a, b). For the case of two media interacting across a vacuum an interesting feature emerged from our calculations. We demonstrated that unlike the result for simple dielectrics, the work done against van der Waals forces and the surface free energy differ by a 'healing' or 'cleavage' energy. A similar result has been obtained independently by Harris and Griffin (1975) and Wikborg and Inglesfield (1975). The origin of this energy is quite simple to understand. In order to create a surface in this model from a bulk

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medium it is necessary to cleave the medium first by erecting a reflecting barrier before pulling the surfaces apart against van der Waals forces. Now because of the nature of specular reflection, the set of modes for a medium of width 2L differ from those appropriate to two adjacent media each of width L. The energy involved is therefore non-zero and contributes to the surface energy. In a recent paper Heinrichs (1975b) argues that the surface energy is to be identified solely with the work done against van der Waals forces and that the cleavage energy given by the model is unphysical. Now in a more realistic system, which accounts in more detail for the readjustment of charge density, at an interface, at the moment of cleavage, one will not obtain such a simple splitting between 'cleavage' and van der Waals free energy. However there must be a 'cleavage' contribution. Only a study of a more realistic model can resolve the question of its magnitude.

The effects of spatial dispersion on van der Waals interactions have also been studied recently by Agarwal (1975) and Barnes (1975). Agarwal's model differed slightly in that he imposed diffuse reflection of charges at an interface rather than specular reflection. In this case it is not possible to obtain a result valid for a general dielectric permittivity but a particular choice must be made and Agarwal used the hydrodynamic model for the permittivity. In terms of this model the diffuse boundary condition effectively says that $J = \lambda J'$ where J' is the normal derivative of the normal component of the current $\boldsymbol{J}$ and λ is a model-dependent parameter which tends to zero in the limit of no spatial dispersion. (Specular reflection insists that $J = 0$.) The final result obtained by Agarwal does not appear to differ qualitatively from that obtained using specular boundary condition; however, no detailed comparisons have been made.

Having obtained the result for the non-retarded van der Waals interaction between two spatially dispersive media across vacuum, we computed the expression for the particular case of two like media characterized by the familiar hydrodynamic dielectric permittivity. We found, as did Harris and Griffin, that spatial dispersion significantly reduced the van der Waals interaction energy from the value given by Lifshitz theory at distances comparable with the inverse term wavenumber, k_{F}^{-1}. What we did not expect however was that reductions of up to 10% would be still evident at distances $\sim 10k_{\mathrm{F}}^{-1}$ where retardation effects were also beginning to come into play. Now complete characterization of the interparticle potential is of some importance in this régime for colloid science applications; therefore it is necessary to evaluate fully van der Waals interaction energy in this régime. This is the object of this paper. The method we follow is essentially that used in our earlier papers in that the solution for the inhomogeneous system is constructed using a set of auxiliary homogeneous systems. However rather than evaluating a response function we merely obtain the secular determinant for the normal mode frequencies of the surface plasmons and use this directly to obtain the van der Waals interaction energy following standard prescriptions (van Kampen *et al* 1968; Richmond and Ninham 1971; Mitchell and Richmond 1974). The details of the derivation of the free energy of interaction are given in §2 and §3. A model calculation is then done in which the spatially dispersive medium is modelled using hydrodynamic-type permittivities.

2. Retarded response function

To obtain the free energy of interaction of two spatially dispersive media interacting across a vacuum gap within the framework of our model it is first necessary to obtain the response of a uniform, homogeneous spatially dispersive medium to a fluctuating surface current (Chan and Richmond 1975b, Flores 1973). Consider then a uniform medium subject to a planar surface current $\tilde{\boldsymbol{J}}(x; y)\delta(z - z')$. (The z component of the current vector is zero.) The retarded response is determined by Maxwell's equations. Thus, in an obvious notation,

$$\nabla \times \tilde{\boldsymbol{E}} = (\mathrm{i}\omega/c)\ \tilde{\boldsymbol{B}} \tag{2.1}$$

$$\nabla \times \tilde{\boldsymbol{H}} = (4\pi/c)\tilde{\boldsymbol{J}} - (\mathrm{i}\omega/c)\tilde{\boldsymbol{D}} \tag{2.2}$$

$$\nabla \cdot \tilde{\boldsymbol{D}} = 4\pi\tilde{\rho} \tag{2.3}$$

$$\nabla \cdot \tilde{\boldsymbol{B}} = 0. \tag{2.4}$$

In the following we shall ignore magnetic effects and assume $\tilde{\boldsymbol{B}} = \tilde{\boldsymbol{H}}$. Now from equations (2.1) and (2.2) we have

$$\nabla(\nabla \cdot \tilde{\boldsymbol{E}}) - \nabla^2\tilde{\boldsymbol{E}} - (\omega^2/c^2)\tilde{\boldsymbol{D}} = (4\pi\,\mathrm{i}\omega/c^2)\tilde{\boldsymbol{J}}. \tag{2.5}$$

Now we introduce Fourier transforms such that

$$\tilde{A}(\boldsymbol{r}) = \int \frac{\mathrm{d}^3\boldsymbol{q}}{(2\pi)^3}\exp(\mathrm{i}\,\boldsymbol{q} \cdot \boldsymbol{r})A(\boldsymbol{q}). \tag{2.6}$$

Equation (2.5) then becomes

$$-\boldsymbol{q}(\boldsymbol{q} \cdot \boldsymbol{E}) + q^2\boldsymbol{E} - (\omega^2/c^2)\boldsymbol{D} = (4\pi\,\mathrm{i}\omega/c^2)\boldsymbol{J}. \tag{2.7}$$

It is convenient to resolve the electric field into longitudinal and transverse components i.e.,

$$\boldsymbol{E} = \boldsymbol{E}_{\mathrm{L}} + \boldsymbol{E}_{\mathrm{T}}$$

where

$$\boldsymbol{E}_{\mathrm{L}} = \boldsymbol{q}(\boldsymbol{q} \cdot \boldsymbol{E})/q^2; \qquad \boldsymbol{E}_{\mathrm{T}} = (\boldsymbol{q} \times \boldsymbol{E}) \times \boldsymbol{q}/q^2. \tag{2.8}$$

The displacement vector is related to the electric field via the longitudinal and transverse permittivities ϵ_{L}, ϵ_{T} i.e.,

$$\boldsymbol{D} = \epsilon_{\mathrm{L}}\boldsymbol{E}_{\mathrm{L}} + \epsilon_{\mathrm{T}}\boldsymbol{E}_{\mathrm{T}}. \tag{2.9}$$

The solution to equation (2.7) is now readily obtained. Thus

$$\boldsymbol{E} = \frac{4\pi\,\mathrm{i}\omega}{c^2(q^2 - \omega^2\epsilon_{\mathrm{T}}/c^2)}\frac{(\boldsymbol{q} \times \boldsymbol{J}) \times \boldsymbol{q}}{q^2} + \frac{4\pi}{\mathrm{i}\omega\epsilon_{\mathrm{L}}}\frac{\boldsymbol{q}(\boldsymbol{q} \cdot \boldsymbol{J})}{q^2} \tag{2.10}$$

and

$$\boldsymbol{D} = \frac{4\pi\,\mathrm{i}\omega\epsilon_{\mathrm{T}}}{c^2(q^2 - \omega^2\epsilon_{\mathrm{T}}/c^2)}\frac{(\boldsymbol{q} \times \boldsymbol{J}) \times \boldsymbol{q}}{q^2} + \frac{4\pi}{\mathrm{i}\omega}\frac{\boldsymbol{q}(\boldsymbol{q} \cdot \boldsymbol{J})}{q^2}. \tag{2.11}$$

Taking the Fourier transform of equation (2.1) and using equation (2.10) gives the magnetic induction

$$\boldsymbol{B} = \frac{4\pi\mathrm{i}}{c(q^2 - \omega^2\epsilon_{\mathrm{T}}/c^2)}(\boldsymbol{q} \times \boldsymbol{J}). \tag{2.12}$$

In order to later match the boundary conditions across the planar interfaces of our inhomogeneous system we must invert these transforms with respect to k, the z component of the vector $\boldsymbol{q} = (\boldsymbol{K}, k)$. It is convenient to introduce the vectors

$$\hat{\boldsymbol{K}} = \boldsymbol{K}/K; \hat{\boldsymbol{k}} = \boldsymbol{k}/k; \boldsymbol{J} = (\boldsymbol{J}_s, 0) \tag{2.13}$$

and note the relations

$$\begin{aligned}&\hat{\boldsymbol{K}} \cdot \boldsymbol{q} = K; \qquad \hat{\boldsymbol{k}} \cdot \boldsymbol{q} = k;\\ &\hat{\boldsymbol{K}} \cdot (\boldsymbol{q} \times \boldsymbol{J}) = (k/K)|\boldsymbol{J}_s \times \boldsymbol{K}|; \qquad \hat{\boldsymbol{k}} \cdot (\boldsymbol{q} \times \boldsymbol{J}) = |\boldsymbol{K} \times \boldsymbol{J}_s|.\end{aligned} \tag{2.14}$$

We now obtain the component of $\boldsymbol{D}$ perpendicular to the planar surface from

$$D^{\perp}(\boldsymbol{K}; z, z') = \frac{4\pi}{\mathrm{i}\omega} \int_{-\infty}^{\infty} \frac{\mathrm{d}k}{2\pi} \exp[\mathrm{i}k(z - z')] \frac{k}{(q^2 - \omega^2 \epsilon_{\mathrm{T}}/c^2)} (\boldsymbol{K} \cdot \boldsymbol{J}_s); \tag{2.15}$$

the component of the electric field $\boldsymbol{E}$ parallel to $\boldsymbol{K}$ from (2.10),

$$E^{\parallel}(\boldsymbol{K}; z; z') = \frac{4\pi}{\mathrm{i}\omega} \left(\frac{\boldsymbol{K} \cdot \boldsymbol{J}_s}{K}\right) \int_{-\infty}^{\infty} \frac{\mathrm{d}k}{2\pi} \exp[\mathrm{i}k(z - z')] \left(\frac{K^2}{q^2 \epsilon_{\mathrm{L}}} - \frac{(\omega^2/c^2)k^2}{(q^2 - \omega^2 \epsilon_{\mathrm{T}}/c^2)q^2}\right); \tag{2.16}$$

the normal component of $\boldsymbol{B}$ from (2.12)

$$B^{\perp}(\boldsymbol{K}; z; z') = \frac{4\pi \mathrm{i}}{c} \frac{|\boldsymbol{K} \times \boldsymbol{J}_s|}{K} \int_{-\infty}^{\infty} \frac{\mathrm{d}k}{2\pi} \exp[\mathrm{i}k(z - z')] \frac{1}{(q^2 - \omega^2 \epsilon_{\mathrm{T}}/c^2)}; \tag{2.17}$$

the component of $\boldsymbol{B}$ parallel to $\boldsymbol{K}$ from (2.12)

$$B^{\parallel}(\boldsymbol{K}; z; z') = \frac{4\pi \mathrm{i}}{c} |\boldsymbol{K} \times \boldsymbol{J}_s| \int_{-\infty}^{\infty} \frac{\mathrm{d}k}{2\pi} \exp[\mathrm{i}k(z - z')] \frac{k}{(q^2 - \omega^2 \epsilon_{\mathrm{T}}/c^2)}. \tag{2.18}$$

Our solution must satisfy the following boundary condition:

$$B^{x,y}(z'_+; z') - B^{x,y}(z'_-; z') = 4\pi J_s^{y,x}/c.$$

From equation (2.11) we see that this implies

$$\int_{-\infty}^{\infty} \frac{\mathrm{d}k}{2\pi} \frac{\mathrm{i}k\, \mathrm{e}^{\mathrm{i}k0^+}}{q^2 - \omega^2 \epsilon_{\mathrm{T}}/c^2} - \int_{-\infty}^{\infty} \frac{\mathrm{d}k}{2\pi} \frac{\mathrm{i}k\, \mathrm{e}^{\mathrm{i}k0^-}}{q^2 - \omega^2 \epsilon_{\mathrm{T}}/c^2} = -1. \tag{2.19}$$

To see this consider the following integral†

$$I = \lim_{z \to 0} \int_{-\infty}^{\infty} \frac{\mathrm{d}k}{2\pi} \frac{\mathrm{i}k\, \mathrm{e}^{\mathrm{i}kz}}{q^2 - \omega^2 \epsilon_{\mathrm{T}}/c^2}. \tag{2.20}$$

Noting that $\lim_{q \to \infty} \epsilon_{\mathrm{T}}(q; \omega) \to 1 + \mathrm{O}(q^{-n}), n \geqslant 2$, we have

$$I = \lim_{z \to 0} \left(\int_{-\infty}^{\infty} \frac{\mathrm{dk}}{2\pi} \frac{\mathrm{i}k\, \mathrm{e}^{\mathrm{i}kz}}{q^2 - \omega^2/c^2} - \frac{\omega^2}{c^2} \int_{-\infty}^{\infty} \frac{\mathrm{d}k}{2\pi} \frac{\mathrm{i}k(1 - \epsilon_{\mathrm{T}})\, \mathrm{e}^{\mathrm{i}kz}}{(q^2 - \omega^2/c^2)(q^2 - \omega^2 \epsilon_{\mathrm{T}}/c^2)} \right]. \tag{2.21}$$

† We are grateful to Dr B Davies for this derivation.

If we make the physically reasonable assumption that ϵ_T is a function of $|\boldsymbol{q}|$ only we may let $z \to 0$ with impunity in the second term on the RHS and the integrand is then seen to be well behaved as $k \to \infty$ and is an odd function of k. The integral is therefore zero. The first integral may be evaluated after it is noted that ω must have a small positive imaginary part to ensure we are dealing with retarded time-dependent quantities. This determines the position of the poles in the complex k plane and we obtain

$$I = -\tfrac{1}{2}\,\mathrm{sgn}\,(z). \tag{2.22}$$

Equation (2.19) readily follows from equation (2.22).

3. Retarded free energy of interaction

Consider now two semi-infinite half spaces of spatially dispersive media separated by a vacuum. The bulk dielectric permittivities are $\epsilon_{1,\mathrm{L}}, \epsilon_{1,\mathrm{T}}, \epsilon_{3,\mathrm{L}}$ and $\epsilon_{3,\mathrm{T}}$. The vacuum layer has width $2l$ and we shall choose the axis of a cartesian coordinate system perpendicular to the interfaces which coincide with the planes $z = \pm l$. The free energy of interaction is then given by the following:

$$F = k_{\mathrm{B}}T \sum_{\xi_n=0}^{\infty}{}' \int \frac{\mathrm{d}^2\boldsymbol{K}}{(2\pi)^2} \ln D(\boldsymbol{K}, \mathrm{i}\xi_n) \tag{3.1}$$

where $D(\boldsymbol{K}, \mathrm{i}\xi_n)$ is a secular determinant evaluated at imaginary frequencies $\mathrm{i}\xi_n = \mathrm{i}\,2n\pi k_{\mathrm{B}}T/\hbar$. The secular determinant may be obtained from the mode equations for electromagnetic surface waves in the above system. Strictly $D(\mathrm{i}\xi)$ is the analytic continuation of $D(\omega)$ which is obtained by including incoming and outgoing waves. However it may be demonstrated that $D(\mathrm{i}\xi)$ may be obtained by simply considering 'outgoing waves' evaluated at the imaginary frequencies $\mathrm{i}\xi_n$ (Schram 1973, Langbein 1973).

Thus following the procedure in I and substituting $\omega \to \mathrm{i}\xi$ in equations (2.15)–(2.18) of the previous section we obtain

$$E^{\parallel}(\boldsymbol{K}; z) = \begin{cases} -\dfrac{4\pi}{\xi K}\,\boldsymbol{K}\,.\,\boldsymbol{J}_{\mathrm{s}}^{4} \displaystyle\int_{-\infty}^{\infty} \frac{\mathrm{d}k}{2\pi} \exp[\mathrm{i}k(z-l)] \left(\frac{K^2}{q^2\epsilon_{3,\mathrm{L}}} + \frac{(\xi^2/c^2)k^2}{(q^2+\xi^2\epsilon_{3,\mathrm{T}}/c^2)q^2}\right) & z > l \qquad (3.2) \\[2ex] -\dfrac{4\pi}{\xi K}\left[\boldsymbol{K}\,.\,\boldsymbol{J}_{\mathrm{s}}^{3} \displaystyle\int_{-\infty}^{\infty} \frac{\mathrm{d}k}{2\pi} \exp[\mathrm{i}k(z-l)] \left(\frac{K^2}{q^2} + \frac{(\xi^2/c^2)k^2}{(q^2+\xi^2/c^2)q^2}\right)\right. & \\[2ex] \qquad \left. +\ \boldsymbol{K}\,.\,\boldsymbol{J}_{\mathrm{s}}^{2} \displaystyle\int_{-\infty}^{\infty} \frac{\mathrm{d}k}{2\pi} \exp[\mathrm{i}k(z+l)] \left(\frac{K^2}{q^2} + \frac{(\xi^2/c^2)k^2}{(q^2+\xi^2/c^2)q^2}\right)\right] & |z| < l \qquad (3.3) \\[2ex] -\dfrac{4\pi}{\xi K}\,\boldsymbol{K}\,.\,\boldsymbol{J}_{\mathrm{s}}^{1} \displaystyle\int_{-\infty}^{\infty} \frac{\mathrm{d}k}{2\pi} \exp[\mathrm{i}k(z+l)] \left(\frac{K^2}{q^2\epsilon_{1,\mathrm{L}}} + \frac{(\xi^2/c^2)k^2}{(q^2+\xi^2\epsilon_{1,\mathrm{T}}/c^2)q^2}\right) & z < -l \qquad (3.4) \end{cases}$$

$$B^{\perp}(\boldsymbol{K};z) = \begin{cases} \dfrac{4\pi\mathrm{i}}{cK}|\boldsymbol{K}\times \boldsymbol{J}_{\mathrm{s}}^4| \displaystyle\int_{-\infty}^{\infty} \frac{\mathrm{d}k}{2\pi}\frac{\exp[\mathrm{i}k(z-l)]}{(q^2+\xi^2\epsilon_{3,\mathrm{T}}/c^2)q^2} & z>l \quad (3.5) \\ \dfrac{4\pi\mathrm{i}}{cK}\left[|\boldsymbol{K}\times \boldsymbol{J}_{\mathrm{s}}^3| \displaystyle\int_{-\infty}^{\infty} \frac{\mathrm{d}k}{2\pi}\frac{\exp[\mathrm{i}k(z-l)]}{q^2+\xi^2/c^2} + |\boldsymbol{K}\times \boldsymbol{J}_{\mathrm{s}}^2| \int_{-\infty}^{\infty} \frac{\mathrm{d}k}{2\pi}\frac{\exp[\mathrm{i}k(z+l)]}{q^2+\xi^2/c^2}\right] & \\ |z|<l & (3.6) \\ \dfrac{4\pi\mathrm{i}}{cK}|\boldsymbol{K}\times \boldsymbol{J}_{\mathrm{s}}^1| \displaystyle\int_{-\infty}^{\infty} \frac{\mathrm{d}k}{2\pi}\frac{\exp[\mathrm{i}k(z+l)]}{q^2+\xi^2\epsilon_{1,\mathrm{T}}/c^2} & z<-l \quad (3.7) \end{cases}$$

$$D^{\perp}(\boldsymbol{K};z) = \begin{cases} -\dfrac{4\pi}{\xi}|\boldsymbol{K}\times \boldsymbol{J}_{\mathrm{s}}^4| \displaystyle\int_{-\infty}^{\infty} \frac{\mathrm{d}k}{2\pi}\frac{\exp[\mathrm{i}k(z-l)]k}{(q^2+\xi^2\epsilon_{3,\mathrm{T}}/c^2)} & z>l \quad (3.8) \\ -\dfrac{4\pi}{\xi}\left[|\boldsymbol{K}\times \boldsymbol{J}_{\mathrm{s}}^3| \displaystyle\int_{-\infty}^{\infty} \frac{\mathrm{d}k}{2\pi}\frac{\exp[\mathrm{i}k(z-l)]k}{q^2+\xi^2/c^2} + |\boldsymbol{K}\times \boldsymbol{J}_{\mathrm{s}}^2| \int_{-\infty}^{\infty} \frac{\mathrm{d}k}{2\pi}\right. & \\ \quad \left.\times \dfrac{\exp[\mathrm{i}k(z+l)k}{q^2+\xi^2/c^2}\right] & |z|<l \quad (3.9) \\ -\dfrac{4\pi}{\xi}\left[|\boldsymbol{K}\times \boldsymbol{J}_{\mathrm{s}}^2| \displaystyle\int_{-\infty}^{\infty} \frac{\mathrm{d}k}{2\pi}\frac{\exp[\mathrm{i}k(z+l)]k}{q^2+\xi^2\epsilon_{1,\mathrm{T}}/c^2}\right] & z<-l \quad (3.10) \end{cases}$$

$$B^{\parallel}(\boldsymbol{K};z) = \begin{cases} \dfrac{4\pi\mathrm{i}}{c}|\boldsymbol{K}\times \boldsymbol{J}_{\mathrm{s}}^4| \displaystyle\int_{-\infty}^{\infty} \frac{\mathrm{d}k\,\exp[\mathrm{i}k(z-l)]k}{2\pi(q^2+\xi^2\epsilon_{3,\mathrm{T}}/c^2)} & z>l \quad (3.11) \\ \dfrac{4\pi\mathrm{i}}{c}\left[|\boldsymbol{K}\times \boldsymbol{J}_{\mathrm{s}}^3| \displaystyle\int_{-\infty}^{\infty} \frac{\mathrm{d}k}{2\pi}\frac{\exp[\mathrm{i}k(z-l)]k}{q^2+\xi^2/c^2} + |\boldsymbol{K}\times \boldsymbol{J}_{\mathrm{s}}^2| \int_{-\infty}^{\infty} \frac{\mathrm{d}k}{2\pi}\right. & \\ \quad \left.\times \dfrac{\exp[\mathrm{i}k(z+l)]k}{q^2+\xi^2/c^2}\right] & |z|<l \quad (3.12) \\ \dfrac{4\pi\mathrm{i}}{c}|\boldsymbol{K}\times \boldsymbol{J}_{\mathrm{s}}^1| \displaystyle\int_{-\infty}^{\infty} \frac{\mathrm{d}k\,\exp[\mathrm{i}k(z+l)]k}{2\pi(q^2+\xi^2\epsilon_{1,\mathrm{T}}/c^2)} & z<-l. \quad (3.13) \end{cases}$$

The currents $\boldsymbol{J}^1$ to $\boldsymbol{J}_{\mathrm{s}}^4$ are now *fictitious* fluctuating surface currents of our inhomogeneous system and are determined by imposing the usual boundary conditions. Thus continuity of $E^{\parallel}$ at $z = \pm l$ gives

$$\left(\frac{\xi}{c\hat{\epsilon}_{3,\mathrm{T}}} + \frac{K}{\hat{\epsilon}_{3,\mathrm{L}}}\right)(\boldsymbol{K}\,.\,\boldsymbol{J}_{\mathrm{s}}^4) = s\,\mathrm{e}^{-2sl}(\boldsymbol{K}\,.\,\boldsymbol{J}_{\mathrm{s}}^2) + s(\boldsymbol{K}\,.\,\boldsymbol{J}_{\mathrm{s}}^3) \tag{3.14}$$

$$\left(\frac{\xi}{c\hat{\epsilon}_{1,\mathrm{T}}} + \frac{K}{\hat{\epsilon}_{1,\mathrm{L}}}\right)(\boldsymbol{K}\,.\,\boldsymbol{J}_{\mathrm{s}}^1) = s(\boldsymbol{K}\,.\,\boldsymbol{J}_{\mathrm{s}}^2) + s\,\mathrm{e}^{-2sl}(\boldsymbol{K}\,.\,\boldsymbol{J}_{\mathrm{s}}^3) \tag{3.15}$$

where

$$\frac{1}{\hat{\epsilon}_{\alpha,\mathrm{T}}} = \frac{2\xi}{c}\int_{-\infty}^{\infty} \frac{\mathrm{d}k}{2\pi}\frac{k^2}{q^2(q^2+\xi^2\epsilon_{\alpha,\mathrm{T}}/c^2)} \tag{3.16}$$

$$\frac{1}{\hat{\epsilon}_{\alpha,\mathrm{L}}} = 2K\int_{-\infty}^{\infty} \frac{\mathrm{d}k}{2\pi}\frac{1}{q^2\epsilon_{\alpha,\mathrm{L}}} \tag{3.17}$$

and

$$s^2 = K^2 + \xi^2/c^2$$

The terms on the RHS of equations (3.14)–(3.15) are obtained by evaluating the integrals in equation (3.3).

Similarly continuity of $B^{\perp}$ at $z = \pm l$ gives

$$\frac{1}{\eta_3}|\boldsymbol{K} \times \boldsymbol{J}_s^4| = |\boldsymbol{K} \times \boldsymbol{J}_s^3| + \mathrm{e}^{-2sl}|\boldsymbol{K} \times \boldsymbol{J}_s^2| \tag{3.18}$$

$$\frac{1}{\eta_1}|\boldsymbol{K} \times \boldsymbol{J}_s^1| = |\boldsymbol{K} \times \boldsymbol{J}_s^3|\,\mathrm{e}^{-2sl} + |\boldsymbol{K} \times \boldsymbol{J}_s^2| \tag{3.19}$$

where

$$\frac{1}{\eta_\alpha} = 2s\int_{-\infty}^{\infty}\frac{\mathrm{d}k}{2\pi}\frac{1}{q^2 + \xi^2\epsilon_{\alpha,\mathrm{T}}/c^2}. \tag{3.20}$$

Matching $D^{\perp}$ and $B^{\parallel}$ and evaluating all the integrals (using arguments similar to those invoked to derive equation (2.19) to evaluate those arising from equations (3.8), (3.10), (3.11), and (3.13)) we obtain

$$(\boldsymbol{K}.\boldsymbol{J}_s^4) = \mathrm{e}^{-2sl}(\boldsymbol{K}.\boldsymbol{J}_s^2) - (\boldsymbol{K}.\boldsymbol{J}_s^3) \tag{3.21}$$

$$(\boldsymbol{K}.\boldsymbol{J}_s^1) = -(\boldsymbol{K}.\boldsymbol{J}_s^2) + \mathrm{e}^{-2sl}(\boldsymbol{K}.\boldsymbol{J}_s^3) \tag{3.22}$$

$$|\boldsymbol{K} \times \boldsymbol{J}_s^4| = \mathrm{e}^{-2sl}|\boldsymbol{K} \times \boldsymbol{J}_s^2| - |\boldsymbol{K} \times \boldsymbol{J}_s^3| \tag{3.23}$$

$$|\boldsymbol{K} \times \boldsymbol{J}_s^1| = -|\boldsymbol{K} \times \boldsymbol{J}_s^2| + \mathrm{e}^{-2sl}|\boldsymbol{K} \times \boldsymbol{J}_s^3|. \tag{3.24}$$

Equations (3.14), (3.15), (3.21) and (3.22) yield the 'secular determinant' for electric modes (P modes).

$$D_{\mathrm{E}}(\boldsymbol{K}; \mathrm{i}\xi) = 1 - \Delta_1\Delta_3\,\mathrm{e}^{-2sl} \tag{3.25}$$

where

$$\Delta_\alpha = \frac{\xi/c\hat{\epsilon}_{\alpha,\mathrm{T}} + K/\hat{\epsilon}_{\alpha,\mathrm{L}} - s}{\xi/c\hat{\epsilon}_{\alpha,\mathrm{T}} + K/\hat{\epsilon}_{\alpha,\mathrm{L}} + s} \tag{3.26}$$

Similarly equations (3.18), (3.19), (3.23) and (3.24) yield the 'secular determinant' for magnetic modes (*S* modes)

$$D_{\mathrm{M}}(\boldsymbol{K}; \mathrm{i}\xi) = 1 - \bar{\Delta}_1\bar{\Delta}_3\,\mathrm{e}^{-2sl} \tag{3.27}$$

where

$$\bar{\Delta}_\alpha = (1 - \eta_\alpha)/(1 + \eta_\alpha) \tag{3.28}$$

The function D required to compute the free energy of interaction according to equation (3.1) is now given by

$$D = D_{\mathrm{E}}D_{\mathrm{M}} \tag{3.29}$$

Further, the conditions when the denominators of Δ and $\bar{\Delta}$ vanish, namely

$$\frac{\xi}{c\hat{\epsilon}_{\mathrm{T}}} + \frac{K}{\hat{\epsilon}_{\mathrm{L}}} + s = 0 \tag{3.30}$$

and

$$1 + \eta = 0 \tag{3.31}$$

correspond, as expected, to the surface plasmon modes dispersion relations for a vacuum/medium interface (see for example Kliewer and Fuchs 1968).

4. Results and discussion

We have computed the free energy of interaction for two identical semi-infinite half spaces using for the permittivities ϵ_T and ϵ_L forms appropriate to a hydrodynamic model. Thus we chose

$$\epsilon_L(\boldsymbol{q}; i\xi) = 1 + \frac{\omega_p^2}{\xi^2 + \beta^2 k^2} \tag{4.1}$$

and

$$\epsilon_T(\boldsymbol{q}; i\xi) = 1 + \omega_p^2/\xi^2. \tag{4.2}$$

These are appropriate to a model jellium in which only compression forces are allowed (Davies and Ninham 1972). Shear waves are supposed not to exist. This is the reason why the transverse permittivity is independent of $\boldsymbol{q}$. One point we note here is that ϵ_T and ϵ_L given by equations (4.1) and (4.2) do not satisfy the general relations (Ehrenreich 1966)

$$\epsilon_L^{-1}(\boldsymbol{q}, \omega) = 1 - 4\pi\tilde{\alpha}(\boldsymbol{q}, \omega)$$

$$\epsilon_T^{-1}(\boldsymbol{q}, \omega) = [(4\pi\tilde{\alpha} + 1)c^2q^2 - \omega^2]^{-1}[(4\pi\tilde{\alpha} - 1)\omega^2 + c^2q^2]$$

where $\tilde{\alpha}(\boldsymbol{q}, \omega)$ is the macroscopic polarizability. However, we note that if we were to use a $\boldsymbol{q}$-dependent transverse permittivity, the difference would be an enhancement of the effect of spatial dispersion obtained below. The advantage of using the above simple forms is that $\hat{\epsilon}_T$, $\hat{\epsilon}_L$ and η can all be easily derived analytically. Thus from the definitions (equation (3.16), (3.17) and (3.20)) we obtain

$$\frac{K}{\hat{\epsilon}_L} = \left(\xi^2 + \frac{\omega_p^2 K\beta}{[(K\beta)^2 + (\omega_p^2 + \xi^2)]^{1/2}}\right)\frac{K}{(\xi^2 + \omega_p^2)} \tag{4.3}$$

$$\frac{\xi/c}{\hat{\epsilon}_T} = \{-K + [K^2 + \xi^2/c^2 + \omega_p^2/c^2]^{1/2}\}\frac{\xi^2}{\xi^2 + \omega_p^2} \tag{4.4}$$

and

$$\eta = \left(\frac{K^2 + \xi^2/c^2 + \omega_p^2/c^2}{K^2 + \xi^2/c^2}\right)^{1/2}. \tag{4.5}$$

The parameter β is chosen so that the longitudinal permittivity yields the correct dispersion relation for bulk plasmons in the long-wavelength limit. Thus $\beta^2 = (3/5)v_F^2$ where v_F is a Fermi velocity. This may be related to the plasma frequency ω_p and Fermi energy E_F as follows: $v_F = (16e^2/3\pi h)(E_F/h\omega_p)^2$.

In figure 1 we show our results for an aluminium jellium for which $\hbar\omega_p = 14{\cdot}2\,\text{eV}$ and $E_F = 11{\cdot}64\,\text{eV}$. The Fermi wavelength $k_F^{-1} = 3\,\text{Å}$. We have chosen to plot the effective 'Hamaker constant' H which is related to the free energy of interaction $F(l)$ by the formula

$$H = -\frac{12\pi l^2}{k_B T}F(l) \tag{4.6}$$

Curve A is the usual Lifshitz interaction free energy without any spatial dispersion (i.e. $\beta = 0$). As would be expected H is constant at small distances; at larger distances retardation sets in and $H \propto 1/l$ such that the free energy of interaction $F(l) \propto 1/l^3$.

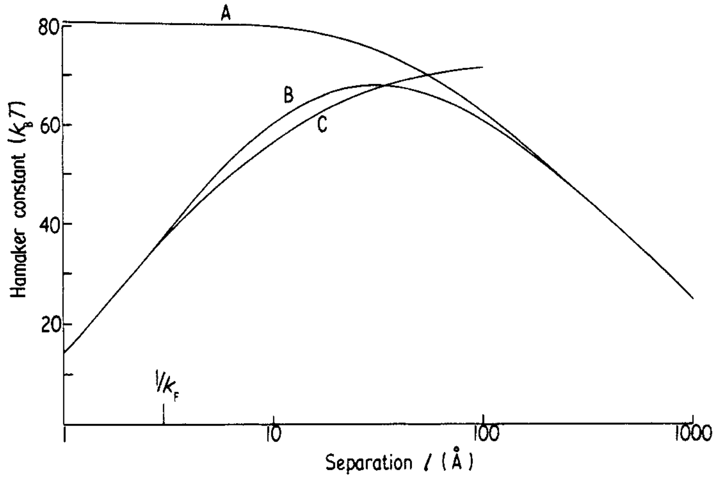

Figure 1. The Hamaker constants in units of k_BT as a function of separation for aluminium calculated using (A) Lifshitz theory with retardation but without spatial dispersion, (B) present theory, (C) non-retarded theory with spatial dispersion (reference I).

Curve B is the result obtained by including spatial dispersion. Clearly the difference becomes quite marked at distances less than ~ 50 Å. At small distances ($\sim 4/k_F$) we expect that our results will start to become inaccurate due to overlap of the electronic charge distributions from each half space. Nevertheless at this distance, which for our example is 12 Å, spatial dispersion has resulted in a 20% reduction in the Hamaker constant given by the conventional Lifshitz theory and we emphasize again our comment that if a wavevector-dependent expression for ϵ_T is used this reduction will be even greater. Furthermore we note that the hydrodynamic model is only valid for small wavenumbers, as it has the wrong asymptotic behaviours at large q, and we expect that the present calculation in common with others using the hydrodynamic model gives an estimate of the effects of spatial dispersion only at small distances.

Finally we have plotted (curve C) the results for a non-retarded spatially dispersive interaction ($c \to \infty$). The effect of the magnetic terms can be seen to reduce slightly the effect of spatial dispersion.

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