J. Phys. C: Solid State Phys., Vol. 8, 1975. Printed in Great Britain. © 1975

Free energies of inhomogeneous spatially dispersive media: II. Thin films

Derek Chan† and Peter Richmond
Unilever Research, Port Sunlight Laboratory, Port Sunlight, Wirral, Merseyside L62 4XN

Received 6 May 1975

Abstract. Using a general formalism developed in earlier papers we calculate an expression for the free energy of interaction across a film or slab of spatially dispersive medium in contact on either side with dielectric. The result is expressed in terms of bulk dielectric properties. The Lifshitz or Debye–Hückel results are recovered in appropriate limits.

1. Introduction

In a previous paper we have developed a general method which yields free energies for inhomogeneous media which contain spatially dispersive components (Chan and Richmond 1975a, b—henceforth referred to as I). We considered in I the relatively simple case of two spatially dispersive semi-infinite half spaces separated by a vacuum, and derived expressions for the interaction and surface free energies in terms of the dielectric response functions $\epsilon(\boldsymbol{q}, \omega)$ which characterize the *bulk* media. Similar expressions have also recently been deduced by Wikborg and Inglesfield (1975a, b). Now of considerable interest in many areas is a knowledge of the interaction energy for the inverse problem, for example, wetting of dielectrics by liquid metals or electrolytes or the interaction of colloidal particles across electrolytes. In both of these important applications it is necessary to know the interaction free energy between two dielectrics interacting via a spatially dispersive medium. The former case involving metals has only been studied using a hydrodynamic model (Chang *et al* 1971, Davies and Ninham 1972, Heinrichs 1973). However, this model, when combined with the normal mode method, contains some inconsistencies connected with the zero frequency contribution or classical limit of the interaction free energy. The classical limit appropriate to electrolytes was first considered by V A Parsegian (1972) (remark in a seminar at the Research School of Physical Sciences, Australian National University), and has been studied within the Debye–Hückel approximation (V A Parsegian and B W Ninham 1972 unpublished, and outlined in Mahanty and Ninham 1975, Mitchell and Richmond 1974, Richmond 1974, Barnes and Davies 1975).

The aim of this paper is to obtain a general expression for the interaction free energy for situations involving spatially dispersive media without introducing a specific form for the dielectric permittivity. We shall see that, to handle the case where the spatially

† CSIRO post doctoral research fellow.

dispersive medium is sandwiched between dielectrics, it is necessary to generalize the procedure used in I in a non-trivial manner. The paper is set out as follows. In the next section we review briefly the theoretical groundwork and discuss in a qualitative manner the generalizations referred to above. In § 3 we then derive the response function and associated free energy of interaction. In § 4 we demonstrate how our result reduces to well known limiting cases; § 5 contains a brief summary.

2. Formulation

For our system, the interaction Hamiltonian may be written as

$$V = -\tfrac{1}{2}\int \mathrm{d}^3 r\, \boldsymbol{P}(\boldsymbol{r})\,.\,\boldsymbol{E}(\boldsymbol{r}) \tag{2.1}$$

where $\boldsymbol{P}(\boldsymbol{r})$ is the local polarization density and $\boldsymbol{E}(\boldsymbol{r})$ is the local electric field. The corresponding free energy is

$$F = F_0 - \frac{1}{\beta}\left[\sum_{n=0}^{\infty\prime}\int_0^1 \frac{\mathrm{d}\lambda}{\lambda}\int \mathrm{d}^3 r \sum_\alpha G_\alpha(\boldsymbol{r}; \mathrm{i}\xi_n; \lambda)\right] \qquad \alpha = x, y, z. \tag{2.2}$$

The imaginary frequency $\mathrm{i}\xi_n = \mathrm{i}2n\pi/\beta\hbar$ where $\beta = 1/k_\mathrm{B}T$; k_B is Boltzmann's constant and T the absolute temperature. F_0 is the free energy of our system in the absence of electrical interactions. The Green function, G, is the analytic continuation onto the imaginary axis of $G_\alpha(\boldsymbol{r}; \omega; \lambda)$ which may, using linear response theory, be shown to be the αth component of the induced polarization at $\boldsymbol{r}$ due to the αth component of a unit test dipole at $\boldsymbol{r}$.

This function may be calculated classically in terms of macroscopic bulk permittivities $\epsilon(\boldsymbol{q}, \omega)$. The coupling constant, λ, may be introduced by making the substitution

$$\epsilon(\boldsymbol{q}, \omega) = 1 + 4\pi\chi(\boldsymbol{q}, \omega) \rightarrow \epsilon(\boldsymbol{q}, \omega|\lambda) = 1 + 4\pi\lambda\chi(\boldsymbol{q}, \omega). \tag{2.3}$$

This particular approximation gives results equivalent to a Random Phase Approximation. For further details of this approach we refer the reader to the literature (for example, see Mitchell and Richmond 1974, Richmond 1974, Pines 1962).

Now we saw in I that the essential step was to specify the response of the semi-infinite media. Within the spirit of our classical approximation, this took the form of an additional boundary condition which ensured that polarization currents at the interface induced in our spatially dispersive medium were specularly reflected. For

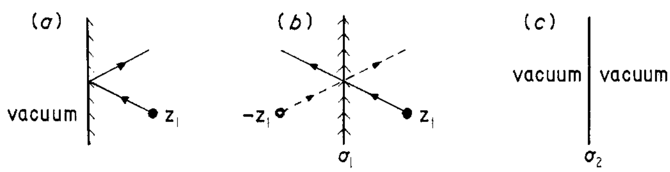

Figure 1. (*a*) A semi-infinite spatially dispersive medium in contact with vacuum. A real test charge is at z_1. The line indicates how a current is reflected specularly at the interface. (*b*) An auxiliary system of spatially dispersive medium. The supplementary test charge at $-z_1$ produces a current on the RHS such that to an observer in the RH half space it would appear that the currents are reflected specularly at the interface. (*c*) The second auxiliary system.

example, consider a single semi-infinite half space which contains a single oscillating test charge at z_1 as shown in figure 1(*a*). Currents emanating from the test charge are reflected as shown. The solution to this problem was constructed from two auxiliary homogeneous systems. In system 1 (figure 1*b*) the whole space is occupied with the spatially dispersive phase with bulk dielectric constant $\epsilon(\boldsymbol{q}, \omega)$. The test charge at z_1 is supplemented with an additional charge at $-z_1$. This produces a current shown by the broken line. Clearly the total current on the RHS is equivalent to the required specular current in figure 1(*a*). In addition we have a surface charge σ_1 at the interface. The second auxiliary system is a vacuum with a surface charge σ_2 in the plane $z = 0$ (figure 1*c*). The potential response for the homogeneous system is readily obtained. The solution to the inhomogeneous system is then determined by matching across the plane $z = 0$ the potential $\phi(\boldsymbol{r})$ and normal component of the electric displacement $\boldsymbol{D}(\boldsymbol{r})$ using the RH solution of system 1(*b*) and the LH solution of system 1(*c*).

We require to solve the system shown in figure 2(*a*). The test charge now induces currents which are multiply reflected as shown. Clearly we can simulate these specularly

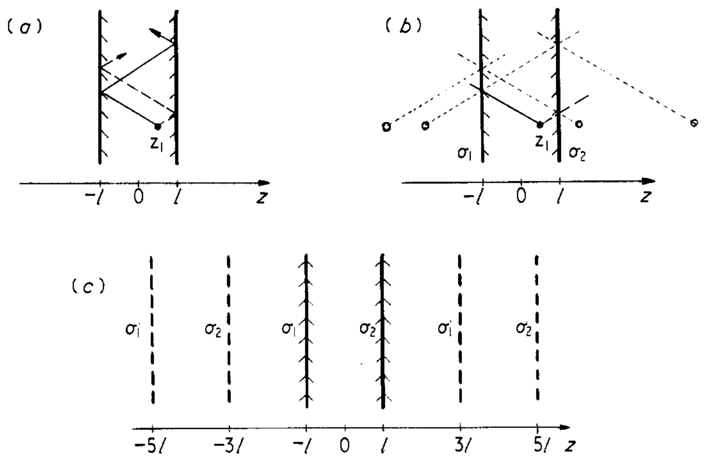

Figure 2. (*a*) A thin slab of spatially dispersive medium. The arrows indicate how the currents are reflected specularly at the boundaries. (*b*) An auxiliary system of spatially dispersive medium, including supplementary point charges which produce currents in the slab such that to an observer in the slab it appears that currents from the test charge in the slab are reflected specularly. (*c*) This shows how the surface charges must also be imaged in order that currents from the induced surface charges at the interfaces $z = \pm l$ are also effectively reflected specularly.

reflected currents by introducing charges at the appropriate image points as shown in figure 2(*b*). However, the potential corresponding to this system within the region $-l < z < l$ will not yield the correct answer. The reason becomes clear when we realize that the currents due to the induced surface charges must also be specularly reflected. That is, currents from σ_1 at $z = -l$ must be reflected at $z = l$; similarly, currents from σ_2 at $z = l$ must be reflected at $z = -l$. This is arranged by introducing surface charges at image planes as illustrated in figure 2(*c*). The potential in the range $-l < z < l$ for a system with image test charges and image surface planes is the appropriate solution we require.

3. Response function and free energy

We shall now derive the free energy of interaction for a system consisting of a slab of spatially dispersive media of width $2l$ and bulk dielectric permittivity $\epsilon(\boldsymbol{q}, \omega)$ in contact with vacuum. (The introduction of dielectric is a trivial extension.) Following the qualitative discussion of the previous section and the method pursued in I we may write the potentials and displacement vectors for the case when a unit test charge is at $\boldsymbol{r}_1$ ($|z_1| < l$). Thus to ensure specular reflection in the slab of currents from the test charge we introduce into our auxiliary homogeneous system the (test and auxiliary) charge density

$$\begin{aligned}\rho(z) = \delta(z - z_1) &+ \sum_{n=0}^{\infty} \delta(z - [2(2n+1)l - z_1]) + \sum_{n=1}^{\infty} \delta(z + [2(2n)l - z_1]) \\ &+ \sum_{n=0}^{\infty} \delta(z + [2(2n+1)l + z_1]) + \sum_{n=1}^{\infty} \delta(z - [2(2n)l + z_1]) \\ &+ \sigma_2 \sum_{n=-\infty}^{\infty} \delta(z - [4n-1]l) + \sigma_3 \sum_{n=-\infty}^{\infty} \delta(z + [4n-1]l). \end{aligned} \tag{3.1}$$

The electrical potential in the region $|z| < l$ for our inhomogeneous system is then

$$\begin{aligned}\phi = \phi_2 = 4\pi G_2(z; z_1) &+ \sum_{n=0}^{\infty} \{G_2(z; 2(2n+1)l - z_1) + G_2(z; -[2(2n+1)l + z_1])\} \\ &+ \sum_{n=1}^{\infty} \{G_2(z; 2(2n)l + z_1) + G_2(z; -[2(2n)l - z_1])\} \\ &+ \sigma_2 \sum_{n=-\infty}^{\infty} G_2(z; (4n-1)l) + \sigma_3 \sum_{n=-\infty}^{\infty} G_2(z; -(4n-1)l) \end{aligned} \tag{3.2}$$

where

$$G_2(z; z') = \int_{-\infty}^{\infty} \frac{dk}{2\pi} \frac{\exp[ik(z - z')]}{q^2 \epsilon(\boldsymbol{q}, \omega)}; \qquad \boldsymbol{q} = (\boldsymbol{K}, k) \tag{3.3}$$

is the potential response at z to a test charge of strength $\frac{1}{4}\pi$ at z'.

The electric displacement is

$$\begin{aligned}\boldsymbol{D} = \boldsymbol{D}_2 = 4\pi[\![\boldsymbol{G}(z; z_1) &+ \sum_{n=0}^{\infty} \{\boldsymbol{G}(z; 2(2n+1)l - z_1) + \boldsymbol{G}(z; -[2(2n+1)l + z_1])\} \\ &+ \sum_{n=1}^{\infty} \{\boldsymbol{G}(z; 2(2n)l + z_1) + \boldsymbol{G}(z; -[2(2n)l - z_1])\} \\ &+ \sigma_2 \sum_{n=-\infty}^{\infty} \boldsymbol{G}(z; (4n-1)l) + \sigma_3 \sum_{n=-\infty}^{\infty} \boldsymbol{G}(z; -(4n-1)l)]\!] \end{aligned} \tag{3.4}$$

where

$$\begin{aligned}\boldsymbol{G}(z; z') = \int_{-\infty}^{\infty} \frac{dk}{2\pi} \frac{(-i\boldsymbol{q})}{q^2} \exp[ik(z - z')] &= \left(-\frac{i\boldsymbol{K}}{2K}, \tfrac{1}{2}\operatorname{sign}(z - z')\right) \\ &\times \exp(-K|z - z'|) \end{aligned} \tag{3.5}$$

is the electric displacement response at z to a test charge of strength $\frac{1}{4}\pi$ at z'.

In the vacuum domains we have

$$\phi = \begin{cases} \phi_1 = 4\pi G(z; -l)\sigma_1 & z < -l \\ \phi_3 = 4\pi G(z; l)\sigma_4 & z > l \end{cases} \qquad \begin{matrix}(3.6)\\(3.7)\end{matrix}$$

where

$$G(z; z') = \int_{-\infty}^{\infty} \frac{\mathrm{d}k}{2\pi} \frac{\exp[\mathrm{i}k(z - z')]}{q^2} = \frac{1}{2K} \exp(-K|z - z'|)$$

and

$$\boldsymbol{D} = \begin{cases} \boldsymbol{D}_1 = 4\pi \boldsymbol{G}(z; -l)\sigma_1 & z < -l \\ \boldsymbol{D}_2 = 4\pi \boldsymbol{G}(z; l)\sigma_2 & z > l. \end{cases} \qquad \begin{matrix}(3.8)\\(3.9)\end{matrix}$$

It is now a straightforward matter to impose the usual boundary conditions, namely that ϕ and D^z are continuous across the planes $z = \pm l$. Consider for example the displacement vector at $z = -l$. From equations (3.4) and (3.9) we obtain

$$\begin{aligned} G^z(-l^-; -l)\sigma_1 = {} & G^z(-l^+; z_1) + \sum_{n=0}^{\infty} \{G^z(-l^+; 2(2n+1)l - z_1) \\ & + G^z(-l^+; -[2(2n+1)l + z_1])\} + \sum_{n=1}^{\infty} \{G^z(-l^+; [2(2n)l + z_1]) \\ & + G^z(-l^+; -[2(2n)l - z_1])\} + \sigma_2 \sum_{n=-\infty}^{\infty} G^z(-l^+; (4n-1)l) \\ & + \sigma_3 \sum_{n=-\infty}^{\infty} G^z(-l^+; -(4n-1)l). \end{aligned} \qquad (3.10)$$

Using equation (3.5) we see that the z component of the first five terms on the RHS of equation (3.4) may be written as follows:

$$\begin{aligned} & \tfrac{1}{2}\Big\{ \operatorname{sign}(z - z_1) \exp(-K|z - z_1|) - \sum_{n=0}^{\infty} \exp[-Kl2(2n+1)l] \exp[K(z + z_1)] \\ & \quad + \sum_{n=0}^{\infty} \exp[-Kl2(2n+1)] \exp[-K(z + z_1)] \\ & \quad + \sum_{n=1}^{\infty} \exp[-Kl4n] \exp[-K(z - z_1)] \\ & \quad - \sum_{n=1}^{\infty} \exp[-Kl4n] \exp[K(z - z_1)]\Big\} \\ & = \Big\{\tfrac{1}{2}\operatorname{sign}(z - z_1) \exp[-K|z - z_1|] - \left(\frac{\exp(-2Kl)}{1 - \exp(-4Kl)}\right) \exp[K(z + z_1)] \\ & \quad + \left(\frac{\exp(-2Kl)}{1 - \exp(-4Kl)}\right) \exp[-K(z + z_1)] + \left(\frac{\exp(-4Kl)}{1 - \exp(-4Kl)}\right) \\ & \quad \times \exp[-K(z - z_1)] - \left(\frac{\exp(-4Kl)}{1 - \exp(-4Kl)}\right) \exp[K(z - z_1)]\Big\}. \end{aligned} \qquad (3.11)$$

If we now substitute $z = -l$ (equation 3.11), this expression reduces identically to zero. We also have

$$\sum_{n=-\infty}^{\infty} G^z(-l^+;(4n-1)l) = \tfrac{1}{2} \sum_{n=-\infty}^{\infty} \operatorname{sign}(-4n)\exp(-K|4n|l) = \tfrac{1}{2} \quad (3.12)$$

and

$$\sum_{n=-\infty}^{\infty} G^z(-l^+;-(4n-1)l) = \tfrac{1}{2} \sum_{n=-\infty}^{\infty} \operatorname{sign}(4n-2)\exp(-K|4n-2|l) = 0. \quad (3.13)$$

Substituting expressions (3.12)–(3.13) into equation (3.10) readily yields

$$\sigma_1 = -\sigma_2. \quad (3.14)$$

Similarly we obtain, by matching D^z, at $z = l$:

$$\sigma_4 = -\sigma_3. \quad (3.15)$$

The potential ϕ may be matched in a similar manner. Thus we obtain

$$\sigma_2 f(l) + \sigma_3 k(l) = h(l;z_1) \qquad z = l \quad (3.16)$$

and

$$\sigma_2 k(l) + \sigma_3 f(l) = h(l;-z_1) \qquad z = -l \quad (3.17)$$

where

$$h(l;z) = 2\int \frac{dk}{2\pi}\frac{1}{q^2\epsilon(q)}\left[\frac{\exp[ik(l+z)] + \exp[ik(l+z)]}{\exp(2ikl) - \exp(-2ikl)}\right] \quad (3.18)$$

$$g(l) = \int \frac{dk}{2\pi}\frac{1}{q^2\epsilon(q)}\left[\frac{1+\exp(4ikl)}{1-\exp(4ikl)} + \frac{1}{2K}\right] \quad (3.19)$$

and

$$f(l) = 2\int \frac{dk}{2\pi}\frac{1}{q^2\epsilon(q)}\left[\frac{\exp(2ikl)}{1-\exp(4ikl)}\right]. \quad (3.20)$$

in order to evaluate the sums in equations (3.2) and (3.4) to obtain these results, it is necessary to take the contour of the k integral to be just above the real axis in the complex k plane to ensure convergence i.e. $\mathrm{Im}(k) > 0$.

Solving equations (3.16) and (3.17) yields

$$\sigma_2 = [h(l;z_1)f(l) - h(l;-z_1)g(l)]/[f^2(l) - g^2(l)] \quad (3.21)$$

and

$$\sigma_3 = [h(l;-z_1)f(l) - h(l;z_1)g(l)]/[f^2(l) - g^2(l)]. \quad (3.22)$$

It is now a straightforward matter to obtain the appropriate dipole response function necessary to evaluate the free energy according to equation (2.2). In fact

$$G_\alpha(r) = \frac{1}{4\pi}\lim_{r\to r_1}\left[\frac{\partial D^\alpha}{\partial r_{1,\alpha}}(r;r_1) + \frac{\partial^2\phi(r;r_1)}{\partial r_\alpha \partial r_{1,\alpha}}\right] \quad (3.23)$$

where

$$\left.\begin{matrix}\phi(r;r_1)\\ \boldsymbol{D}(r;r_1)\end{matrix}\right\} = \int \frac{d^2\boldsymbol{K}}{(2\pi)^2}\exp[i\boldsymbol{K}\cdot(s-s_1)]\left\{\begin{matrix}\phi(z;z_1)\\ \boldsymbol{D}(z;z_1).\end{matrix}\right. \quad (3.24)$$

Applying this prescription we obtain

$$\sum_{\alpha} G_{\alpha}(r) = \int \frac{d^2 K}{(2\pi)^2} G(K|z) \tag{3.25}$$

where

$$\begin{aligned} G(K|z) = {} & \int \frac{dk}{2\pi}\left(\frac{1}{\epsilon(q)} - 1\right) + \int \frac{dk}{2\pi}\frac{1}{q^2\epsilon(q)}\Bigg((K^2 - k^2)\sum_{n=0}^{\infty}\{\exp(-4nikl)\exp[2ik(z-l)] \\ & + \exp(4nikl)\exp[2ik(z+l)]\} + q^2\sum_{n=1}^{\infty}\{\exp(-4nikl)\exp(4inkl)\}\Bigg) \\ & + K^2\int \frac{dk}{2\pi}\frac{1}{q^2}\left(\frac{1}{\epsilon(q)} - 1\right)\exp[ik(z+l)]\sum_{n=-\infty}^{\infty}\exp(-4nikl)\sigma_2(z) \\ & + \int \frac{dk}{2\pi}\frac{ik}{q^2}\left(\frac{1}{\epsilon(q)} - 1\right)\exp[ik(z+l)]\sum_{n=-\infty}^{\infty}\exp(-4nikl)\frac{\partial\sigma_2(z)}{\partial z} \\ & + K^2\int \frac{dk}{2\pi}\frac{1}{q^2}\left(\frac{1}{\epsilon(q)} - 1\right)\exp[ik(z-l)]\sum_{n=-\infty}^{\infty}\exp(4nikl)\sigma_3(z) \\ & + \int \frac{dk}{2\pi}\frac{ik}{q^2}\left(\frac{1}{\epsilon(q)} - 1\right)\exp[ik(z-l)]\sum_{n=-\infty}^{\infty}\exp(4nikl)\frac{\partial\sigma_3(z)}{\partial z}. \end{aligned}$$

We now require to integrate the response function $G(K|z)$ with respect to z. Using the relation $\sigma_3(z) = \sigma_2(-z)$, we obtain (after some algebra and an integration by parts):

$$\begin{aligned} \int_{-l}^{l} dz\, G(K|z) = {} & 2l\int \frac{dk}{2\pi}\left(\frac{1}{\epsilon(q)} - 1\right) + \tfrac{1}{2}\left(\frac{1}{\epsilon(K,0)} - 1\right) + 4l\int \frac{dk}{2\pi}\left(\frac{1}{\epsilon(q)} - 1\right) \\ & \times\left(\frac{\exp(4ikl)}{1-\exp(4ikl)}\right) + 2\int \frac{dk}{2\pi}\left(\frac{1}{\epsilon(q)} - 1\right)\exp(ikl)\sum_{n=-\infty}^{\infty}\exp(-4nikl) \\ & \times\int_{-l}^{l} dz\exp(ikz)\sigma_2(z) + 2\int \frac{dk}{2\pi}\frac{ik}{q^2}\left(\frac{1}{\epsilon(q)} - 1\right)\exp(ikl)\sum_{n=-\infty}^{\infty}\exp(-4nikl) \\ & \times\int_{-l}^{l} dz\frac{\partial}{\partial z}[\exp(ikz)\sigma_2(z)]. \end{aligned} \tag{3.27}$$

Using the relation

$$\begin{aligned} \sum_{n=-\infty}^{\infty}\exp(-4nikl) &= \sum_{n=1}^{\infty}\exp(-4nikl) + \sum_{n=-\infty}^{0}\exp(-4nikl) \\ &= \frac{\exp(-4ikl)}{1-\exp(-4ikl)} + \frac{1}{1-\exp(4ikl)} \end{aligned}$$

the fifth term on the RHS of equation (3.27) becomes:

$$2\int\frac{\mathrm{d}k}{2\pi}\frac{ik}{q^2}\left(\frac{1}{\epsilon(q)}-1\right)\frac{\exp(-4\,ikl)}{1-\exp(-4\,ikl)}\left[\sigma_2(l)\exp(2\,ikl)-\sigma_2(-l)\right]$$

$$+2\int\frac{\mathrm{d}k}{2\pi}\frac{ik}{q^2}\left(\frac{1}{\epsilon(q)}-1\right)\frac{1}{1-\exp(4\,ikl)}\left[\sigma_2(l)\exp(2ikl)-\sigma_2(-l)\right]=0. \quad (3.28)$$

In the first integral, the poles of the integrand are avoided in the lower complex k plane; in the second integral, the poles of the integrand are avoided in the upper complex k plane. Changing the first integral into one in the upper half k plane by letting $k \to -k$ the equality follows. The fourth term on the RHS of equation (3.25) can, after some algebra, be shown to equal:

$$2\int\frac{\mathrm{d}k}{2\pi}\left(\frac{1}{\epsilon(q)}-1\right)\int\frac{\mathrm{d}k'}{2\pi}\frac{1}{q'^2\epsilon(q')}\left[\left[\frac{4P}{\mathrm{i}}\left\{\frac{\exp(2ikl)}{1-\exp(4ikl)}-\frac{2Q}{\mathrm{i}}\left[\frac{1+\exp(4\,ikl)}{1-\exp(4ikl)}\right]\right\}\frac{k'}{k'^2-k^2}\right.\right.$$

$$\left.\left.+\left\{\frac{4P}{\mathrm{i}}\frac{\exp(2ik'l)}{1-\exp(4ik'l)}-\frac{2Q}{\mathrm{i}}\left[\frac{1+\exp(4ik'l)}{1-\exp(4ik'l)}\right]\frac{k}{k^2-k'^2}\right\}\right]\right] \quad (3.29)$$

where

$$P=\frac{f}{f^2-g^2} \quad \text{and} \quad Q=\frac{g}{f^2-g^2}. \quad (3.30)$$

Both the k and k' integrals are taken above the real axis and we now specify that $\mathrm{Im}(k') > \mathrm{Im}(k)$. Thus consider the integral

$$\int_{-\infty+i\epsilon}^{\infty+i\epsilon}\frac{\mathrm{d}k'}{2\pi}f(k;k')\frac{k'}{k'^2-k^2} \qquad \text{where } f(k;k')=f(k;-k').$$

It is readily shown that this may be written as follows:

$$\tfrac{1}{2}\oint_{\mathrm{c}}\frac{\mathrm{d}k'}{2\pi}\frac{f(k;k')}{k'-k}$$

where the contour c encircles the real axis in the negative sense. Providing $f(k;k')$ has no singularities within this contour, this integral equals

$$-\tfrac{1}{2}\mathrm{i}\,f(k;k).$$

On the other hand we have

$$\int_{-\infty+i\epsilon}^{\infty+i\epsilon}\frac{\mathrm{d}k}{2\pi}f(k;k')\frac{k}{k^2-k'^2}=0.$$

Equation (3.27) becomes therefore

$$-\int\frac{\mathrm{d}k}{2\pi}\left(\frac{1}{\epsilon(q)}-1\right)\frac{1}{\epsilon(q)q^2}\left\{4P\left[\frac{\exp(2\,ikl)}{1-\exp(4\,ikl)}\right]-2Q\left[\frac{1+\exp(4ikl)}{1-\exp(4\,ikl)}\right]\right\}. \quad (3.31)$$

From equations (2.2), (3.25), (3.26) and (3.29) we have the free energy per unit area

$$\Delta F=-\frac{1}{\beta}\sum_{n=0}^{\infty}{}'\int\frac{\mathrm{d}^2\boldsymbol{K}}{(2\pi)^2}\int_0^1\frac{\mathrm{d}\lambda}{\lambda}\left\{2l\int\frac{\mathrm{d}k}{2\pi}\left(\frac{1}{\epsilon(q)}-1\right)\right.$$

$$+\tfrac{1}{2}\left(\frac{1}{\epsilon(\boldsymbol{K},0)}-1\right)+4l\int\frac{\mathrm{d}k}{2\pi}\left(\frac{1}{\epsilon(q)}-1\right)\left[\frac{\exp(4\mathrm{i}kl)}{1-\exp(4\mathrm{i}kl)}\right]$$

$$+2\int\frac{\mathrm{d}k}{2\pi}\left(\frac{1}{\epsilon(q)}-1\right)\frac{1}{\epsilon(q)q^2}\left[\frac{\exp(2\mathrm{i}kl)}{1-\exp(4\mathrm{i}kl)}\right]Q$$

$$-4\int\frac{\mathrm{d}k}{2\pi}\left(\frac{1}{\epsilon(q)}-1\right)\frac{1}{\epsilon(q)q^2}\left[\frac{1+\exp(4\mathrm{i}kl)}{1-\exp(4\mathrm{i}kl)}\right]P\Bigg\} \tag{3.32}$$

and it is understood in equation (3.32) that we have introduced the dependence of $\epsilon(q)$ on the coupling constant into the integrand. When this dependence is given by the simple relation (2.3) then the coupling constant integral may be done when we note that

$$\frac{\partial\epsilon}{\partial\lambda}=\left(\frac{\epsilon-1}{\lambda}\right)$$

$$\frac{\partial f}{\partial\lambda}=\frac{2}{\lambda}\int\frac{\mathrm{d}k}{2\pi}\left(\frac{1}{\epsilon}-1\right)\frac{1}{\epsilon q^2}\frac{\exp(2\mathrm{i}kl)}{1-\exp(4\mathrm{i}kl)} \tag{3.33}$$

and

$$\frac{\partial k}{\partial\lambda}=\frac{1}{\lambda}\int\frac{\mathrm{d}k}{2\pi}\left(\frac{1}{\epsilon}-1\right)\frac{1}{\epsilon q^2}\left[\frac{1+\exp(4\mathrm{i}kl)}{1-\exp(4\mathrm{i}kl)}\right]. \tag{3.34}$$

Thus we have from equations (3.30)–(3.33)

$$\Delta F=\frac{1}{\beta}\sum_{n=0}^{\infty}{}'\int\frac{\mathrm{d}^2\boldsymbol{K}}{(2\pi)^2}\Bigg\{2l\int\frac{\mathrm{d}k}{2\pi}\ln\epsilon(\boldsymbol{q}\,|\,\mathrm{i}\xi_n)$$

$$+\tfrac{1}{2}\ln\epsilon(\boldsymbol{K},0\,|\,\mathrm{i}\xi_n)+4l\int\frac{\mathrm{d}k}{2\pi}\ln\epsilon(\boldsymbol{q}\,|\,\mathrm{i}\xi_n)\frac{\exp(4\mathrm{i}kl)}{1-\exp(4\mathrm{i}kl)}$$

$$+\ln\left[\frac{g^2(l\,|\,\lambda=1)-f^2(l\,|\,\lambda=1)}{g^2(l\,|\,\lambda=0)-f^2(l\,|\,\lambda=0)}\right]\Bigg\}. \tag{3.35}$$

The first term corresponds to a bulk energy and has been studied at length elsewhere (see for example, Pines 1962). The remaining terms comprise surface and interaction energies.

To obtain the surface energy, ΔF_s, we take the limit $l\to\infty$. Noting that all the k integrals are taken in the upper half complex plane we obtain from equations (3.19), (3.20) and (3.34)

$$\Delta F_s=\frac{1}{\beta}\sum_{n=0}^{\infty}{}'\int\frac{\mathrm{d}^2\boldsymbol{K}}{(2\pi)^2}\left\{\tfrac{1}{2}\ln\epsilon(\boldsymbol{K},0\,|\,\mathrm{i}\xi_n)+2\ln\left[\frac{1+\hat{\epsilon}(\boldsymbol{K}\,|\,\mathrm{i}\xi_n)}{2\hat{\epsilon}(\boldsymbol{K}\,|\,\mathrm{i}\xi_n)}\right]\right\} \tag{3.36}$$

where

$$\frac{1}{\hat{\epsilon}}=2K\int\frac{\mathrm{d}k}{2\pi}\frac{1}{q^2\epsilon(q)}. \tag{3.37}$$

Noting that our slab has two surfaces we see that this result agrees with that obtained in I and also by Wikborg and Inglesfield (1975a, b). The free energy interaction is now obviously given by

$$\Delta F(l) = \frac{1}{\beta}\sum_{n=0}^{\infty}{}' \int \frac{d^2\boldsymbol{K}}{(2\pi)^2}\left\{4l\int \frac{dk}{2\pi}\ln\epsilon(q)\frac{\exp(4ikl)}{1-\exp(4ikl)}\right.$$
$$\left. + \ln\left[\frac{g^2(l|\lambda=1)-f^2(l|\lambda=1)}{g^2(\infty|\lambda=1)}\right] - \ln\left[\frac{g^2(l|\lambda=0)-f^2(l|\lambda=0)}{g^2(\infty|\lambda=0)}\right]\right\} \tag{3.38}$$
$$= \frac{1}{\beta}\sum_{n=0}^{\infty}{}' \int \frac{d^2\boldsymbol{K}}{(2\pi)^2}\left\{4l\int \frac{dk}{2\pi}\ln\epsilon(q)\frac{\exp(4ikl)}{1-\exp(4ikl)}\right.$$
$$+ \ln\left\{\left[1 - \frac{2\int(dk/2\pi)[1/q^2\epsilon(q)][\exp(2ikl)/1+\exp(2ikl)]}{(1/2K)[1+(1/\hat{\epsilon})]}\right]\right.$$
$$\left.\left.\times\left[1 + \frac{2\int(dk/2\pi)[1/q^2\epsilon(q)][\exp(2ikl)/1-\exp(2ikl)]}{(1/2K)[1+(1/\hat{\epsilon})]}\right]\right\}\right.$$
$$\left. + \ln[1-\exp(-4kl)]\right\}. \tag{3.39}$$

This result is clearly somewhat more complicated in form than those given by the Lifshitz expression for dielectrics or the Debye–Hückel approximation for electrolytes. It is clearly necessary to establish that our expression reduces to these forms in the appropriate limits.

4. Special limits

(i) Consider first the case where the permittivity is independent of q. If we recall now that the k integrals are taken above the real axis we now see immediately that the first term on the RHS of equation (3.39) is zero since the integral has no poles in the upper half of the complex k plane. The k integrals in the second term are readily evaluated. Thus:

$$\int \frac{dk}{2\pi}\frac{1}{q^2}\frac{\exp(2ikl)}{1\pm\exp(2ikl)} = \frac{1}{2K}\frac{\exp(-2Kl)}{1\pm\exp(-2Kl)} \tag{4.1}$$

and after some simple algebra we obtain the Lifshitz result (Dzyaloshinskii *et al* 1961):

$$\Delta F(l) = \frac{1}{\beta}\sum_{n=0}^{\infty}{}' \int \frac{d^2\boldsymbol{K}}{(2\pi)^2}\ln\left[1-\left(\frac{\epsilon-1}{\epsilon+1}\right)^2\exp(-4Kl)\right]. \tag{4.2}$$

(ii) In the Debye–Hückel approximation we have the static dielectric permittivity

$$\epsilon(q) = 1 + K^2/q^2 \tag{4.3}$$

where κ is the usual Debye–Hückel screening parameter. Now recalling that we require only the zero frequency term, the first term on the RHS of equation (3.38) becomes

$$\frac{1}{2\beta}\int\frac{d^2\boldsymbol{K}}{(2\pi)^2}4l\int\frac{dk}{2\pi}\ln\left(\frac{k^2+s^2}{K^2+k^2}\right)\frac{\exp(4ikl)}{1-\exp(4ikl)} \tag{4.4}$$

where

$$s^2 = K^2 + \kappa^2. \tag{4.5}$$

To evaluate the k integral, the contour is closed in the upper half-plane and must be indented to avoid the branch line arising from the logarithm. (Split the logarithm as follows: $\ln[(k^2+s^2)/(K^2+k^2)] = \ln(k+\mathrm{i}s) + \ln(k-\mathrm{i}s) - \ln(k+\mathrm{i}K) - \ln(k-\mathrm{i}K)$.) The integral can then be shown to equal

$$\frac{1}{2\beta}\int\frac{\mathrm{d}^2\boldsymbol{K}}{(2\pi)^2}\ln\left[\frac{1-\exp(-4sl)}{1-\exp(-4Kl)}\right]. \qquad (4.6)$$

The remaining k integrals are readily evaluated. Thus

$$\int\frac{\mathrm{d}k}{2\pi}\frac{1}{q^2\epsilon(q)}\frac{\exp(2\mathrm{i}kl)}{1\pm\exp(2\mathrm{i}kl)} = \frac{1}{2s}\frac{\exp(-2sl)}{1\pm\exp(-2sl)} \qquad (4.7)$$

and using the relation $\hat{\epsilon} = s/K$ we readily obtain

$$\Delta F(l) = \frac{1}{2\beta}\int\frac{\mathrm{d}^2\boldsymbol{K}}{(2\pi)^2}\ln\left[1-\left(\frac{s-K}{s+K}\right)^2\exp(-4sl)\right]. \qquad (4.8)$$

This is the well known Debye–Hückel limiting form which has been studied by workers in colloid science (Mitchell and Richmond 1974, Gorelkin and Smilga 1973).

5. Summary

In the paper we have obtained a general expression for the free energy of interaction across a slab of spatially dispersive material. The result (equation 3.38) is expressed in terms of the bulk dielectric permittivities for the component media. The result reduces subject to appropriate approximations to all the well known limits derived elsewhere. However, it does not appear to be equal to that given by application of the normal mode method (van Kampen *et al* 1968). This result now enables a study to be made of the stability and associated disjoining pressures for thin liquid metal films. Alternatively one can study the interaction between voids which have been observed in metals (Lucas 1973).

We conclude by noting that our method will also yield information relating to surface plasmons. In fact the imaginary part of the charge response function $\sum_\alpha G_\alpha(\boldsymbol{K}|\omega)$ is essentially the spectral density function for such excitations.

References

Barnes C and Davies B 1975 *J. Chem. Soc.*: *Faraday Trans. II* submitted
Chan D and Richmond P 1975a *Phys. Lett.* **51** A 323–4
—— 1975b *J. Phys.* C: *Solid St. Phys.* **8** 2509–21
Chang D B, Cooper R L, Drummond J E and Young A C 1971 *Phys. Lett.* A **37** 311
Davies B and Ninham B W 1972 *J. Chem. Phys.* **56** 5797
Dzyaloshinskii I E, Lifshitz E M and Pitaevskii L P 1961 *Adv. Phys.* **10** 168
Gorelkin V N and Smilga V P 1973 *Sov. Phys.–Dokl.* **36** 761
Heinrichs J 1973 *Solid St. Commun.* **13** 1595
van Kampen N G, Nijboer B R A and Schram K 1968 *Phys. Lett.* **26** A 307
Lucas A A 1973 *Phys. Rev.* B 3527
Mahanty J and Ninham B W 1975 *Dispersion Forces* (New York: Academic Press)
Mitchell D J and Richmond P 1974 *J. Coll. Int. Sci.* **46** 118
Pines D 1962 *The Many Body Problem* (New York: Benjamin)
Richmond P 1974 *J. Chem. Soc. Faraday Trans. II* **70** 1650
Wikborg E and Inglesfield J E 1975a *Solid St. Commun.* **16** 335
—— 1965b *Phys. Stat. Solidi* at press